A Manual for the CHEMICAL ANALYSIS of METALS

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ASTM Manual Series: MNL 25
ASTM Publication Code Number (PCN)
28-025096-50

100 Barr Harbor Drive, West Conshohocken, PA 19428-2959

Library of Congress Cataloging-in-Publication Data

Dulski, Thomas R., 1942–
A manual for the chemical analysis of metals/Thomas R. Dulski.
p. cm.—(ASTM manual series; MNL 25)
Includes bibliographical references (p. –) and Index.
ISBN 0-8031-2066-4
1. Metals—Analysis—Handbooks, manuals, etc. I. Title.
II. Series.
QD132.D85 1996
669'.92–dc20 96-1836
CIP

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Printed in Ann Arbor, MI
March 1996

Dedication

THIS BOOK IS DEDICATED to my father, Frank Dulski, who was both a gentleman and a gentle man.

Acknowledgments

THERE ARE three levels of indebtedness that I would like to acknowledge. First, there are those individuals, living and deceased, who for over 32 years have taught me from their deep knowledge of classical and instrumental analysis: Charles J. Byrnes, Silve Kallmann, Ralph M. Raybeck, James O. Strauss, Alfons Suk, and George Vassilaros. These cherished friends have contributed to this book in countless unrecognized ways. Next, there are those who have given their time and their efforts in the review of the manuscript: their names and affiliations are listed below. The suggestions and corrections of these individuals have been an invaluable aid in the preparation of the final text. Finally, there are my friends, coworkers, and associates, including the members of ASTM Committee E-1, and my family—my wife, Grace, my daughter, Brittany, and my mother, Stephanie—who have in their respective ways supported and sustained me in this work. Thank you, all.

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Foreword

THIS PUBLICATION, *A Manual for the Chemical Analysis of Metals,* was approved by ASTM Committee E-1 on Analytical Chemistry for Metals, Ores, and Related Materials. This is Manual 25 in ASTM's manual series.

Cover photo from the collection of Isabel and Alfred Bader.

Disclaimer

MUCH OF THE METHODOLOGY described in this book is potentially hazardous. The author, his affiliation, Carpenter Technology Corporation, and the publisher, ASTM, assume no liability whatsoever for any material, financial, or personal loss or injury incurred from the implementation of the equipment, chemicals, or procedures described herein.

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Introduction

WHILE THE ANCIENTS WERE intuitively aware of the particulate nature of matter and had developed a keen understanding of proportions and mathematics, it was not until the eighteenth century, when the mists of alchemy began to clear, that mankind first peeked into the heart of a substance. The insights that followed were in every sense as profound as those that followed the somewhat earlier ponderings of force and light. Analytical chemistry, as a more or less clearly defined discipline, has been around now for about 200 years. The intimate connection between the analysis of materials and the understanding of the laws governing their nature has remained a hallmark and an impetus of both since that time.

Among the earliest insights of those nascent days was the very notion that certain substances were, in fact, divisible. Air, for example. Leonardo da Vinci had suspected and Joseph Priestley had proved that it was a mixture, but Antoine Lavoisier gave *quantity* to its components. And today, watching those two perfectly proportioned peaks emerge when a sample of air is injected into a gas chromatograph, who can deny a key historical role to compositional analysis?

The analysis of metals was among the earliest applications of analytical chemistry, but it is also interesting to note that fire assay techniques used to assess the purity of gold antedated the scientific discipline by 3000 years. In the nineteenth century, the Bessimer process (introduced in 1856) made the large-volume production of steel a reality. This was followed shortly by the open-hearth (1864) and electric furnace (1890) processes. The latter led to the production of high-purity alloy steels and the need for accurate quantitative measurement of product composition. Brass and bronze foundries, derived from a centuries-old tradition, began to employ new processes and to produce new alloys. And in the 1890s the Hall process gave birth to the aluminum industry. Each of these developments required innovations from analytical chemistry—to analyze their products and raw materials, to assess their recoveries, and to fine tune their processes.

In the second half of the twentieth century, nickel- and cobalt-base high-temperature alloys came into their own for critical aerospace applications, followed closely by titanium alloys. The nuclear industry required zirconium and beryllium alloys. These and other metals industries made unprecedented demands on the analytical chemist for accuracy, precision, and sensitivity. And at the same time, the new high-speed production processes in "traditional" industries—the basic oxygen furnace, the argon-oxygen decarburization (AOD) vessel, the continuous caster—were adding a new demand for nearly instantaneous results.

The evolution of techniques for the analysis of metals and alloys followed these metallurgical developments very closely.[1] Late nineteenth and early twentieth century metals analysis laboratories employed gravimetric and titrimetric methods. As the demand for timely reports increased, time-honored approaches were modified. Factor weights and burets calibrated in element percent circumvented time-consuming hand calculations. A major innovation at the time was the color intensity comparator, a subjective application of Beer's law. In the 1920s and 1930s instrumentation began to ease the analyst's burden: pH meters, filter photometers, electrogravimetric analyzers.

But it was in the 1940s that instrumental approaches began to dominate. Spectrophotometers extended molecular absorption approaches to new levels of sensitivity and

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[1] For a brief chronology of the developments in both fields, see Appendix I.

broadened the useful wavelength range to the near ultraviolet and infrared. Emission spectroscopy became a practical tool. In the 1950s, X-ray fluorescence began to revolutionize the field, taking the idea of rapid analysis into a new realm. In the 1960s, atomic absorption spectrophotometry promised a revolution in solution-based analysis. In the 1970s and 1980s, it was the plasma emission techniques. Today, inorganic mass spectrometry appears poised to take the lead, and computerization promises a paperless lab. Each of those past developments has delivered nearly all that it had initially promised, and each has contributed immeasurably to the metals industry.

Today, a modern control laboratory in, for example, a large integrated steel mill can deliver analytical results for 25 elements to two or three decimal-place accuracy within 5 min of receipt of the sample. And work is now underway to develop robot labs and furnace-side probes for even faster compositional analysis. The size of the work force in a large steel mill laboratory has dropped from several hundred before World War II to, perhaps, 15 to 20 today. And the new robot laboratories have further reduced the personnel required to two or three largely maintenance positions. Such robot facilities incorporate completely automated sample preparation and may include optical emission and X-ray fluorescence spectrometers and carbon, sulfur, oxygen, and nitrogen determinators. The instruments automatically select and run standards, and if validation criteria are not met, they automatically recalibrate themselves.

One would think by pondering this picture that the present and future needs of the metals industry are now well on their way to being adequately met. In fact, there are some dark clouds on this high-tech horizon. To properly describe the problem, it is necessary to first point out some fundamental distinctions in the formalism by which a substance can be analyzed. In the days when gravimetry and titrimetry were the only options available for a metals analyst, results were being generated independent of any matrix-matched certified reference material. These are sometimes termed *definitive* methods, and even today there are only a few techniques that can be added to the list (coulometry and isotope dilution mass spectrometry come immediately to mind). In gravimetry, a pure compound (or element) is weighed and related to the analyte's abundance in the test material. In volumetric work based on normality, the analyte reacts with a precisely measured amount of a pure compound. In both cases, the only function for a certified metal alloy standard is to *validate* the skill of the operator.

The situation changed in a fundamental way when high-speed instrumental methods began to be introduced. Optical emission and X-ray fluorescence spectrometers for all their blinding speed are powerless to operate without metal alloy standards. So much so, in fact, that an argot of terms has formed around the subject. Thus we have "drift standards," "type standards," "calibration standards," "standardization standards," "control standards," "precontrol standards," and several others. Similarly, modern carbon, sulfur, nitrogen, oxygen, and hydrogen determinators are designed with metal alloy standards as their primary means of calibration. These methods are said to be *comparative*. We have traded for speed, and what we gave up was independence.

And so today there are uncounted numbers of standards in metals analysis laboratories throughout the world. Each lab has its small or large personalized suite, selected to meet its particular requirements. Many of these have been purchased over many years from standardizing agencies like the National Institute of Standards and Technology (formerly, the National Bureau of Standards). Some are cherished remnants of days when classical chemical analysis was being used to develop "in-house" standards for instrument calibration. For the sad truth is that few organizations have had the foresight to retain *any* wet chemical analysis capability, let alone the ability to perform definitive methods. Moreover, while the resources available to standardizing agencies, governmental or private, have always been limited, the traditionally employed interlaboratory cooperative round robin is breaking down because the ability to perform the necessary work no longer exists.

Each time a solid spectrometric standard is resurfaced, some material is lost and stocks of standards available for sale are being exhausted. Often they are replaced with reference materials whose certificate values show much greater uncertainty. Even more often, they are not being replaced at all.

The result of this trend will be a deterioration in the veracity of the results produced by those high-speed/low-overhead analytical engines. For undoubtedly some will suggest that we make a standard by *comparing* it to a standard, ignoring the enormous potential for runaway systematic error, and, like a photograph copied from a copy, truth will quickly blur. The alternatives will be almost equally painful to sharp-penciled accountants—either allow those speedy engines to grind to a halt or reinstate some sort of "wet lab" to work on standards.

The situation is, perhaps, not quite as bleak as I have just pictured. In certain metals companies (not always the largest), and particularly in metals research facilities, some classical analytical chemistry is still in evidence. Besides the need for in-house standards, there are a number of excellent practical reasons for maintaining a "wet lab." First, the great flexibility of chemical techniques can accommodate many sample sizes and shapes (fine wire or small parts, for example) that are difficult or impossible by solids spectrometric methods. Unlike those approaches, chemical methods can effectively handle a moderate degree of sample inhomogeneity by linking wet chemistry to a rational sampling plan. Chemical methods are immune to thermal history effects that sometimes harass solids techniques. Chemical techniques *may* be more accurate, more precise, or more sensitive than particular solids spectroscopic approaches. Certainly they are *different* and thus represent a valuable check on data quality and can serve as umpires between instruments, between laboratories, and between vendor and consumer industries. In the absence of suitable standards, sometimes a classical definitive method is contractually specified as part of a compositional certification test plan for a key element in a critical application alloy.

Such agreements are rare, however. The fact is the definitive methods, in the strict application of that term, are rare as well. Today, much of what remains of wet analytical chemistry occupies a mid-ground between definitive and comparative protocols. Currently, what many call "wet analysis" consists of dissolving the sample, diluting it to some fixed volume, and presenting it to some instrument that has been calibrated with pure (or matrix-matched) solutions of the analyte.

While this methodology evinces all the advantages associated with a solution-based approach, it is fraught with potential errors: calibrant purity, linearity limits, spectroscopic line interferences, and chemical effects, to name a few. It is reasonably rapid, however, and requires only a moderate degree of manipulative skill. Spectroscopic knowledge is needed, of course, to anticipate line overlaps and sensitivity problems, but the solutions found for these problems are typically instrumental ones: alternate line selection, interelement correction factors, off-peak background correction, and others. It rarely occurs to today's analysts that many classical chemical separation schemes are directly applicable to spectroscopic problems. And yet just such a hybrid classical/instrumental approach often yields the highest quality analysis in the least amount of time. As a cost-effective measure when the best level of work is needed and solids techniques are not a viable option, returning to the chemistry in this way makes sense.

Which leads us finally to the *raison d'etre* of this book. The last quarter of the twentieth century has witnessed a prodigious loss of classical analytical chemistry lore from the industrial workplace. I have used the word "lore" advisedly, because other aspects of this discipline—theory, good laboratory practices, and specific methods—can still be extracted from public, university, and industrial libraries. But with the exception of a few long-out-of-print and somewhat dated texts, there is no source from which to learn the thinking and manipulative skills that make a classical analyst. "Lore" also implies a degree of art that must accompany the science—the things that work even though their chemistry is poorly understood.[2] But the unfortunate fact is that most of the lore has been lost as wet labs were closed and classical analysts were retired without replacement. As we have seen, these decisions have been short-sighted and potentially disastrous.

An equally disturbing trend is the recent spread into industry laboratories of a dogma, widely held by lawyers and bureaucrats, that any human act, no matter how involved and complex, can be precisely specified in a written set of instructions. This credo is patently false, as anyone who reflects a moment on the works of man can plainly see. That is why there is only one Sistine Chapel ceiling, why all violins do not sound like a Stradivarius, and why open heart surgery is not offered as a correspondence school course. The simple fact is that no written protocol, even when the last "t" is crossed and the last "i" is dotted, can ever reduce the analyst to that hypothetical "pair of hands"—

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[2] The notion of lore is not new to science, nor is it antiscience. Rather, it precedes science. How many lives have been saved, for example, by drugs whose mode of action is only dimly understood?

a cheap, readily available, ultimately disposable "human resource," in the ultimate implication of that term. Well-written analytical procedures, such as ASTM standard methods are, of course, indispensable recipes, but one does not become a great chef, or even a good cook, by reading recipes.

This book is an attempt to describe and explain some of the intangibles and many of the details associated with the analysis of metals. It is not a recipe book of specific methods, but rather a training manual and a reference source that can complement a laboratory quality control manual and a suitable array of analytical procedures. Emphasis has been placed on skills, knowledge, and approaches to problem solving that are typically not described in either QC manuals or specific method documents. Clearly, no book can summarize all the tricks of this or any other trade with sufficient detail to substitute for a good "hands-on" on-the-job training program. But modern industrial realities being what they are, the time and talent for such programs is no longer available. The knowledge in many cases has been lost. Lone analysts are frequently placed in the position of either sinking or swimming along a *tsunami* of a learning curve. And because few have the time or resources for an adequate literature search, the wheel is reinvented many times.

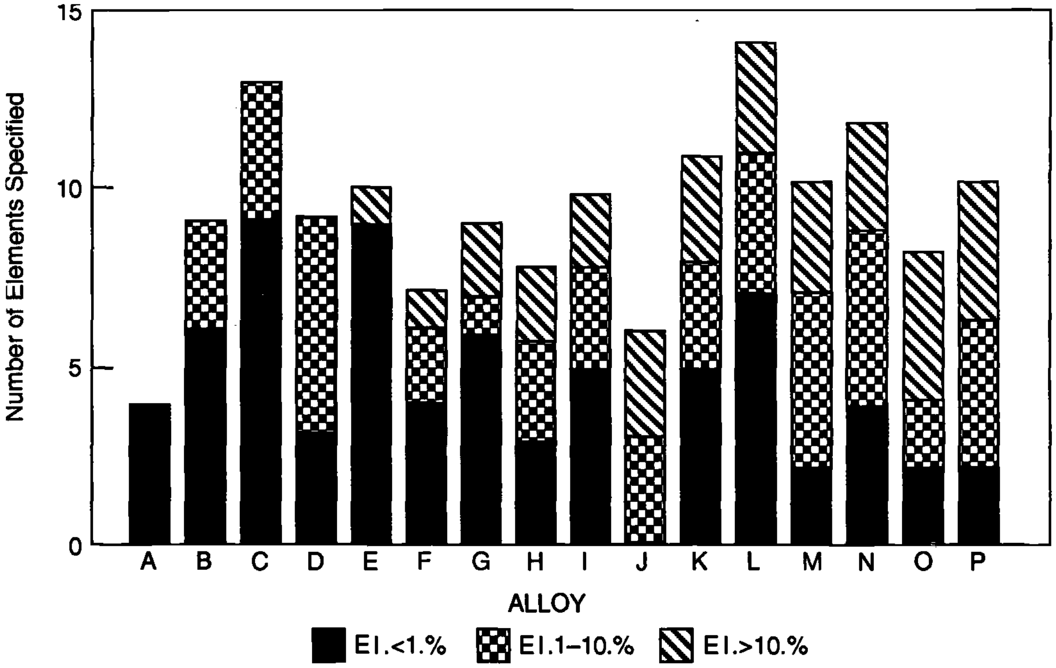
And so, what is being attempted here is to provide some guidance for those who find themselves alone in the trenches, perhaps professionally trained in chemistry, but inexperienced in the trade of metals analysis. They may be alone or in charge of a staff of inexperienced or partially trained personnel. They may have access to high-speed spectrometers and other equipment that has been purchased to lower overhead costs, but that never quite meets all the demands placed upon it.

Unfortunately, academic credentials are an inadequate preparation for this sort of career. The universities and colleges have de-emphasized analytical chemistry and, in particular, classical analytical chemistry. And descriptive inorganic chemistry has largely been replaced by theory. While these changes may serve larger needs, they have hurt certain pragmatic concerns, among them, metals analysis. It is entirely possible that an individual may be awarded a Ph.D. in chemistry and have no idea of the colors of vanadium ion in aqueous solution. This observation is not meant to reflect on individual achievement, academic standards, or the quality of academic programs, but simply to illustrate that industry's perhaps parochial concerns are not being met. Certainly college training provides the foundation for scientific problem solving, and any specific fact can be extricated, but no one has bothered to inform the industrial marketplace that all their problems may not be instantly solved by their next hire.

Training in another related field of industrial analytical chemistry can be a useful preparation for an assignment in metals analysis; however, the professional manager type of individuals may find themselves adrift without the technical knowledge to guide their staff. Today, with the analytical workforce severely limited in size and often shrinking, technical guidance from management is required much more urgently than in earlier times when expertise could emanate from a line of "sublieutenants."

The complexity of the analytical task, of course, varies widely between industry laboratories. Some are called upon to analyze comparatively few metal alloy compositions, while 500 standard stocks are not uncommon in others. A research environment or a "jobber" type of mill is much more likely to routinely encounter the nonroutine. One measure of the comparative complexity of the work is the number and frequency of measured analytes and, in particular, the number and frequency of such analytes present at levels of 10% and above (since the need for wet chemical support increases dramatically at about that level). This point is illustrated in Fig. I-1, which uses a few selected alloys from a number of metals industries to suggest trends. A metals analyst may in the course of a career analyze half a hundred different elements in major, minor, and trace amounts. High-temperature superalloys, in particular, represent a challenge to the analyst; their only rival in the inorganic field may be in the complex area of mineral analysis.

It should also be recognized that few laboratories are exclusively engaged in metals analysis. Most are also called upon to analyze an array of other materials—slags, refractories, water, air particulates, process gases, plating and pickling baths, and a host of other materials. While these are not the main subject of this volume, they are part of the overall task and thus cannot be completely ignored. Many of the skills, some of the separations, and a lot of the thinking involved in solving metals analysis problems are directly transferrable to other matrices.



NOTE: See key below for alloy designations.

A: Plain Carbon Steel (AISI 1040)
B: Alpha-Beta Titanium Alloy (UNS R56620)
C: High-Strength Low Alloy Steel (ASTM A871)
D: High-Speed Tool Steel (AISI M42)
E: Wrought Aluminum (AA No. 1070)
F: Ferritic Stainless Steel (AISI 405)
G: Cast Aluminum Alloy (AA No. 384.2)
H: Austenitic Stainless Steel (AISI 316L)
I: Aluminum Bronze (Copper No. C63020)
J: Permanent Magnet Alloy (Alnico 9)
K: Iron-base High Temperature Alloy (A286; ASTM A-453)
L: Nickle-base High Temperature Alloy (Waspaloy; AISI 685)
M: Cobalt-base High Temperature Alloy (S-816; AMS 5765)
N: Nickle-base High Temperature Alloy (AF115)
O: Cobalt-base High Temperature Alloy (L605; AMS 5759)
P: Iron-base High Temperature Alloy (S-590; AMS 5770)

FIG. I-1—Frequency of analyte concentrations (miscellaneous alloy specifications).

The basic message of this book is: *Learn the chemistry*; know, at least in a general way, what is happening or expected to happen at each step in the analytical process. That *dictum* includes not just the ideal "paper" reactions of textbooks, but also the often ignored real-world deviations from ideal behavior—the way equilibria are shifted at high dilutions or the way cations are adsorbed on vessel walls, for example. That knowledge combined with an appropriate array of manipulative skills is principally the key to all forms of analytical problem solving. It is hoped that this book will be used as an aid in such problem solving for the analysis of metals. It is written for the laboratory technician, the chemist, and the lab manager who are faced with detection limit difficulties, or spectroscopic line interferences, with precision problems at high concentrations, or perhaps with an alloy that takes too long to dissolve.

Much of the material in this volume is gleaned from older ways of doing things, some is from the current literature, and some may never have been published before. Many of the older techniques and procedures are, of course, outdated and have been left to moulder on library shelves. But a judicious selection from the antiquarian lore still includes the most accurate and definitive procedures in many cases. And some of these methods contain manipulative steps that are valuable additions to the instrumental world of the sleek and the swift. I have tried my best to keep the focus on only those techniques that *can* and *should* be used today and in the years to come. Many of them will be needed only rarely, others will find use every day. But none have been included as curiosities. This is not a history.

The organization generally follows the analytical process: materials, samples, separations, measurement, and quality issues. There is also a large appendix that summarizes the analytically important chemical behavior of certain elements. Hopefully, this manual will be useful as a direct guide to specific problem solving.

Before closing this introduction, I must admit to at least two biases that may color the tone of this work. First, much of my own training and experience comes from the steel industry, in particular from that branch of the steel industry that produces specialty alloys. Second, I am by training and predilection a classical wet chemist. The former admission means that this book will have some leaning towards the problems related to iron-, nickel-, and cobalt-based alloys. The latter admission means that there will be a tendency to solve problems chemically, rather than by instrumental means. I do not believe that either bias will be fatal to my intended purpose since any addition to an analyst's bag of tricks has to be of some use. I am reminded of the introduction to that classic text, *Applied Inorganic Analysis*, where the authors compare the determination of an element in pure form to finger exercises, while its analysis in complex mixtures requires the skills of a virtuoso pianist. I think that in today's world of high-speed instruments and understaffed laboratories, the appropriate analogy is not Chopin but jazz. We must know when it is our turn to play, and we must know how to improvise.

REFERENCES

Beck, C. M., *Analytical Chemistry*, Vol. 66, No. 4, 1994, pp. 224A–239A.

Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley and Sons, New York, 1953.

Jaffe, B., *Crucibles: The Story of Chemistry*, Fawcett, Greenwich, CT, 1957.

Kallmann, S., *Analytical Chemistry*, Vol. 56, No. 9, 1984, pp. 1020A–1028A.

Slavin, W. and Epstein, M. S., Eds., *Spectrochimica Acta B* (Special Issue: *Reference Materials and Reference Methods*), Vol. 46B, No. 12, 1991, pp. 1571–1652.

Van Nostrand's Scientific Encyclopedia, 4th ed., Van Nostrand, Princeton, NJ, 1968.

Woldman's Engineering Alloys, 7th ed. , J. P. Frick, Ed., American Society for Metals International, Materials Park, OH, 1990, pp. 1425-1495.

Part I: Materials

"Being now inflamed with a great desire to begin working, I told his Excellency that I had need of a house where I could install myself and erect furnaces, in order to commence operations in clay and bronze, and also, according to their separate requirements, in gold and silver. I knew that he was well aware how thoroughly I could serve him in those several branches, and I required some dwelling fitted for my business."

—*Autobiography of Benvenuto Cellini* (1562)

"I implore you, take some interest in those sacred dwellings meaningly described as laboratories.*"*

—Louis Pasteur (1868)

1

Laboratory Design

ONLY A SMALL NUMBER OF individuals ever have the opportunity to participate in the planning and design of a new laboratory facility. And those who do rarely have complete control over the final configuration, which is always a compromise of needs and means. In fact, what usually shakes out is a hodgepodge of different individual's ideas. Architects, corporate financial planners, builders, and others in the decision line may have quite a different agenda than the chemist who plans to work there. There is another sense, though, in which nearly everyone who works in a laboratory for any length of time participates in lab design because laboratories change with changing needs and evolving technology.

Like the discipline of chemistry itself, chemistry laboratories have evolved with time, and a great deal has been learned about how work in a laboratory can be facilitated. Anyone who has seen woodcuts and paintings of alchemical laboratories (such as those in the Fisher Scientific Company collection in Pittsburgh, for example) knows that early labs, at least in the popular conception, were dark, dreary, cluttered places, inhabited by crazed folk who could never keep their stockings up.[1] A fireplace with a natural draft chimney served as hot plate and hood. And the dirt and disorder were probably very real, considering some of the activities that went on there (Fig. 1–1). Clearly the Occupational, Safety and Health Administration (OSHA) was not involved.

Robert Boyle's laboratory (1670) near Covent Garden, outside of London, is often called the first "modern" chemistry lab. Joseph Priestley's expatriation to the fledgling United States resulted in a landmark facility in northeastern Pennsylvania (1794). Other notable stops on the road to the present are: the Royal Institution of Great Britain (1799) where Davy and Faraday worked, the laboratory of von Liebig at Geissen in Germany (1850), the Clarendon at Oxford (1872), and the Cavendish at Cambridge (1874). Industrial laboratories began to emerge in the late nineteenth century, first in Europe, where the German dye industry drove developments.

The early metals analysis laboratories were control labs associated with alloy production (Fig. 1–2). Today it is difficult to imagine the complex logistics of wet chemical control at an early electric furnace steel shop that produced "rustless" steel. In the 1920s such a lab might employ 30 men on each of three shifts. Test castings and finished pieces were turned into chips in the drill room, usually on the first floor of the laboratory building. One or more "weigh-boys" weighed the samples in the balance room on the second floor laboratory level. The weighed chips then passed to the specialized labs, each set up for the efficient chemical determination of carbon, sulfur, phosphorus, silicon, manganese, chromium, nickel, and molybdenum. The silicon lab had its funnel racks, hot plate, and muffle furnace; the chromium lab, its own hot plate, burets, and reagents.

Of course, there were always one or more areas devoted to special work—unusual elements or new methods development—and these had their own sets of nondedicated equipment. One or more stockroom workers prepared all reagent and standard solutions. There might be hand-cranked calculators scattered around and slide rules abounded, but many methods were set up so that results could be read from a buret or from a look-up table. Such labs were manned by promotion from the labor force, and the analyst often had little knowledge of, or interest in, the underlying chemistry. The chief chemist thus was the key technical element of the entire operation. He set up the methods, tested them, and trained the foremen. He often did research, not only in chemistry, but in metallurgy as well. He also ordered supplies, hired and fired, and performed all the management functions normally associated with such a position today.[2]

Such a lab would serve no purpose today. Control laboratories, for the most part, can no longer afford the time involved in wet chemistry of any kind. But the metals industries began to establish research facilities after World War II where new alloys and new metallurgical processes were developed. To support this activity, analytical chemistry labs were included, and many people experienced in the older wet chemical control labs transferred their considerable skills to this new environment. In this chapter, we will explore some idealized laboratory designs for different needs of today's metals industries.

THE BUILDING

The design of a metals analysis laboratory must first consider the constraints of the physical plant in which it will reside. Metals analysis labs today are almost never stand-alone structures with no other function, but rather constitute a part—sometimes a very small part—of a structure whose primary purpose may be alloy production, manufacturing, research, or even corporate administration.

It is common to locate chemistry labs on the top floor of a building to minimize the stack length of hood ducts. This strategy reduces the size and power requirements for exhaust

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[1] An early Renaissance conceit for a distracted mind.

[2] Dr. C. M. Johnson, chief chemist at Crucible Steel's Park Works in Pittsburgh, was perhaps the model for this description, although there were a handful of others in the steel industry.

FIG. 1-1—"The Alchemist," a painting by Cornelis Bega completed around 1660, is one of the best known works in the collection of alchemical paintings. From the collection of Isabel and Alfred Bader.

fan motors to achieve a given face velocity at the hoods. There is little inherent safety advantage to locating labs on the top floor, however, since fire, explosion, chemical, or water damage *may* be more difficult to contain in this sort of arrangement. Most modern buildings are of steel framework construction with supporting walls, although there are many of center-post/curtain-wall construction that allow floor-to-ceiling glass walls that support no weight. Often the lab building, of whatever construction plan, will incorporate windows that do not open—a distinct disadvantage in the event of power failure when hoods are in use. Such a design militates for a back-up generator and even an evacuation plan for power outages.

Maximum utilization of natural lighting is a central part of many architectural designs; this is always supplemented with fluorescent lighting, which may be embedded in a dropped ceiling that conceals service mains. It is important that lighting fixtures, wall switches, and electrical outlets be tailored to the needs of the chemistry lab even if this requires some deviation from the conventions employed in other parts of

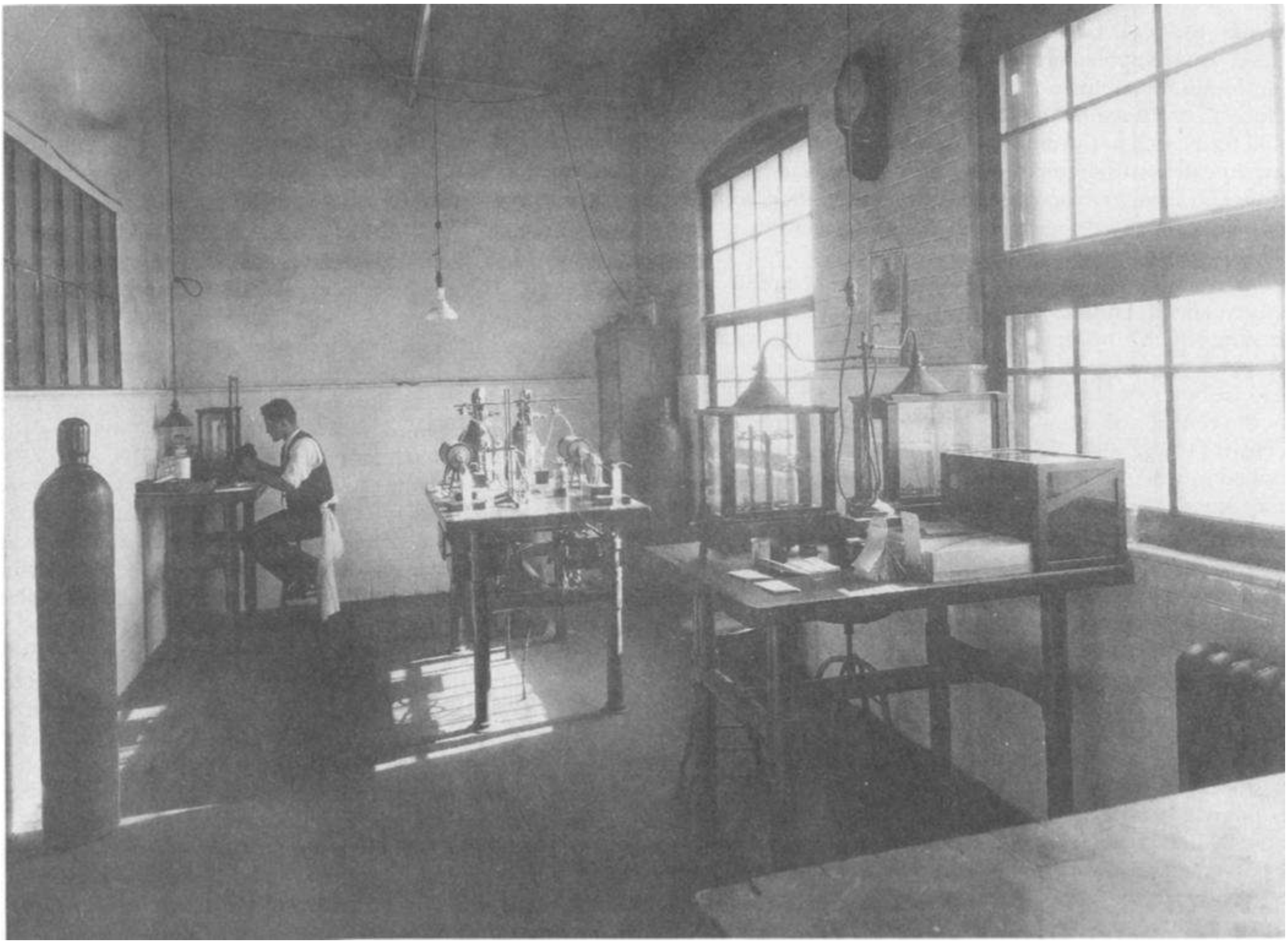


FIG. 1–2—An early metals analysis laboratory (1929).

the building plan. Thus resistance to corrosive fumes should be considered for materials in electrical fixtures to prevent an eventual rain of iron oxide particles from above, oxidized wall sockets that do not work, or wall switches that short out.

Floor material coverings like vinyl tile are more comfortable to stand on and more attractive (at least, at first) than concrete, but they are basically impractical. There is not a commercial floor covering available that can withstand chemical spills in a lab where strong mineral acids are routinely used. Moreover, the cracks between the tiles can catch and hold minute droplets of spilled mercury, creating a potentially serious vapor hazard.

Heat and air conditioning are usually provided by forced air systems that service the entire building. Occasionally heat is supplemented with steam or hot water baseboard units along outer building walls. Without any additional planning, these forced air systems are inadequate for the wet chemical laboratory area, which requires a large volume of forced (and in winter, heated) make-up air when hoods are in operation. An average laboratory requires at least 4 to 8 complete air exchanges per hour when the hoods are off, but this rises dramatically with the hoods running. And even with an adequate make-up air design, laboratory doors must be equipped with louvers to help balance the air supply. If particulate contamination proves to be a problem, final filters must be fitted to the room air vents and replaced in a regular maintenance program.

Utility service to the laboratory must be viewed differently as well. Power requirements are greater and more diverse than for an office area, and certain rooms will need specially stabilized line voltage. Outlets for 110 V, heavy-duty 110 V, and 220 V are common. Certain instruments may require cooling water at high pressure, and so adequately sized cold water pipes must be part of the design.

Sewage handling from a laboratory requires a great deal of planning, including close consideration of all municipal and state ordinances. Borosilicate glass sewage pipes are the best choice, resisting most problem chemicals, but the connections have very tight tolerances and installation and replacement require considerable skill. High-silicon iron (e.g., Duriron) is a less desirable alternative, as is polyvinyl chloride. Some laboratory drains empty into an on-site neutralizer or other waste treatment facility before the effluent passes into a sanitary sewer system.

A central water still (or a reverse osmosis system) is an important part of the building design if high-purity water needs will be great enough to justify the cost. Such facilities are often part of R & D facilities where other technical needs for distilled water supplement the metals analysis requirement. The minimum size for a central still should be a unit that produces 5 or 10 gal (19 or 38 L) per hour. Any smaller size should be located in the analysis area and reserved for its use alone. A central still should be sized for the needs of the entire facility. Too large a capacity may risk contamination and CO_2 pickup. Too small a design may result in warm water, which is often in short supply.

Water from the building mains should ideally be pretreated by large-capacity, mixed-bed ion exchange columns *before* it enters the still. This scheme virtually eliminates the frequent cleaning of tap water salts from the still boiler, which would otherwise be a regular maintenance headache. Distilled water from the central still should be collected in glass-lined sealed reservoirs [100 gal (378.5 L) or larger]. These containers may be linked in series to a gravity-fed system of plastic (or high-quality stainless steel) pipes for distribution throughout the building. The reservoirs should each be fitted with an overflow and a sealed UV lamp to prevent the growth of algae and bacteria. Such a system is conveniently located in a service loft or roof shed with easy access by maintenance and repair personnel.

Of course, floor loading factors must be taken into account since considerable weight will be involved. Since the preliminary mixed-bed columns will have to be replaced every few weeks, they can be located most conveniently on the laboratory level, where they can also provide a plentiful source of reasonably good water for uses less critical than those requiring distilled water. Also, some metals analysis operations and much environmental work will require very high-purity water produced by recirculating polisher systems in certain laboratory rooms fed by the distilled water pipes. Table 1–1 lists some typical purity levels encountered when using different sources of water.

TABLE 1–1—Typical water purity levels.

Source	Resistivity, megohm-cm, 25°C	Total Solids, mg/L
A. Tap water (A)	0.003	200.
B. High-capacity deionizer system (A + B)	1.0	20.
C. Tin-lined still (A + B + C)	2.0	0.6
D. Recirculating polisher (A + B + C + D)	18.0	1.4[a]

[a] Based on work by the author. The increase in dissolved solids may be due to compounds flushed from the polisher resin.

Certainly all laboratories will need a natural gas supply—for burners, hot plates, and glass-working torches. Some of the latter require high flow and thus a mains pipe of sufficient size. Fire assay labs may need even larger pipes to supply gas-fired muffles. Some labs are designed with color-coded and labeled wall tap service for all common gases. These are fed by banks of cylinders connected to manifolds in some outdoor, roofed, and fenced area near the building. Sometimes gases are stored as liquids in large outdoor tanks, and the high-purity expanded top gas is used to feed lines in the building.

Special attention must be paid to ensure leak-free connections when the system is installed. If flammable or toxic gases are to be part of a piped system, extra scrutiny needs to be given to the system design, which in this case should include strategically placed sensor alarm systems to warn of leakage. Piping such gases can only be justified by anticipated high-volume usage. Only proper piping material must be used (e.g., all use of copper must be avoided in acetylene systems to avoid the formation of explosive compounds). Piping materials must also be chosen to minimize corrosion and contamination. All piped gas systems should be designed in a manner that allows easy maintenance access to all parts of the system.

Central steam or vacuum lines are seldom useful in inorganic analytical labs, and these utilities are best provided by equipment located in laboratory rooms where these services will be needed. Similarly, central supplies of chilled or near-boiling water, while occasionally useful, are luxuries that most labs can best generate locally.

Spectrometry labs make special demands on building services, including special electrical circuits and humidity control. In these rooms, continuous temperature and humidity monitors may be needed. Raised floors for underfoot cabling are common, and a halon dump emergency system for electrical fires is a frequently employed precaution.

Safety is a major concern for the entire laboratory facility, of course, and the building plan must meet not only local fire codes, but must also incorporate design features derived from a detailed study of the anticipated use of the work areas. Lab doors should swing out into the hallway rather than the reverse. To avoid disruption of traffic in the corridor, the best design utilizes a recessed vestibule at each doorway.

Floor plans should include unimpeded routes to clearly marked exits and strategic placement of smoke detectors, fire alarms, fire hoses, and emergency lighting. Specialized emergency equipment, such as self-contained breathing apparatus and stretchers, should be stored at well-marked locations outside, but adjacent to, work areas. Fire exits should be well marked, and emergency evacuation routes and rally areas should be prominently posted. Some locations may require a sprinkler system, although this should be avoided in situations where certain chemical and electrical fire hazards exist. Safety design is discussed further in the sections below, which deal with certain specific work areas.

TYPES OF METAL ANALYSIS LABORATORIES

Each laboratory facility will have special needs requiring a different array of specialized rooms for metals analysis. These can be broadly categorized by the nature of the service they are expected to provide: hot metal control, raw material verification, finished product certification, and research support. While some labs are engaged exclusively with only one of these activities, most perform two or more, requiring a hybrid design.

Hot Metal Control

These laboratories operate under extreme time constraints, so the greatest emphasis is placed upon efficiency (Fig. 1–3).

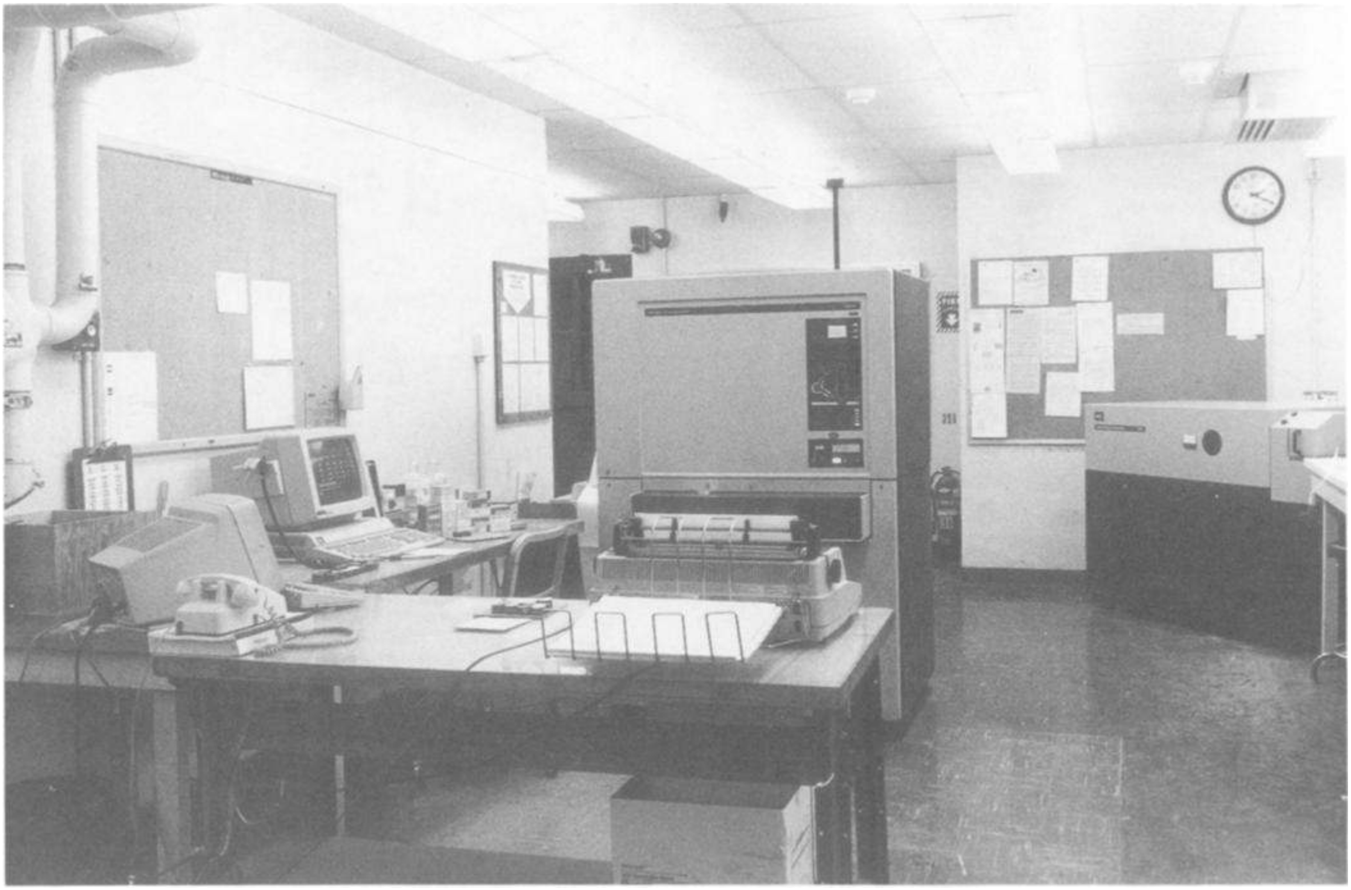


FIG. 1–3—A modern control laboratory.

They are all extensively computerized and often more closely resemble data processing centers than chemistry labs. They also generally combine highly sensitive equipment with a surrounding hostile environment of dirt, heat, and vibration, so that an extreme measure of planning must go into their design. Since a sample of chilled hot metal must be rapidly transported to the laboratory, sometimes by courier, often by a pneumatic tube system, these labs are frequently located adjacent to the melt shop floor.

A typical arrangement might consist of: a sample preparation room; a "combustion" or hot extraction lab containing equipment for the determination of carbon, sulfur, nitrogen, oxygen, and hydrogen; an X-ray fluorescence lab; an optical emission lab; perhaps a computer room; a sample storage room; and an office area. The financial implications of instrument failure can be extreme in this sort of endeavor, and so complete back-up systems are common.

The rooms must be designed as a vibration-damped, dust-free, air-conditioned oasis with a spike-free electrical power supply. Occasionally highly specialized needs introduce other equipment into this environment—mass spectrometers for trace constituents or even solution-based techniques like inductively coupled plasma-optical emission spectrometry (ICP-OES), with their attendant sample preparation requirements, but these are rare except for the most time-tolerant metallurgical processes. The current apex of hot metal control, still at a nascent stage, is the robotic or "container" lab (Fig. 1–4). Here the entire analytical process including sample preparation, instrument calibration, and sample measurement is conducted without human intervention.

Purchased Material Verification

This category includes two quite separate industrial situations. In metal alloy production, raw material labs analyze ore, coke, limestone, refractories, scrap, ore concentrates, process solutions, and various furnace charge materials. In manufacturing facilities, purchased alloys are analyzed to verify their composition. The two types of laboratory are quite different in their function and intent, but they share a common rationale in that both are designed to confirm that material specifications have been met, and both are usually under somewhat more tolerant time constraints. In short, both types of laboratories are designed to provide data on whether a particular material is usable for a production process.

Here the features of a chemistry lab begin to emerge, although these facilities are often heavily instrumented. Since there is time for sample preparation, solution-based tech-

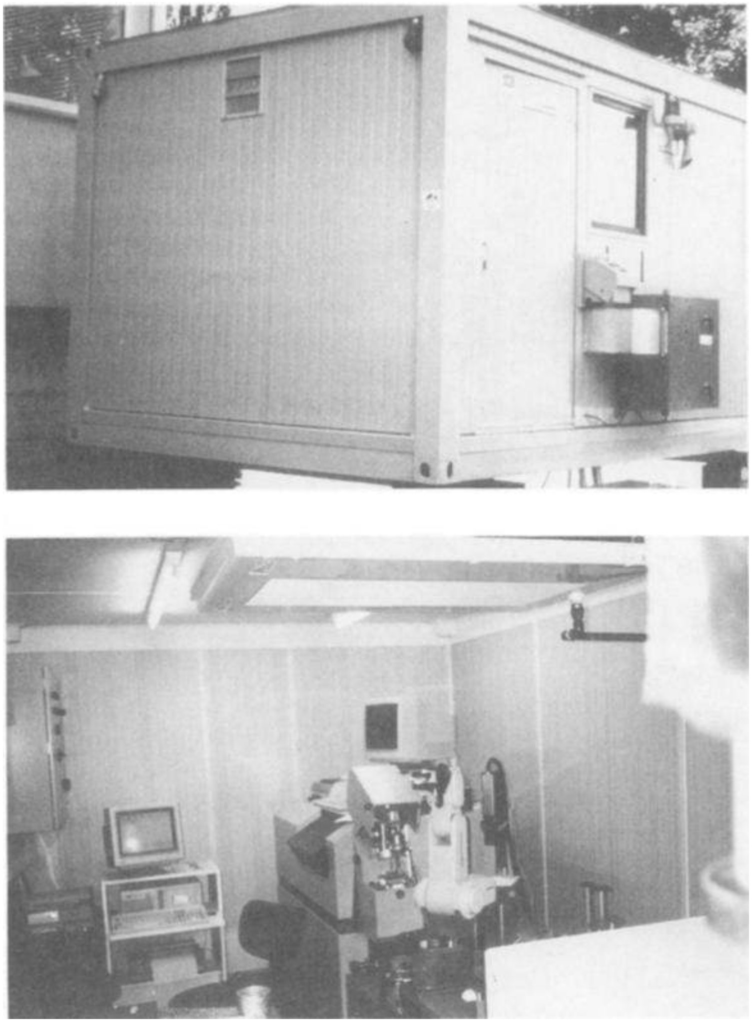


FIG. 1-4—A robotic "container" laboratory (top: external view; bottom: inside view). Photo courtesy of Fisons Instruments.

niques are common but usually not dominant. X-ray spectrometers and optical emission spectrometers are frequently sequential, not simultaneous, to allow some flexibility in line selection. The sample preparation area may include grinding and pulverizing equipment, milling machines as well as drill presses, and diamond saws as well as abrasive cut-off wheels.

There will probably be a hood or two and some reagents and glassware, as well as a microwave digestion system. There may be equipment for melting alloy buttons and perhaps an automated fluxing apparatus to produce molten salt disks. Flame atomic absorption and solution ICP-OES are common, while graphite furnace atomic absorption is, perhaps, less so in this environment. It is here that the semiquantitative survey by optical emission can be most effectively employed. The size and personnel requirements for these labs vary widely. Recent developments on the quality assurance front have actually led to a decline in the number of these facilities. As consumer industries audit and accredit vendor industries, they learn to rely on the analysis that accompanies incoming material (as well as on their own legal staffs).

Finished Product Certification

This lab assigns a final compositional signature to a commodity, declaring the exact elemental makeup of what is being offered for sale. In some metals industries, more time and a greater variety of equipment are required than for hot metal control. X-ray and optical emission direct readers are frequently supplemented with trace analysis equipment like graphite furnace atomic absorption spectrophotometers or, possibly, a glow discharge mass spectrometer. Special high-sensitivity optical emission techniques (hollow cathode or carrier distillation, for example) might be called for. There is likely to be at least a small wet lab where samples are prepared for flame and electrothermal atomic absorption (AA) and possibly ICP-OES and inductively coupled plasma mass spectrometry (ICP-MS) as well.

R & D Support

If hot metal control is the epitome of speed and efficiency, R & D support is the epitome of finesse and versatility. These labs must be prepared to analyze all the oddball samples, determine all the nonroutine analytes, and measure all the unusual concentration levels that an organization might require. They are often engaged in research of their own— methods development or process monitoring—as well as providing analytical support for metallurgical product and process development. Sometimes they oversee other corporate labs by administering an interlaboratory test program. Sometimes they develop in-house standard materials for calibration and verification. In the absence of separate environmental and industrial hygiene analysis laboratories, these functions may be absorbed as well. If there is a last refuge of traditional classical wet chemistry, it is here.

There are usually several wet labs with considerable hood and bench space and an extensive stock of reagents and glassware. There may be a balance room and perhaps a small instrument room where UV-visible spectrophotometers, polarographs, and other equipment find refuge from corrosion. Of course, large instruments abound as well, but they are generally selected for versatility rather than throughput. Thus, sequential optical emission spectrometry (OES) and X-ray fluorescence (XRF) are the most common choices.

One might also find here a number of state-of-the-art instruments performing specialized jobs or being evaluated and calibrated for eventual transfer to a production environment. If organic analysis (coatings work, for example) is done at all, it will likely reside here, and a room or two may be reserved for gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS), high-performance liquid chromatography (HPLC), and Fourier transform infrared spectometry (FTIR) and other instruments and the associated sample preparation. While some labs of this type maintain their own "drill room"—sometimes an elaborate affair with several drill presses, milling machines, crushers, and grinders—others rely on a centralized machine shop to provide properly prepared samples.

THE LABORATORY ROOMS

Metals analysis laboratories of all types and combinations are assembled from a small selection of basic room patterns. The size and number of each room pattern must, of course, be tailored to each organization's needs as determined from the anticipated nature and quantity of the work. Some module styles may not be required at all, while others may be required in sizeable numbers, and for some tasks the best course will be to combine room patterns.

Office Areas

There is little that distinguishes the office area in a chemistry lab from other types of business offices. In early steel mill control labs, the chief chemist's office was an inner sanctum of comparative calm amid the bustle of laboratory activity. It was usually adjoined to the offices of the chief clerk and the lab secretary, who handled the considerable paperwork associated with the operation of a large laboratory. Today a laboratory information management system terminal is likely to sit on the lab manager's desk. Such a system—part of a local area network of computers throughout the chemistry lab—is likely to be linked to a larger mainframe system for transfer of chemical composition data to a central certification file.

Today banks of filing cabinets are being displaced by small rows of diskette and magnetic tape records. In R & D labs, in particular, a "bull-pen" of office cubicles may be reserved for analysts and professional staff, although in many cases desks and files are kept in the work areas themselves. There are convincing arguments for both arrangements, and some chemists have the luxury of two desks. Regardless of the exact layout, it is important to provide clean, well-lighted, and quiet refuge where workers can calculate and enter data, write reports, and study. Some labs maintain a mini-library—often a satellite of a corporate or R & D library— for the analysts' use. And this is likely to include a copy of the lab's quality assurance manual, as well as copies of reference texts, which are in frequent use.

Balance Room

(With apologies), lab planners must *weigh* the need for a balance room. Early labs were often dirty, dusty places, prone to noise and vibration from the operation of nearby heavy machinery. Today many lab environments are sufficiently isolated from drafts, contamination, and vibration to allow analytical balances—even semi-micro- and microbalances—to be located in the analytical work areas. If this course is taken, it is still usually advisable to provide a balance table or shock-absorbing platform to isolate the balances from floor tremors and to choose an area of the lab room well clear of hoods, sinks, hallway doors, and forced-air vents.

The major problem with this scheme is likely to be corrosion. While modern electronic analytical balances are designed for use in a chemically hostile environment, they *will* corrode in the presence of acid fumes, and the potential for an expensive accident is always present. Another argument in favor of having a balance room is that it can also serve as a central repository for primary and secondary standard materials—alloys, high-purity metals, oxides, and other compounds—anything that is regularly selected and weighed for calibration, matrix synthesis, or the validation of a procedure. If a balance room is decided upon, its placement should be selected to provide a central location so that weighed samples need not be transported long distances.

It should also be as far removed from constant or intermittent sources of vibration as practical planning will allow. Sometimes special features can be incorporated in the building design to control vibration in a balance room. Certainly, grinders, forges, presses, or other heavy equipment should not be in use in any room with an adjoining wall. Forced-air heating and air conditioning flows must be filtered, and, if the central filters are inadequate, final filters must be installed in the balance room vents. If this approach is necessary, a regular program of filter change must be established.

The size of a balance room is, of course, directly related to the size and scope of the associated laboratory area. Laboratories generally keep and maintain more balances than they really need. This is because analysts tend to favor certain balances and to associate a specific balance with certain work assignments. This personal proclivity aside, there are usually legitimate reasons for keeping a variety of balances on hand based on differences in capacity, sensitivity, and speed and ease of use.

The standard laboratory balance—the workhorse of the metals analysis lab—has a maximum capacity of about 160 g and an analytical tolerance of ±0.2 mg, readable to ±0.1 mg. The original versions of these instruments were double-pan, sapphire knife-edge devices. The earliest models required a set of calibrated weights and a platinum wire rider to establish the last decimal place on a ridged, calibrated balance beam. Later versions included the keyboard selection of weights or incorporated the so-called "chain-o-matic" principle, all of which simplified the weighing process.

A few of these instruments remain in use today—a testament to their accuracy and to how efficiently they can be used in experienced hands. The mechanical single-pan balance became common in the 1960s and represented a breakthrough in convenience and speed. Many of these instruments are still in current use, as are semi-micro- (readable to ±0.01 mg) and micro- (readable to ±0.001 mg) versions. The modern electronic balance emerged in the 1980s and is still being refined.

Today's versions are similar in weight limits, tolerances, and readability to the best mechanical balances and incorporate many features that were unimagined only a few years ago. Many of the room environment concerns of the past are now automatically compensated for. And, no doubt, future developments will carry this trend further. Most laboratories, however, cannot afford to change their balances with each advance in the technology. And so the balance room is often an interesting mix of technology spanning many decades.

The heavy marble balance tables are probably still a good idea to control low-frequency vibration, even with the state-of-the-art balances. These tables are expensive, however, and a roomful of these monoliths must be planned for in the weight loading design of the room's floor support. The balance room should be equipped with comfortable, adjustable height stools and adequate levels of fluorescent lighting. Window light is a bad idea because of the effect of thermal currents on the most sensitive measurements. Any windows in the room should be fitted with shades to prevent an errant sunbeam from falling on the balance pans.

If balances are arranged along opposing walls, adequate aisle space should be provided to allow room for the passage of lab carts. Top-loading electronic balances, like their mechanical counterparts, the "trip" balances, do not belong in a balance room. Their primary functions are for weighing reagents and the recently popular practice of aliquotting by weight. As such, they belong in suitable locations in the lab rooms where the analytical work requires their use. In general, reagents and solutions should be kept out of the balance room as much as possible. Everything practical should be done to ensure a contamination-free environment in the balance room. In particularly dusty buildings, special air filters and "tacky" floor mats at the entrance may be called for. In all cases, a regular program of "housekeeping" for this area should be established.

Small Instrument Room

Arguments in favor of a balance room also apply to establishing a room for spectrophotometers, polarographs, ion chromatographs, and other benchtop-sized instruments. In addition to corrosion damage, instruments with exposed optical systems tend to degrade in lab work areas due to the formation of UV-polymerized films of organic vapors on lenses, mirrors, and gratings. Also, it is frequently convenient to line stabilize the electrical circuits in an entire room where instruments that require stable line voltage will be used and where equipment like pumps, which may produce line surges, will *not* be used.

The exact array of equipment included in a small instrument room will, of course, reflect the nature of the analytical work, but ion, gas, and liquid chromatographs, IR spectrophotometers, and other equipment that does not require venting and that generates few chemical fumes is probably appropriate. Thus, equipment like pH meters, electrolytic plating cells, and mercury cathode cells belong in the wet chemical laboratory and not here. A sink and a small hood and especially a sink *in* a small hood may be useful in this room, especially if much organic work is to be done. As in the balance room, aisle space should be adequate for the passage of carts.

The "Spec" Labs

The number and size of the spectrometry laboratories must be tailored to reflect the instrumentation expected to be employed immediately and the anticipated expansion of instrumental needs for the future. The reason is that, despite significant downsizing in recent designs, spectrometers require significant space and have specialized service and utility requirements. It is much easier to install a new spectrometer in an area set aside for it than to convert wet labs, storage space, or an office area into a spectrometry lab.

Of course, each type (and even model) of spectrometer has its unique needs for space, services, and environment. A large laboratory will want separate rooms for optical emission (one for arc/spark and one for solution plasma), X-ray fluorescence, atomic absorption (one for flame atomic absorption (FAA) and one for graphite furnace atomic absorption (GFAA), and mass spectrometry. Smaller labs might settle for grouping two or three instrument types in one room. Grouping instruments requires some forethought, however, because some instruments are more compatible than others. The air-acetylene or nitrous oxide-acetylene flame of an atomic absorption premix burner is more likely to affect room temperature control than the hotter but much more confined optical emission sources, even inductively coupled plasma (ICP) and direct current plasma (DCP). An X-ray fluorescence unit requires personnel to wear film badges to monitor radiation exposure. Large mass spectrometers and Zeeman background corrected GFAA instruments will generate magnetic fields that may affect the operation of other instruments.

If instruments must be grouped, it is best to combine solids-based techniques in one room and solution-based techniques in another. Thus, for example, an optical emission direct-reader, a sequential X-ray, and a glow discharge mass spectrometer might share space in one room, while a flame AA, a graphite furnace AA, and an ICP-OES might occupy another room. The former group might share adjoining belt or disk-sanding equipment, perhaps even darkroom facilities, while the latter group might share an adjoining wet chemical preparation area.

X-ray fluorescence spectrometers require a source of cooling water and appropriate electrical service, but little else except possibly some cylinder-supplied gases such as helium or "P10" counter gas. The room must be posted at all doors as a radiation area. If the instrument is designed to operate overnight in an unattended automatic mode, it is essential that an "X-rays On" light be clearly visible without entering the room. Of course, the room should *not* contain a night watchman's turnkey station and should be avoided on regular rounds. As with all overnight operations, a list of emergency phone numbers should be prominently posted, in this case just outside the room.

An atomic absorption laboratory may contain several AA units and a rack or cabinet for hollow cathode and electrodeless discharge lamps.. If there are multiple instruments, they may be semi-permanently configured into flame, graphite furnace, cold vapor, or hydride generation modes to save the time and the possible trouble involved in conversion. If acetylene, nitrous oxide, argon, and air are to be supplied by cylinder, a designated area for the tanks, with appropriate anchoring equipment and preferably out of the aisle way of the room, should be part of the room plan.

Adequate space to transport and maneuver cylinders should be incorporated in the floor plan design. If in-wall service for these gases is to be provided, great care should be given to the acetylene and nitrous oxide systems layout. Copper or plastic tubing or pipe should be avoided for the acetylene lines. Copper may eventually form explosive compounds, and plastic may dissolve in the acetone present in the acetylene cylinders. Both acetylene and nitrous oxide gas manifolds should be located in a covered, secured fenced area outside the building.

Both systems should be fitted with valves designed to automatically switch between cylinders or between banks of cylinders when inlet pressure drops to a preset level. A regular program for checking and replacing the spent cylinders must be established. The systems should be regularly inspected for leaks, and alarm systems should be incorporated in the design. The air supply should be final filtered of oil and dust at or near the wall tap. Small exhaust hoods must be provided just above each atomizer on each AA instrument. These may be connected to a common manifold provided there is adequate air velocity at each outlet. Stainless steel is recommended for at least the lower portions of this system since it will be exposed to heat and corrosive vapors. Cooling water is needed for the graphite furnace instrument, and connections should be of a permanent or "semi-permanent" design to prevent disastrous water damage from a loose connection. The room should be posted with a strong magnetic field warning if the GFAA has a Zeeman effect background correction system.

An inductively coupled plasma optical emission spectrometer (ICP-OES) laboratory will have similar requirements to an atomic absorption lab. The hood exhaust above the ICP torch is often of a more robust design than those used for AA simply because the larger ICP units are less likely to be relocated. The hood exhaust must be adequate to handle the significant volume of argon that some torch designs employ. The argon can be supplied from cylinders, but the usage rate usually justifies either a liquid argon tank or an in-wall piped system supplied by a bank of cylinders.

The top gas from a liquid argon tank is high purity and will supply the needs of all but the busiest labs, but the tanks are heavy and difficult to transport. If the instrument may be expected to sit idle for extensive periods, a liquid argon tank is a bad choice since the warming liquid will eventually begin to vent gas and all the argon will be lost through the safety valve. Because of this venting, liquid gases must be stored in an area of good air circulation and preferably outdoors since a venting tank can rapidly displace the air in an enclosed space.

Arc/spark optical emission laboratories are usually regarded as permanent, dedicated installations, custom designed for an anticipated type and level of work. Electrical connections for the source units are likely to involve special wiring, and the excitation chambers must be vented with draw-out ducting. Close access to an area where samples can be belt- or disk-sanded must be provided, although it is less desirable to have these facilities in the same room as the instruments. High-purity argon is required in many installations, and here liquid argon systems are especially desirable since traces of oxygen in the arc chamber atmosphere are a problem.

All optical emission instruments are adversely affected by room temperature fluctuations, although newer designs have the optical tank thermostatically maintained with heaters above the room ambient. Room air humidity can be a problem for air excitation. Some facilities have opted for a completely separate environmental control system for their optical emission labs in order to closely control these variables. Dynamic temperature and humidity control is often monitored with continuous recording readout of room air sensors.

Despite the relatively recent development of solid-state, pixel-based detectors, many photographic plate installations are still in place. These require adjacent darkroom facilities for the development of plate spectra. Darkrooms require either light-trap entrances or an "in-use" indicator light, and having both is preferable. They should be painted with light-colored walls, and they should be provided with incandescent lights as well as "safety" lights. Fluorescent lights are a poor choice since the phosphors in the tube may luminesce even after the current is shut off. Also, the frequent switching that occurs in a darkroom is uneconomical for this type of lamp. Darkrooms also require a source of distilled water, an impervious flooring material, and good ventilation.

Mass spectrometers require a level of vacuum that the inorganic analyst may be unaccustomed to dealing with. Oil diffusion pumps, turbomolecular pumps, and gettering pumps have special maintenance problems associated with them. Spark source units require equipment to machine sample electrodes. Old-style photographic plate systems require the same darkroom facilities that old-style optical emission systems utilize. Even with newer instruments, "down time" is a frequent problem and so there must be a scrupulously clean area where critical components can be disassembled and cleaned.

The Wet Lab

There is no area in a metals analysis facility that requires more planning than the area where classical chemical analysis is performed. This statement may surprise some people who may view the dabbling with beakers and chemicals as a low-tech anachronism. On the contrary, the variety and complexity of the tasks performed there and the potential for serious accidents require that every detail of a wet chemical laboratory be carefully studied.

The first step, as in every design plan, is to anticipate every operation that will likely occur in the room. For classical wet chemistry, this is a task that nearly defies analysis, but there are certain broad outlines that can be traced. All such facilities will require hoods and acids and close access to the balance room where samples are weighed. Labware storage and reagent stores must be close at hand. Safety equipment, like eyewash stations and emergency showers, must be provided only steps away from work areas. These are basic requirements even if no chemistry beyond sample solution preparation is anticipated.

A lab that will do separations will require significantly more hood and bench space; reagent storage requirements and labware needs will increase; and space for specialized equipment, like ion exchange columns and mercury cathode electrolysis devices, will have to be provided. A full-fledged classical analytical chemistry lab, however, is very much like a chemical research and development lab in that space and equipment must be provided for techniques and processes that are only infrequently used. And safety planning must accommodate situations that arise infrequently.

Fume hoods are the most costly and most essential part of a wet chemical analysis lab. By far the best material of construction for metals analysis work is Alberene stone, a form of soapstone quarried in Virginia. It has high strength, good thermal shock resistance, and low liquid absorbency. A distant second choice are various forms of impregnated hard sandstone sold commercially under names such as Kemrock, Labrock, Imperial Stone, Shelrock, and Metrock. These generally have low absorbency, but do not withstand much heat. Even less desirable are cement asbestos compositions, such as Kemstone and Colorlith, that have high liquid absorbency.

Some labs make do with hoods constructed of high-quality austenitic stainless steel. These have the advantage of comparative ease of construction, and they can be readily fitted with a tempered-glass paneled sliding window to further restrict airflow. Their drawback is corrosion, which can be a problem even for highly resistant alloy compositions (such as commercially pure or palladium-bearing titanium). Also, the glass panel is a dangerously inadequate safety shield and should never be used as such when an explosion hazard exists.

Today, most laboratory building designs can accommodate hoods located anywhere in a laboratory room, although the most common plan involves hoods placed next to the hallway walls. This is so that hood stacks line up in an attic way above the lab level, where exhaust fans and motors are arrayed for maintenance, service, and replacement. Some labs have roof exhausts for each hood; others combine exhausts in a manifold. Frequently there are problems with the exhaust placement due to fumes reentering the building through air intakes, especially with certain directions of wind movement. Any stack exhaust design must address this potential problem. A few labs have incorporated water scrubbers in their design to meet local emission regulations. These systems are effective, but quite elaborate in design, involving time delay relays and recirculating pumps.

Perchloric acid is used in abundance in the metals analysis laboratory. Indeed, it is difficult to imagine most metals labs operating, as many other types of laboratories do, with a regulatory ban on the use of perchloric acid. For this reason, all or most hoods must be designed with built-in wash-down facilities. This extra expense is essential since the buildup of perchlorate salts in hood stacks is a severe explosion hazard.

A proper perchloric acid hood is designed with water sprays at the top of the stack and in the hood area and with a recessed trough and sewer drain across the back of the hood work surface. A regular wash-down procedure, somewhere between weekly and biweekly, must be maintained. In labs where perchloric acid fuming is employed intensively, an even more frequent program is called for. Such a program affords an opportunity to maintain an accompanying program of housekeeping in other areas of the laboratory as well.

If there are other types of hoods in the laboratory, they must be on a completely separate exhaust system. And they must be prominently marked with signs indicating that they are not for use with perchloric acid. The materials used for hood stacks, fan housings, and impellers vary widely; cost and corrosion resistance are the selection criteria. Materials as varied as high-silicon cast iron, austenitic stainless steel, and even titanium alloy have been used for some hood components.

The hood surface itself should be designed with a front ridge that prevents the dripping of spilled liquids out of the hood area. Most hoods are designed with a back baffle that facilitates the airflow by restricting the opening to the stack and handles both heavy and light fumes equally effectively (Fig. 1–5). Hot plates may be either gas or electric. Gas models must stand above the hood surface; they have the advantage of higher temperatures and more adjustable heating levels. Electric hot plates may either stand above or be built into the hood work surface. Built-in hot plates have the advantage that beakers or flasks may be slid on or off the heat without lifting. In any case, the hot plate should occupy one third or less of the total work surface of the hood.

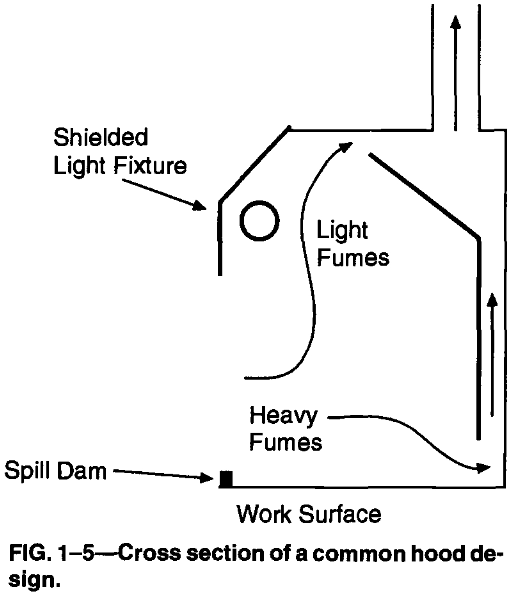


FIG. 1–5—Cross section of a common hood design.

Air velocity over the face of the hood should be in the range of 60 to 125 linear feet (18.3 to 38.1 m) per minute. The exact rate for a given hood design must reflect its intended use and location. Nearby doors can generate drafts that can cause fumes to blow out of a hood with an otherwise adequate face velocity. Thus, a degree of overdesign may be called for. Hoods should be fitted with electric, gas, and possibly air and vacuum service, all controlled from outside the hood work area. An externally controlled water supply for a built-in cup sink is essential. Light should be supplied by a shielded fixture also controlled from the outside. Electrical connections, lights, switches, and receptacles must be of a sealed, explosion-proof design.

There are other types of hoods that may be required in the wet chemical lab. Canopy hoods are necessary over muffle furnaces and are useful or essential in a variety of other situations. They are usually constructed of austenitic stainless steel sheet. They should be designed to overlap the fume-producing region by at least 25% of the vertical height from the source of the fumes, and the stack velocity should be 40 to 100 ft^3/min (1.1 to 2.8 m^3/min). Canopies in excess of 4 ft (1.2 m) in length will require two stacks. Trace or ultra-trace analysis may require a Class 100 laminar-flow hood. These special systems have integral high-efficiency filters to flush the work surface with air from which particulate contamination has been removed. Fumes are exhausted through louvers at the back of the hood. These hoods are not suitable for use with perchloric acid and should be posted with that warning.

Lab bench designs vary widely and are closely related to the room size and the building's service main design. "Island" and "peninsula" patterns are the usual choices for center-room benches, with wall-hugging benches running perpendicular to the building corridor (Figs. 1–6 and 1–7). The aisle-way distance between benches should be 4 to 6 ft (1.2 to 1.8 m) to allow room for lab cart movement and other activity. Services usually enter a lab from right angle taps from hallway ceiling runs or from vertical "pipe chases" in corridor closets.

Gas, air, and electrical taps should be provided at frequent intervals along the wall-bench service panels and either along a service box mounted at the back of the work surface or from fixtures mounted in the work surface for the center-room benches. Water taps and cup sinks are a good idea and are frequently indispensable, but if they are not used the drain traps will dry out and sewer fumes may enter the lab. The bench tops themselves should be made of the best material a lab's budget will allow. As with hoods, Alberene stone is the material of choice for most metals analysis laboratories.

And as with service outlets, one usually finds that there are never enough sinks in a wet chemistry laboratory. If some thought is given to the number and placement of sinks, time can be saved and safety can be enhanced. A good rule of thumb is to plan on one sink for every 25 to 30 linear feet (7.6 to 9.1 m) of bench work surface. Sinks should be as near to the fume hoods as possible and preferably under a canopy hood themselves. Figures 1–6 and 1–7 show block diagrams of two possible wet chemistry lab arrangements.

Sinks should be provided with a sizeable drainboard surface of a material that is noncontaminating and easily cleaned. Ribbed glass or plastic are suitable materials, although an Alberene stone surface will work since most chemists will cover it with rubberized netting before use. The sink bowl itself may be rubber or stone (in which case it should also be lined with the rubberized netting).

If the building has a central distilled water supply, there should be a self-closing distilled water tap next to the hot and cold water taps. If there is no central distilled water supply, a spigotted plastic carboy of distilled water should be mounted on a raised shelf above the sink. This can be refilled as needed from a plastic-lined 55-gal (208 L) drum on wheels using a small plastic-lined pump. The sink is also one good strategic location for an eyewash station, especially if it has been optimally located near a hood.

Above and around the sink are the ideal locations for pegboard drying racks. If ultra-high-purity distilled water is needed, a recirculating multi-bed polisher system can be mounted on a panel above the sink. Fed from the tap distilled water lines (or from the carboy), these systems produce 18 megohm-cm filtered water. A few labs meet their ultra-high-purity water needs by feeding distilled water into an all-glass still that can be similarly mounted near a sink. Both types of system should be carefully installed to ensure that electrical connections remain dry under all situations.

Reagent storage is a major concern for both safety and work efficiency. Acids should be kept in stone or Teflon-lined cabinets below bench level. There is usually little justification for keeping more than two or three 2-L bottles of most common mineral acids in the lab at any given time. Some labs are under local code or insurance restrictions in this regard. Cabinet storage of solid powder or crystal reagents should be in alphabetical arrangement within separately stored categories. Thus, oxidizing agents, reducing agents, acidic salts, ba-

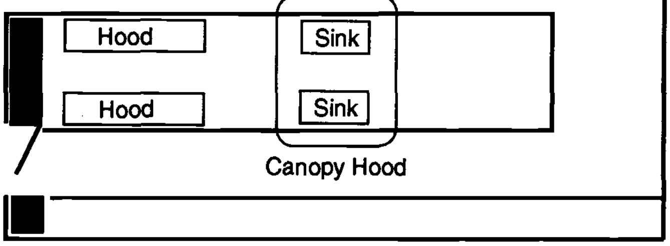


FIG. 1–6—A peninsular bench plan.

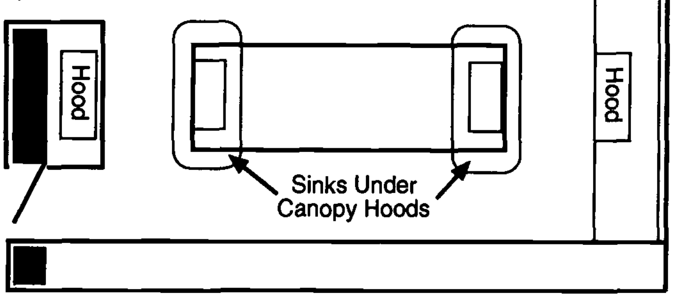


FIG. 1–7—An island bench plan.

sic salts, neutral salts, and organic reagents should be segregated. Organic solvents, flammable or not, should be stored in special-vented, electrically grounded, self-closing steel cabinets that stand on the floor. Refrigerators used to store solvents must be of an approved explosion-proof design. Prepared solutions must also be stored so that incompatibles (acids, bases, oxidizing, and reducing agents) are segregated. Local ordinances and insurance regulations will determine volume limits and the approved forms of storage for all hazardous reagents.

Commercial spill-control kits for acids, bases, organic solvents, and for such special-problem spills as mercury and hydrofluoric acid should be stored either in the wet lab or in prominently marked hallway closets immediately outside the wet lab. Emergency showers are an essential part of the overall safety plan. Conventional wisdom holds that placement of emergency showers in the hallway immediately outside the wet labs is best since a contaminated worker is more likely to be seen and helped by co-workers there. Also, although only a step or two away, it removes him or her from the contaminated area where further injury might be incurred from fumes or other causes.

The "flushometer" style of an emergency shower will douse a worker with 30 to 40 gal (114 to 151 L) of water with each pull of the chain ring. Designs that incorporate floor drains beneath each showerhead are problematic since infrequent use will lead to dry drain traps and sewer fumes. A regular program that tests emergency showers (and eyewash stations) should be maintained and will serve to keep drain traps filled. Gas masks of appropriate design and sets of self-contained breathing apparatus should be maintained in marked corridor closets.

Each room on the laboratory floor must be supplied with fire extinguishers appropriate to the type of fire hazard likely to occur there. Carbon dioxide and dry chemical extinguishers are two types frequently employed for fire hazards in the wet analysis lab. There are also situations in which foam-type extinguishers are appropriate. Extinguishers should be regularly checked and promptly replaced with fully charged devices in the event of use. Other important fire and safety equipment that should be on hand includes fire blankets, stretchers, and fire hoses. In these and related fire and emergency control matters, lab planners must consult with local fire departments for advice and guidance.

Sample Preparation Room

Most metals analysis laboratories prefer to keep control of the sample preparation process rather than relegating the responsibility to either the submitter or to a central machine shop. Sample prep rooms range in scale and complexity from a simple hood, sink, and drill press, to what may be considered a small-scale machine shop/laboratory combination. Metal pieces are pickled in trays on hot plates in the hood, sometimes generating significant fumes, so a good hood face velocity is essential.

Acid and solvent use (the latter for degreasing) are intensive, so proper storage and disposal of these substances must be provided for. Major equipment may include a vertical drill press, a horizontal milling machine, a band saw, a reciprocating saw, an abrasive cut-off wheel (that should have its own vent exhaust if it can operate without water), sheet nibblers or punches, a trepanning machine, a diamond saw, a high removal rate (Swisher style) grinder, belt and disk sanders, a jaw crusher, disk or ball mills, and one or more forms of button casting machines. There is usually a sample log-in area which these days is likely to contain a PC and a bar code label printer. Often there is an adjacent storage area where the excess prepared samples are archived after all analytical work is completed.

Other Rooms and Areas

Knowledge and skills in scientific glassblowing are becoming rare these days, especially in inorganic analysis laboratories. Larger facilities may wish to retain an area where this work can be performed. It requires natural gas, compressed air, and oxygen. A large bench with significant space behind the worker is essential. The bench should have a raised edge to prevent tubes and rods from rolling off. Four-foot lengths of various diameter tubes and rods should be stored in a compartmentalized case designed for this purpose. If high-volume bench burners are to be used, it may be necessary to install a special large-bore natural gas pipe.

Most labs maintain an area for bulk or surplus reagent storage. It is especially important that all the fire, emergency, and spill-control equipment described for the wet labs be available in sufficient quantity here as well. Reagents must be segregated by category and an exact inventory maintained. Many facilities maintain a solvent storage shed for the bulk storage of flammable solvents. This is a locked metal structure in a fenced area some distance from the laboratory building; ventilation is provided with flame-arrestor screened vents. Here, as wherever flammable chemicals are stored or used, proper warning signs must be posted.

A lab may also need an area to store instruments and other equipment that, while not currently needed, may have some utility at a future time. The problem here is that these areas frequently become the lab's "attic," where outdated or broken machines accumulate and are forgotten. Proper housekeeping involves a yearly inventory of stored equipment so that items unlikely to be needed can be removed and discarded.

REFERENCES

The Design of Research Laboratories, Division for Architectural Studies of the Nuffield Foundation, Oxford University Press, London, 1961.

Lewis, H. F., *Laboratory Planning for Chemistry and Chemical Engineering*, Reinhold, New York, 1962.

Munce, J. F., *Laboratory Planning*, Butterworths, London, 1962.

Of Historical Interest

Meade, R. K., *The Design and Equipment of Small Chemical Laboratories*, Chemical Engineer Publishing Co., 1908.

Sisco, F. T., *Technical Analysis of Steel and Steel Works Materials*, McGraw-Hill, New York, 1923.

2

Equipment

TO POSE POLARIZED BROMIDES: while necessity is the mother of invention, one really cannot make a silk purse out of a sow's ear. In other words, there is an extensive array of paraphernalia associated with the metals analyst's work for which even the most innovative substitution simply will not do. It behooves the analyst, therefore, to know his or her tools and materials very well, to have them on hand, and to select among them judiciously.

Anticipation of needs, safety, and convenience are the key elements in any properly equipped laboratory, wet or "dry." In this chapter, however, the classical chemical analysis laboratory will be the sole focus. The reader is referred to later chapters on spectrometric and other forms of instrumental measurement and to the many excellent texts on the applied forms of those techniques (see Bibliography) for equipment needs in those areas.

The wet chemistry laboratory today still bears the stamp of its archetypical heritage. Like the alchemical laboratory, it is a vast assemblage of miscellaneous vessels and devices, although minus a few alembics and retorts and hopefully kept in good order. While this chapter will discuss much of this equipment, any attempt at an exhaustive survey would be futile (as, indeed, it was when the authors of *Applied Inorganic Analysis*—published by John Wiley & Sons, New York, 1953—came to the same conclusion).

The experienced classical analyst is usually a great collector of things that "might come in handy some day," a master at applying things to uses for which they were never intended, and a prodigious fabricator of special-purpose, single-use, usually odd-looking artifacts. Most of these types of objects are stored in the laboratory as well, sometimes for decades, and occasionally some are even used more than once—but here we must avert our eyes.

GENERAL LABWARE

Materials and Their Properties

Glass

Glass vessels are the most familiar form of laboratory equipment. *Borosilicate glass*, developed in 1912 and today known commercially as Pyrex or Kimax, has displaced all other compositions for ordinary lab use because of its low expansion, superior strain point temperature, and low cost. Admittedly, one will still find a few antediluvian flint or soda lime glass artifacts in some laboratories, usually as reagent bottles or large carboys—some may even be in use—but for all practical purposes, borosilicate glass is a baseline requisite, and one should not consider purchasing anything of lesser quality. Its superior thermal shock resistance makes it suitable for over 90% of all laboratory operations.

There *are* occasions, however, when borosilicate glass must be avoided. It is unsuitable for certain manipulations in silicon, aluminum, boron, sodium, or potassium determinations (such as the addition of hydrofluoric acid, hot phosphoric acid, or caustic) because these elements are major constituents of the glass. Usually acid solutions, with the exception of hydrofluoric acid or hot phosphoric acid, present no problems in borosilicate vessels except for determinations in the trace realm, where it is often best to choose another vessel material.

There are definite limits to the amount of thermal shock a borosilicate vessel can withstand, and these limits are inversely related to the wall thickness. For this reason, thick-walled, heavy duty glassware represents no advantage if it is going to be heated. The temperature limit for borosilicate vessels is usually the temperature limit of most gas or electric hotplates; they should not be used in muffle furnaces or other heat sources that can much exceed 450°C. Scratched borosilicate vessels are much more likely to crack when heated even at comparatively low temperatures. Scratched labware should be reserved for room temperature work or discarded. All volumetric glassware sold in the United States is of borosilicate composition. Its thermal expansion is considerably lower than soda lime glass, but still sizeable enough to bear close watching in the most accurate work.

The analyst must keep in mind that most volumetric labware is calibrated at 20°C and temperature deviations in use may require corrections. Pyrex 7740, the standard composition of borosilicate glass for laboratory use, can be distinguished from other types of glass if it "disappears" in a solution of 16 parts of absolute methanol to 84 parts of benzene (by volume). This test, based on matching the refractive index of 1.474, may occasionally be useful for glassblowers who deal with different grades of glass tubing, but it must always be conducted in a hood with proper safety protection due to the very high toxic and carcinogenic hazard of benzene liquid and vapor.

Corex glass (Code 0331) is an *aluminosilicate* composition with mechanical strength and scratch resistance superior to Pyrex. It is used principally in the manufacture of breakage-resistant pipets and centrifuge tubes. This equipment is a bit more expensive than its borosilicate equivalent, but should have a longer average service life. *Vycor* glass (Code 7913) is

TABLE 2-1—Glass labware composition and thermal properties.

Type	Soda Lime (Container)	Alkali Resistant, Boron Free	Alumino-borosilicate (Apparatus Glass)	Borosilicate Low Expansion	96% Silica	99.9% Silica
Common or Trade Name	Flint Glass	Corning 7280	Kimax N51A	Pyrex 7740, Kimax KG-33	Vycor 7913	Fused Quartz
SiO_2%	70–74	71	74.7	81	96	99.9
Al_2O_3%	1.5–2.5	1	5.6	2	0.5	. . .
B_2O_3%	. . .	. . .	9.6	13	3	. . .
ZrO_2%	. . .	15	. . .	. . .	. . .	. . .
Li_2O%	. . .	1	. . .	. . .	. . .	. . .
BaO%	0–0.5	. . .	2.2	. . .	. . .	. . .
Na_2O%	13–16[a]	11	6.4	4	. . .	. . .
K_2O%	13–16[a]	0.5	0.5	0.5	. . .	. . .
CaO%	10–13[b]	. . .	0.9	. . .	. . .	. . .
MgO%	10–13[b]	. . .	. . .	. . .	. . .	. . .
Coefficient of expansion, $\times 10^{-7}$/°C[c]	80–90	64	49	32	8	5.5
Strain point, °C[d]	500	578	538	513	900[e]	1000[f]

[a] Concentration of Na_2O and K_2O combined.

[b] Concentrations of CaO and MgO combined.

[c] The linear coefficient of expansion is the change in length in inches per inch, per degree centigrade change in temperature over the range 0–300°C. This value is a measure of thermal endurance.

[d] The strain point is the maximum temperature to which a glass can be heated without introducing permanent stress. A practical maximum temperature for routine service is always below this temperature.

[e] Short excursions to 1200°C.

[f] Short excursions to 1350°C.

a 96% silica material produced by chemically leaching the boron and sodium oxides from a fabricated borosilicate vessel, then firing the remaining porous silicon structure at 1200°C to achieve a pore-free transparent composition. While quite expensive, it is less costly than fused quartz, which it resembles in thermal properties, ultraviolet light transmission, and chemical resistance.

Vycor labware can withstand muffle furnace temperatures of 900°C and periodic excursions as high as 1200°C. Its thermal stress resistance is about four times better than Pyrex, so that barring gross negligence it is unlikely to crack due to thermal shock. Because the composition retains a little aluminum and boron, it is unwise to add hydrofluoric acid or caustic to Vycor vessels used in determining those elements. Vycor beakers, flasks, crucibles, and evaporating dishes are sold. Rod, tubing, and graded seals (to Pyrex) are available, but Vycor, like fused quartz, requires an oxyhydrogen or oxyacetylene torch to work and demands the special skills of the glassblower.

The ultimate level in glass labware is represented by the materials known variously as *fused quartz* , fused silica, vitreous quartz, or vitreous silica. These terms are often used interchangeably to refer to amorphous SiO_2 products of 99.9% (or better) purity. Frequently the term "vitreous silica" is reserved for the milky translucent version, which contains countless trapped microscopic air bubbles. This product finds use in the form of trays for conveniently transporting sets of crucibles or dishes in and out of muffle furnaces and as the shield tubes for high-temperature thermocouples. The water-clear transparent version is manufactured into a wide variety of dishes, crucibles, beakers, flasks, joints, and seals.

Both types are virtually impervious to thermal shock due to a coefficient of thermal expansion six times lower than that of borosilicate glass. A fused quartz vessel can be removed from a 1500°C furnace and quenched in ice water without cracking. Continuous use above 1150°C can lead to devitrification, which appears as a haze of cristobalite on the transparent labware, but this generally causes no problems. While fused quartz vessels are attacked by hydrofluoric acid, hot phosphoric acid, and caustic, the effect of these treatments adds no serious vessel-wall contaminants except silicon.

There are a few other glasses that the metals analyst may encounter in some laboratories. *Low actinic* or Ray-Sorb glassware is used to protect vessel contents from light wavelengths below 500 nm. Today this type of labware consists largely of borosilicate glass with a permanent red coating. While it is used extensively in biochemical analysis, as in vitamin assays, its use in metals analysis is confined to certain manipulations with silver, mercury, and gold determinations, and to the storage of light-sensitive organic reagents.

A form of *aluminoborosilicate* glass with good resistance to chemical attack, but with less resistance to thermal shock than low-expansion borosilicate glass, is sometimes employed for labware. At one time an *alkali-resistant/boron-free* composition (Corning 7280) was used in the manufacture of labware for special purposes, such as boron determinations. This high-zirconia glass is still in use in many laboratories, although it is very sensitive to thermal shock. When this labware breaks, it can usually be replaced with transparent fused quartz or polytetrafluoroethylene vessels.

Table 2-1 lists some frequently encountered laboratory glasses, their composition, and their relevant thermal properties. They are arranged in order of their thermal shock resistance.

Plastic

When the classic text, *Applied Inorganic Analysis* , was first published, plastic labware, with the exception of a few impractical Bakelite beakers, did not exist. Hydrofluoric acid was sold in wax or hard rubber bottles in those days, and if you needed to use it you had better have invested in some platinumware. Today, there are dozens of plastics in routine laboratory use, each with its special array of properties so that each can be tailored to a specific set of applications.

One of the most common plastics, polyethylene, is commonly found in three forms in the chemical laboratory. *Low-density polyethylene* is a highly branched polymer that is tough and somewhat flexible. *High-density polyethylene* has much less side-chain branching, resulting in a more rigid, but also somewhat more brittle structure. *Linear low-density polyethylene* is both tough and rigid. All three polyethylenes show good low-temperature chemical resistance. All three are translucent, and none can be heated except in a low-temperature water bath.

Polypropylene is similar to high-density polyethylene in some properties; as a screw cap material, it makes a leakproof seal for both low-density and high-density polyethylene reagent storage bottles. Beakers made of polypropylene are relatively inexpensive, but they must be heated in a steam or boiling water bath, and they are translucent. The material serves better in room temperature applications as funnels, vacuum filtration flasks, and other equipment, including volumetric flasks.

Polyallomer consists of alternating ethylene and propylene groups (as such, it is termed a copolymer); it manifests some of the properties of both polyethylene and polypropylene. It has been used for centrifuge tubes and wash bottles. *Polystyrene*, unlike the previous polymers, is transparent; it is rigid and brittle and will craze when repeatedly exposed to many chemicals. It is used for disposable petri dishes and single-use filtration units, and some rod and tubing may have been used to fabricate home-made devices in the lab.

Polycarbonate is also transparent and much stronger than polystyrene, but it also reacts with many chemicals. Its impact resistance and its impervious blockage of ultraviolet light between 200 and 360 nm make it an ideal material for safety shields. It is also used for centrifuge tubes and storage bottles.

Polymethyl methacrylate, also water-clear, is another engineering polymer that shows up in the laboratory as equipment component parts. Although readily soluble in organic solvents, thick-walled tubing shows some acid resistance. Commercial versions of this material are known as Plexiglas and Lucite.

Polyvinyl chloride is actually polyethylene with a chlorine atom on each repeating monomer. This form is somewhat flexible, transparent with a bluish tint, and shows low gas permeability. It is used as reagent storage bottles. Other formulations, still often known as PVC, are chemically different. The clear, pliable tubing known as Tygon is a mixture of polyvinyl chloride with phthalate esters. Condensed copolymers with polyvinylacetate are superior in certain properties. Many forms of PVC are opaque, rigid, strong, and resist many chemicals. And polyvinyl dichloride is even better than PVC for some applications.

Polymethylpentene is a comparatively new material in labware applications. It is rigid and transparent and can withstand sustained heating at 150°C. It shows good resistance to most chemicals, except halogenated hydrocarbons. Beakers, Erlenmeyer flasks, graduates, graduated cylinders, bottles, and volumetric flasks have been manufactured from this material. It is roughly twice as expensive as polypropylene, and it will crack or shatter if dropped, but its transparency and its higher temperature limit are real advantages.

Another new material is *polysulfone*. This engineering resin combines the strength and transparency of polycarbonate with good chemical resistance. It has a slight straw color. It has been used for centrifuge tubes, in-line membrane filter holders, and vacuum filtration funnels.

Before passing on to the fluorocarbon polymers, which warrant a separate discussion, it would be well to briefly discuss some additional plastics that the analyst might encounter. *Polyethylene terephthalate G copolymer* from the Dacron/Mylar family is clear and rigid and used for bottles. *Polyacetal*, opaque and sometimes reinforced with glass fibers, is strong and resistant to heat and chemicals. The *nylons* have excellent mechanical properties, but do not resist acids, bases, and many other inorganic compounds. *Polyurethane* is used to make clear tubing nearly as flexible as that made of PVC. The *elastomers* are somewhat of a separate category of polymeric materials used, along with natural latex for tubing, stoppers, gaskets, and O-rings. These include *butadiene-acrylonitrile copolymers* (Buna-N) and *polychloroprene* (Neoprene)—the former with oil resistance, the latter with good solvent and heat resistance. *Silicone rubber* is polydimethylsiloxane that has been cross-linked ("vulcanized"). This white elastomer has a broad useful temperature range and good electrical resistivity.

The unique properties of *fluoropolymers* have made them an essential part of a modern laboratory's tool box. They are not one, but a collection of materials, nearly all at the high-performance end of the engineering resins.

Polytetrafluoroethylene is the material many people think of first in this category of polymers. It is known most familiarly by the registered duPont trademark, "Teflon," or by the acronyms TFE or PTFE. It is an opaque, white, semi-rigid solid that is manufactured into a host of labware forms, including beakers, bottles, funnels, flasks, evaporating dishes, and watchglasses. It is also used to coat metallic equipment like forceps and magnetic stir bars. It is sold in other forms as well—as tape, sheets, "wool," rod, and tubing.

Polytetrafluoroethylene resists attack by all chemicals except elemental fluorine, carbon trifluoride, and molten alkali metals; its temperature limit for continuous service is 250°C. Vessels should not be heated directly on hotplates. But with a sandbath, perchloric acid and even sulfuric acid can be brought to anhydride fumes conveniently. Because of its extremely low coefficient of friction, polytetrafluoroethylene is also used to manufacture stoppers and stopcocks.

Fluorinated ethylene propylene, known by the trademark "Teflon FEP," trades some of TFE's amazing properties for translucence. It is flexible, but feels heavy and has a temperature limit of 205°C; it should not be used with perchloric acid, but it withstands most chemicals (barring those that attack TFE). It is used for reagent bottles and sampling bags for corrosive gas and liquid samples; beakers and erlenmeyer flasks are also available.

Perfluoroalkoxy polymer is a relatively new material with the "Teflon PFA" trademark. It has a slightly higher temperature limit than TFE and has that polymer's chemical resistance. It is translucent like FEP. Its use with perchloric acid has not been tested, so that application is not advised. It is available as bottles and beakers, some of the latter with a molded-in graphite base, allowing direct placement on a hotplate surface.

Other fluoropolymers include *Tefzel ETFE* (ethylene-tetrafluoroethylene copolymer; white, translucent, used for the screw closures of FEP bottles), *Halar ECTFE* (ethylene-chlorotrifluoro-ethylene copolymer; used for beakers), *Kel-F* (polymonochlorotrifluoroethylene; used in fittings), and Viton (a copolymer of vinylidene fluoride and hexafluoropropylene; it is actually a series of fluoroelastomers used in O-rings and gaskets).

Metal

The most important and familiar metal used in classical wet chemical analysis is also the most expensive: *platinum.* In fact, the production of labware was the impetus behind the early beginnings of the platinum fabrication industry. Unalloyed platinum is grayish white and softer than silver (in Spanish, *platina* means "small silver"). Fabricated labware is an alloy of platinum with another platinum group metal (e.g., iridium or rhodium) that hardens it to a more usable form.

The melting point of commercial labware is in excess of 1750°C—a temperature far beyond all common laboratory operations. The expense of platinumware is, in some instances, the most significant initial capital expenditure for wet lab equipment, but it is a partially renewable resource because damaged or severely contaminated vessels can be returned to the manufacturer for replacement at a comparatively reasonable refining and refabrication fee. The prudent lab manager will watch the platinum market prices before returning equipment since market rates prevail in these transactions.

Crucibles, crucible lids, electrolysis electrodes, and possibly evaporating dishes and filter cones constitute most of the needed platinum equipment. In the days of vacuum fusion gas analysis, rod or foil may also have been required. Most labs have a safe for the storage of platinumware and other precious metals; at the very least, it should be kept under lock and key.

Platinum for all its chemical nobility is a fragile material that can easily be abused. Hydroxide and peroxide fusions should never be performed in platinum crucibles. Platinum must never be exposed to mixtures of hydrochloric and nitric acids or to chlorine or bromine water. Platinumware should never be heated in a luminous flame, and large amounts of carbonaceous material must be ignited at a low temperature at the muffle furnace door to provide sufficient oxygen for ignition. The same precaution applies to large amounts of sulfur, phosphorus, arsenic, antimony, selenium, or tellurium compounds. Metal samples should never be fused in platinumware. Dirty crucibles can be burnished with clean sand, and distorted crucibles can be shaped with wood or plastic molds.

After each use, crucibles should be cleaned by fusion with potassium pyrosulfate and the cooled melt leached in boiling 1:1 hydrochloric acid:water. They should then be rinsed in distilled water and dried before storage. Electrodes used for electrogravimetry can be restored to their original shape by carefully molding them by hand. Deposited metals are removed by various techniques; boiling in 1:1 nitric acid:water is frequently employed. They are then rinsed in water and then in some low-residue polar solvent (acetone or HPLC-grade methanol) and dried in a drying oven.

Over the years a few innovations in platinumware were introduced by the fabricators. Some labs may retain platinum articles with a sintered core of another platinum group metal, and platinum-gold alloys are currently being employed for their nonwetting characteristics in casting molten salt sample disks for X-ray fluorescence analysis.

Zirconium, in the form of crucibles and lids, is an indispensable material for any lab that will be required to perform peroxide or hydroxide fusions. Chemists can thank the nuclear industry for the ready availability of zirconium crucibles since zirconium's unique suitability for use in reactors led to the creation of the industry that refines and fabricates it. A new zirconium crucible is shiny and rings like a dinner bell when tapped. After its first heating to about 550°C over a Meker burner, it will have darkened to a purple eggplant color. If it should be placed mistakenly in a muffle furnace at 550°C for a few hours, it will have turned light gray and dull, covered with a powdery white oxide.

The reducing flame of a Meker or Fisher or blast burner is sufficient to prevent the surface formation of ZrO_2, which occurs readily in an air muffle. Thus, zirconium crucibles are unsuitable for the weighing of ignited precipitates. Their utility resides in their unique resistance to molten peroxides and hydroxides. The service life of a zirconium crucible for sodium peroxide fusions may be 20 times that of a nickel crucible, its closest competitive material.

Of course, *some* zirconium *does* dissolve, and there are situations where that is not tolerable. Zirconium is also soluble in hydrochloric and sulfuric acids, two reagents that are frequently employed to acidify the water-leached melt. For many analyses, however, these facts are of no consequence, and zirconium remains the material of choice. Zirconium crucibles should be cleaned by boiling for 1 min in 1:1 hydrochloric acid:water, rinsing thoroughly with distilled water, and drying over a burner.

Nickel crucibles and lids are much less expensive than zirconium and have about four times the service life of iron crucibles for peroxide or hydroxide fusions. If zirconium is to be analyzed or if zirconium interferes in the planned analytical scheme, nickel crucibles may be the best alternative. Since zirconium phosphate is insoluble, if phosphorus is the analyte, nickel crucibles are usually a good choice. Considerable amounts of nickel are dissolved from the crucible with each peroxide fusion, resulting in an average service life of about four such fusions. Sometimes the nickel can be ignored, or removed simply, as in the filtration of the water-leached basic solution, where the nickel hydroxide is retained and analyte elements such as aluminum, molybdenum, or tungsten pass into the filtrate. Nickel is also employed in the lab as combustion boats, "baskets," capsules, and foil for gas determinations of powdered metal samples, and in numerous nickel and nickel-plated tongs, forceps, and similar devices.

Iron crucibles and lids are manufactured from high-purity metal. They should be treated as single-use vessels for peroxide fusions. Massive amounts of iron dissolve in a peroxide fusion. If the method allows, it can be most conveniently removed as described for nickel since a subsequent ammonia separation must contend with large amounts of sodium salts.

Other crucible metals, mostly used for specialized techniques, include *silver*, *gold*, and *tantalum*. Tantalum, because of its high melting point, high-temperature strength, and excellent corrosion resistance, may find use in other forms as well, such as combustion boats and filter cones. Outside of their roles in the actual analytical chemistry of wet labs, many metals and alloys serve as utensils, thermocouples, support structures, fittings, and in other forms.

Only one additional metal will be mentioned here; it is being singled out because of its unique properties and hazards. *Mercury* is the only metal that is a liquid at room temperature (although gallium would melt on a particularly torrid day in the lab). The toxic hazard from mercury is compounded by its slight volatility, and for this reason the exposed metal should be kept covered with a layer of water (or all work should be performed in an efficient fume hood). The water layer also helps to prevent splashing of mercury droplets when the metal is poured.

At one time, large amounts of mercury were used to transfer gases in vacuum fusion equipment (a particularly hazardous arrangement of glass equipment under high vacuum, a high-temperature furnace, and lots of mercury). Today mercury usage is largely confined to various forms of polarography, which utilize a dropping mercury electrode, anodic stripping voltammetry, and the mercury cathode. The mercury cathode requires about 50 mL (about a pound and a half) of mercury per cell. This amount will usually serve to process three to six (1 or 0.5-g) samples. The cell must then be recharged with another 50 mL of fresh mercury. The amalgamated mercury must be safely stored until a sufficient amount has been collected for shipment to a refiner, who distills it for a fee and returns pure mercury.

The hazards associated with working with mercury must be taken very seriously. The nonwetting character of the metal makes spills particularly difficult to clean up. No one should attempt to work with mercury without a full complement of the specialized devices and equipment for dealing with spills: suction bulbs, sponge pad extractors, brushes, activated charcoal, and more. The shipment of contaminated mercury to the refiner must meet Department of Transportation requirements and must be accompanied by a hazardous material manifest.

Miscellaneous Materials

Unlike mercury, which is still very useful, albeit a serious safety concern, *asbestos* is a banned material at many facilities. The hazards associated with the inhalation of asbestos fibers have led to the disposal of a large amount of laboratory equipment. The analyst should be aware that such programs usually overlook things; these items should be properly disposed of when discovered. Certain fiberglass-woven fabric materials make excellent substitutes for asbestos sheeting. Fiberglass cloth and cloth tape and insulating kits are available for most asbestos applications, and work with Gooch crucibles should now employ glass fiber pads for low-temperature work. High-temperature ignitions will require a different kind of filtering crucible.

Glazed and unglazed *porcelain* is still heavily used in many laboratories in the form of crucibles (including high-temperature porous bottom-filtering crucibles), evaporating dishes, Buchner funnels, and such miscellaneous pieces as spot plates, mortar and pestles, and spoons. Crucibles and other vessels that are ignited are best identified by vibro-engraving the glazed side and then impregnating the mark with black porcelain-marking ink and then firing for 1 h at 1000°C. Porcelain vessels, especially when new, require longer time at-temperature to attain constant weight than do many other vessels. They also tend to be somewhat hygroscopic when removed from a desiccator. They stain easily and are difficult to clean. But they *are* comparatively inexpensive.

Graphite is a familiar substance in the laboratory, used as spectrographic counter and sample electrodes, as electrothermal AA tubes, sometimes as powder, and as sample fusion crucibles. The latter have been sold in the conventional, somewhat porous, form and as the more resistant "pyrolytic" form. Both are used for muffle furnace fusions using alkali metal tetraborates and metaborates and boric acid. They have also been used for such fusions using sodium and potassium hydroxide. Leached melts usually have to be filtered to remove some graphite particle contamination. A very dense "glassy" carbon crucible has also been sold.

Other crucible materials sometimes used for specialized applications include *Alundum* (a trademark for fused alumina), *bone ash* (principally, tribasic calcium phosphate), *zirconia*, and a new refractory fabric material that is very light, disposable, and that has a very high cooling rate. Table 2–2 summarizes the utility of the more common crucible materials. Crystalline ceramic compositions like *Pyroceram* (a Corning trademark) are frequently encountered as hotplate and magnetic stirrer surfaces; they withstand everything but

TABLE 2–2—Guide for selecting crucibles.

Flux	Porcelain	Vycor or Fused Quartz	Iron	Nickel	Zirconium	Platinum	Graphite
Na_2CO_3	X	X	X	X	X	E	X
K_2CO_3	X	X	X	X	X	E	X
Li_2CO_3	X	X	X	X	X	E	X
Na_2O_2	X	X	A	G	E	X	X
NaOH	X	X	A	G	E	X	A
KOH	X	X	A	G	E	X	A
$Na_2B_4O_7$	X	X	X	X	X	E	E
$Li_2B_4O_7$	X	X	X	X	X	E	E
H_3BO_3	X	X	X	X	X	E	E
$NaHSO_4$	A	E	X	X	X	E	X
$K_2S_2O_7$	A	E	X	X	X	E	X
Muffle furnace ignitions	A	E	X	X	X	E	X

NOTE: E = Excellent.
Good = Good.
A = Acceptable.
X = Do not use.

hydrofluoric acid, hot phosphoric acid, and basic solutions. Such surfaces must be replaced if damaged because defects can propagate catastrophically.

Shapes and Sizes

In most laboratories beakers are the most frequently used vessels. The lipped low-form (Griffin) style is suitable for over 90% of metals analysis operations. Glass beakers with TFE-coated rims are a questionable advantage. The "dripless" rim may aid the inexperienced analyst in making quantitative transfers, but the coating begins to peel after exposure to few severe heating cycles. The resultant beaker will then actually *impede* good transfers.

Heavy-duty styles with their thick walls are unsuitable for heating and have little to offer the metals analyst. High-form lipless beakers find use in electrolysis and for bromine-methanol dissolutions, but usually need not be stocked in great quantity. Borosilicate beakers should be kept on hand in all sizes. The greatest need will be for 50, 100, 150, 250, 400, and 600-mL capacities. Smaller amounts of 800, 1000, 2000, and 4000-mL sizes will be needed. All should be marked by the manufacturer with approximate volume graduations. And appropriately sized watchglasses (including a few of the ribbed type for rapid evaporations) should be ordered for each beaker size. The most useful polytetrafluoroethylene beaker sizes are 250, 400, 600, and either 800 or 1000 mL. Most other plastic beakers will find use in the 1000-mL size. And a supply of TFE and other plastic lids is essential. Vycor and fused quartz beakers are so expensive that purchased sizes should closely match anticipated needs.

The most useful Erlenmeyer flasks are of 125, 250, 300, and 500-mL capacity; a few 1000 and 3000-mL units should be stored for use. Some labs keep a supply of 125-mL Vycor Erlenmeyer flasks for doing potassium pyrosulfate fusions of metal samples over a burner. For crucibles, the most useful sizes are as follows: platinum—25 and 50 mL; zirconium—50 mL; nickel—50 mL; iron—50 mL; Vycor—50 mL; fused quartz—50 mL; porcelain—25, 50, and 100 mL; graphite—100 mL. Tapered forms with rounded bottom interiors are, in general, an advantage, and appropriate lids are a must (although they will not be needed or desirable for some uses). Evaporating dishes may not be needed at all by some laboratories (although a few porcelain sizes might be stocked for contingencies). Other labs might need Vycor, porcelain, and even platinum dishes in an array of sizes.

A collection of tongs and forceps in a variety of sizes and materials is essential for manipulating vessels and samples. These range from long furnace tongs for moving silica trays and crucibles into and out of high-temperature muffles down to nonmagnetic electronic tweezers for transferring small particles to the balance pan. Beaker tongs with jaws covered by silica-fabric sleeves are essential, as are flask tongs. And nichrome forceps are valuable for manipulating crucibles. Platinum at high temperature should only be handled with platinum-tipped tongs. Plastic or plastic-coated metal instruments will be needed to retrieve crucibles from solutions in beakers. And some special devices like evaporating dish tongs may prove useful. Some labs associated with metal-working facilities have even had special types of tongs custom-forged.

Every lab must stock a collection of bottles to store prepared reagents and standard solutions and samples. Narrow-mouth borosilicate glass bottles with ground glass or plastic stoppers are essential for reagent storage. The 500-mL size with ground glass stopper is convenient for mineral acids and other reagents used at the hood. Larger sizes, 1000 and 2000 mL, are suitable for use at the bench. Still larger sizes become difficult to manage unless fitted with a repipet or siphon. Avoid flint and soda lime glass for these applications and all others. Glass vials and wide-mouth jars are indispensable if powdered metals, slags, ores, or other finely ground materials are analyzed in the laboratory. They are also useful for samples of millings or drillings that are to be analyzed for trace levels of carbon.

The best plastic-capped jars and vials have polytetrafluoroethylene cap liners, which can also be purchased separately. For most work this extravagant precaution is not necessary. Jars can be various sizes depending upon the lab's requirements. In general, as samples tend toward greater inhomogeneity, the larger the sample jars that will be required. The most useful sizes of vials are the 2, 3, and 4-dram capacities (8, 11, and 15 mL). Plastic bottles will be needed in both narrow-mouth and wide-mouth styles. The narrow-mouth bottles are most suitable for standard solutions since the smaller opening affords less evaporative area when the cap is off. The wide-mouth versions serve well for prepared reagent solutions and certain reagent powders.

Unless the sample will attack glass, or important element concentrations will be affected by contact with glass, plastic bottles should not be used for metals analysis lab sample materials. Finely divided materials may develop a static charge in plastic, and carbon contamination may result from the abrasive contact of hard particles with the vessel walls.

High-density polyethylene bottles with polypropylene screw caps are a leak-free combination suitable for 90% of applications. Occasionally, the expense of fluoropolymer bottles is justified by contamination or surface adsorption concerns. In this case, the best choice appears to be the new PFA polymer for both bottle and screw closure. Some of these are sold with polytetrafluoroethylene cap liners. If the lab purchases sub-boiling distilled acids in fluoropolymer bottles, these can be rinsed out and saved as storage bottles. The sizes of plastic bottles that a lab will need vary considerably, but 30, 60, 125, 250, 500, 1000, 2000, and 4000-mL capacities cover the range.

Several 20-L spigotted carboys may also be required, and if these are to be lined up on a raised shelf, the rectangular styles save space. Here again, high-density polyethylene is the best choice. Both glass and plastic wash bottles and dropping bottles are needed. Many analysts still prefer to manufacture their own wash bottles, but several perfectly suitable styles in a range of materials are available from suppliers. Plastic wash bottles should be leak-free, flexible, and able to withstand a range of chemicals. They are sold in a variety of compositions ranging from low-density polyethylene to PFA and FEP fluoropolymers. Both fine-stream and coarse-stream bottles will be needed. The glass wash bottles are needed for hot liquids. Unitized versions with insulated necks and integral pressure bulbs are available. Dropping bottles for dispensing reagents are very convenient, and a collection of 100 and 50-mL sizes in borosilicate and plastic should be kept on hand.

Even if there is no expert or amateur glassblower at the facility, at least one oxymethane hand torch, a few shaping tools, and a pair of didymium safety glasses with wire side shields should be kept in a drawer. And a small assortment of borosilicate tubing and rod should be purchased. The two most useful outside diameters are 6 and 8 mm, with a standard wall of 1 mm for the tubing. For capillary tubing, 6.5 mm with a 1-mm bore will do for manufacturing fine-spray wash bottles. And if much work is done in 150 mL and smaller beakers, a 3-mm O.D. rod will make suitable small diameter stirring rods.

An assortment of flexible hose sizes should also be kept handy. Natural latex tubing is the most pliable, but will not withstand high pressure. Clear PVC tubing is strong and economical for many low to moderate pressure applications. For high-pressure work, heavy-wall black or red rubber tubing or Dacron-braided PVC tubing is best. The most frequently made connections use ¼-in. (6.4-mm) inside diameter tubing.

An assortment of black and green Neoprene solid rubber stoppers should be stocked. Table 2–3 shows the most popular sizes. There is little need to purchase corks, but a good set of cork borers and a sharpening tool) obviates the need to buy rubber stoppers with pre-drilled holes. Keep a pair of needle-nosed pliers handy for extracting the rubber core from the borers. Glass Tuttle covers for Erlenmeyer flasks are useful if procedures are used that require acid reflux in such vessels. Sizes for 250 or 500-mL flasks should be stocked. A selection of separatory funnels is essential. The most commonly used capacities are 125, 250, and 500 mL. A smaller number of 60-mL and one or two 1000-mL funnels will suffice.

All glass funnels should have polyethylene stoppers and polytetrafluoroethylene stopcocks of conventional design. Stopper and stopcock sizes are listed in Table 2–4. Plastic separatory funnels with screw closures are available in polypropylene, Teflon FEP, and Teflon PFA. In these vessels it is difficult to see the solvent interface unless the layers are sharply contrasting. Plasticware should only be resorted to when hydrofluoric acid solutions are extracted. Check the system for leaks by shaking with water before using them with HF solutions. When extracting such samples wear gloves, a rubber apron, and a face shield. For this type of work usually the 125-mL size is adequate.

TABLE 2–3—Rubber stopper sizes.

Size No.	Bottom Diameter, mm	Vessel ID, mm	Flask, mL capacity
00	10	10–13	. . .
0	13	13–15	. . .
1	15	15–17	. . .
2	16	16–18.5	. . .
3	18	18–21	. . .
4	20	20–23	. . .
5	23	23–25	125 (Erlenmeyer)
5½	25	25–26	. . .
6	26	26–27	250 (Erlenmeyer)
6½	27	27–31.5	. . .
7	30	30–34	500 (Erlenmeyer)
8	33	33–37	1000 (Vacuum)
9	37	37–41	1000 (Erlenmeyer)
10	42	42–46	3000 (Erlenmeyer)

Table 2–4—Stoppers and stopcocks for separatory funnels.

Separatory Funnel, mL capacity	Stopper Size[a]	Stopcock Size[b]
30	16	2
60	16	2
125	22	2
250	22	4
500	27	4
1000	27	4
2000	38	6
4000	38	8

[a] Approximate inside diameter of the funnel neck, in mm (NIST Commercial Standard CS-21).

[b] Approximate diameter of the hole through the stopcock plug, in mm (NIST Voluntary Product Standard PS28-70).

VOLUMETRIC LABWARE

Despite the fact that the electronic top-loading balance is beginning to usher in an era in which liquid portions are taken by weight, volumetric equipment still plays a key role in all metals analysis laboratories. Volumetric flasks, pipets, and burets are stocked in both abundance and variety to cover many contingencies.

Volumetric flasks should be almost exclusively the glass Class A accuracy type with polyethylene stoppers. The greatest number of flasks are needed in the 50, 100, 250, 500, and 1000-mL capacities. Lesser numbers of 10, 25, 200, and 2000-mL flasks are usually called for. The 10-mL size should be in a footed style to prevent tipping. These should all be one-mark volumetric flasks. If any two-mark flasks (designed for special tests, such as biological oxygen demand (BOD) or dissolved oxygen) have found their way into the lab, remove them or prominently mark them to avoid inadvertent use. Some flasks have a deep red line in the neck as an aid in reading the meniscus. Some are even square in cross section so that they can be stacked closer together on shelves.

One of the two styles of ground glass stoppers should be available for alternate use with each size of flask. Glass stoppers will be needed if halogenated hydrocarbons are stored in the flasks for extended periods or if the closed flask is subjected to mild heating. Stopper sizes are listed in Table 2–5, and Table 2–6 lists the Class A tolerances.

Plastic volumetric flasks are available in both polypropylene and polymethylpentene, both with polypropylene screw closures. They are not Class A tolerance, but accurate enough for most work. The most useful sizes are 50, 100, 250, and 500 mL. A few 1000-mL flasks will be useful for standard solution and reagent preparation.

Since the two plastics are priced similarly in this product type, the transparency of polymethylpentene makes it the better choice. Because these flasks will be used primarily with hydrofluoric acid solutions, the analyst should use water to check that the closure is leak-free before use. There are two important differences from glass volumetric flasks. First, air bubbles in the solution will adhere to the inside walls of plastic volumetric flasks and must be removed by gently rapping the flask bottom on the benchtop before final dilution to the mark. Second, there is no meniscus but a flat liquid line that should be brought up to superimpose the mark.

If the flasks have been exposed to excessive temperature, or

TABLE 2–5—Stoppers for volumetric flasks.

Volumetric Flask, mL capacity	Stopper Size[a]
10	9
25	9
50	9
100	13
200	13
250	16
500	19
1000	22
2000	27

[a] Approximate inside diameter of the flask neck, in mm (NIST Commercial Standard CS-21).

otherwise abused, and for the most accurate work, the dry-tared flasks can be filled to the mark with 20°C water and weighed to check or adjust their "to contain" volume. This is, of course, usually limited to the smaller-capacity flasks due to weight limits on the more accurate balances. Highly accurate sample aliquotting of hydrofluoric acid solutions, such as when dealing with analyte concentrations above 10%, is best performed on a weight basis using electronic top-loaders.

The modern lab contains a large assortment of pipet types and sizes. The conventional transfer, "to deliver" borosilicate or Corex pipets, still constitute the largest part of this assembly. These should all be Class A tolerance, as described in Table 2–7. In addition to the sizes in Table 2–7, a few each of the following are often useful: 6, 7, 8, 9, 15, and 200 mL.

Some labs use Mohr or serological pipets to dispense small quantities of reagents, but these should never be used for sample or standard solutions or for any work requiring the best accuracy. The analyst who uses certain serological pipets should be aware that many are calibrated "to contain," and, unlike the familiar case, must be blown out. A "to deliver" transfer pipet should only be touched once to the vessel wall after draining. Plastic transfer pipets are not very useful or accurate for most potential applications. They can be kept on hand for contingencies, but should not be used for the most accurate work. These pipets are available in polypropylene; they are "to contain" pipets, designed to be blown out.

It should be hardly necessary to state that mouth pipetting must be a forbidden practice in all laboratories. A variety of sizes of rubber suction bulbs for use with pipets must be made available including: simple red rubber bulbs; black, one-way valved bulbs; and the newer semi-automatic pipetting aids. Automatic pipets are available today that relieve some of the cleaning maintenance associated with glass pipets. These are thumb-action repeating devices, sometimes calibrated for a single volume, sometimes adjustable for a range of volumes. The plastic tips used to withdraw and dispense the solutions are disposable. Attention must be given to these tips because in some cases clinging drops will invalidate the transfer. These automatic pipets rely upon a confined air column that requires an air-tight seal of vacuum grease. Proper maintenance involves regular regreasing of the seal and periodic checking of the accuracy by weighing discharged volumes of water.

The automatic hand pipet began as a microvolume device, and this continues to be its *forte*. Today's laboratory should keep 10, 20, 25, 50, 100, 200, 250, 500, and 1000-μL capabilities. Larger volumes (2, 5, and 10 mL, for example) should also be available. This, of course, involves keeping an assembly of special disposable tips for different manufacturers' pipets and for different volumes. For low volumes there is also a positive displacement micropipet available in which a plunger displaces the liquid.

Burets, in general, are better than pipets for quantitatively dispensing volumes above 0.5 mL provided that an appropriate size is chosen. For volumes between 10 and 50 mL choose a 50-mL buret; for volumes between 0.5 and 10 mL choose a 10-mL microburet. Burets should have a TFE stopcock. Use only the best quality glass burets for quantitative transfers and for titrations. Table 2–8 shows the tolerances for this type of equipment. Reading the meniscus in a buret can be aided by a magnifying eyepiece and a black-and-white contrast card. Schellbach burets have a special stripe that produces an arrow-like image at the meniscus; their use is subject to personal preference.

Plastic burets *are* available in polypropylene and acrylic polymer. These are of limited use because the former is translucent and the latter is strongly attacked by hydrofluoric acid, quickly turning its transparency to an opaque white and rendering the buret useless. If the same solution is to be repeatedly dispensed by a glass buret, it pays to purchase a refilling, self-leveling automatic buret. These are available in several designs, some directly inserted in the reagent storage bottle, others connected to it with flexible tubing. This type of device is a significant advantage as a 5 or 10-mL microburet since manual versions can be difficult to fill. An all-glass version simplifies the dispensing of sulfuric acid solutions, and it is easy to exclude moisture with an indicating silica gel trap on air intakes.

The next step is the digital buret, which can take different forms. These devices are often sold as part of an automatic computerized titration system. A digitally controlled piston

TABLE 2–6—Class A volumetric flask tolerances.

Capacity, mL	Tolerance, ±mL
5	0.02
10	0.02
25	0.03
50	0.05
100	0.08
200	0.10
250	0.12
500	0.20
1000	0.30
2000	0.50

TABLE 2–7—Class A pipet tolerances.

Capacity, mL	Tolerance, ±mL
0.5	0.006
1	0.006
2	0.006
3	0.01
4	0.01
5	0.01
10	0.02
20	0.03
25	0.03
50	0.05
100	0.08

TABLE 2-8—Buret tolerances—ASTM E 287: Specification for Burets (Class A Requirements).

Capacity, mL	Tolerance, ±mL	Subdivisions, mL
10	0.02	0.05
25	0.03	0.10
50	0.05	0.10
100	0.10	0.20

drives a TFE plunger in a glass syringe in most versions. Different capacity syringes can fit on the same housing, so that a given piston excursion represents different dispensed volumes depending on which syringe is mounted. Refilling, flushing, and dispensing are digitally controlled by keyboard commands, and dispensing can be under closed loop control by an electrochemical signal. General-purpose digital dispensing and diluting systems are available, but they are expensive.

As with the automatic micropipets discussed above, one must be aware that the strength of these devices is their precision and not always their absolute accuracy. There are situations where a very precisely dispensed volume that is slightly off in absolute value is all that is required, as when a titer standard is used in a volumetric determination. There are other situations when the absolute value of the dispensed volume is critical. The analyst must know the capabilities of his or her equipment and also know which of these two situations applies.

General volumetric labware, of course, also includes graduated cylinders, pharmaceutical graduates, and double-lipped "beaker graduates" for dispensing less critical volumes. Glass graduated cylinders should be protected from breakage with plastic "tip-over" rings. Graduated cylinders and graduates are also available in polypropylene and polymethylpentene. Included in this category is the "repipet," a glass or plastic reagent dispenser frequently used for mineral acids. These devices are very handy and quite reproducible, although hardly a substitute for pipetting.

FILTRATION EQUIPMENT

The classical analyst does a great deal of filtering of solutions, so it is important to keep the right equipment available and to use it properly. Two sizes of 60° borosilicate glass funnels are needed in quantity: 75 and 100 mm in diameter. About 90% of each of these should be fluted and the remainder unfluted. The flutings are a great aid in gravity filtrations, while sometimes unfluted styles work better for vacuum filtrations. A small number of both sizes in polypropylene will also be useful. One or two 150-mm glass funnels are needed for filtering and transferring reagent solutions.

While on the subject of funnels, it should be mentioned that 35 and 40-mm transfer funnels are invaluable for pouring solutions into small volumetric flasks, and 70-mm wide-stem powder funnels will be needed for transferring solids. Funnel holders and racks will be needed—wooden or plastic-clad wire versions are common. Individual wooden funnel holders that can be lined up in use are handy. For vacuum filtrations with funnels, filter flasks of various sizes will be needed. Platinum or tantalum filter cones placed in the funnel before the filter paper will secure the paper from being sucked into the flask.

If a vacuum pump rather than a water aspirator is used, it should be fitted with both a liquid trap and an acid fume trap. A large empty vacuum flask will serve as the liquid trap, while a small vacuum flask filled with granular-activated charcoal will serve as a suitable trap for acid vapors. Some pumps are more tolerant of abuse than others. The direct-drive centrifugal vane pump is reliable but noisy; belt-driven pumps are quiet and efficient but expensive. Be sure that the latter has a guard around the belt drive and keep both types properly oiled.

The subject of filtration media is broad and growing. There are over a dozen different kinds of filter paper alone, and a good lab needs all or most of them in a variety of sizes. Most gravity filtration is done with 12.5-cm-diameter papers, and most vacuum filtration will require 15.0-cm-diameter papers, but 5.5, 7.0, 9.0, 11.0, and 24.0-cm sizes will be needed as well. It is difficult to speak intelligently and informatively about filter media without mentioning brand names since the products offered vary widely in properties and many are uniquely suited to certain filtering operations.

Filter paper is classed as either qualitative or quantitative based on the weight of ash it leaves upon ignition. Qualitative paper is sometimes useful for filtering reagents, but the majority of the work in a metals analysis lab will be performed with quantitative paper, which is characterized by an ash content of less than 0.01%. Quantitative papers may be either hardened or not. A hardened paper has superior wet strength and acid resistance and often just a bit more ash than an equivalent unhardened paper. Many large laboratory supply companies offer a "house brand" of filter paper; major independent brands include Whatman, Schleicher and Schuell, Reeve Angel, and Ahlstrom. Table 2-9 lists some commercial filter papers and their properties.

Filter pulp is essential for many filtering operations—either added to the solution, to the seated filter paper, or both. A cottony product is offered in bags, and a finer ground powder is available in plastic jars and as pressed disks. These should be agitated with distilled water and stored as a suspension. Pulp helps to retain fine particles, increases the loading capacity of the filter paper, preventing clogging, and helps to support the paper during vacuum filtering.

The (hopefully) familiar stratagem of tearing a corner after folding a filter paper is not a chemist's conceit but really does aid in seating the paper. The filter should be held in place in the funnel while it is filled to the top with distilled water. The paper should be seated with the (scrupulously clean) fingers as the excess water is poured out. A solid column of distilled water in the funnel stem is a good indication that the task has been correctly performed. The pulp suspension should be shaken and added to form about a 1-cm wad when drained. In the case of vacuum filtration, the pulp wad should nearly fill the area supported by the filter cone.

Glass fiber filters are useful for a number of laboratory filtrations. They *can* sometimes be folded like a filter paper and used for gravity filtration, but their poor wet strength militates against this approach. Glass fiber filters are most often used in a membrane filter vacuum filtration apparatus. These consist of a vacuum flask fitted with a one-hole rubber stopper

TABLE 2-9—Filter papers and their properties.

Qualitative Papers					
Whatman	Reeve Angel	S&S	Other	Approximate Retention, μm	Speed
4	202	604	Labcraft 5	15–25	Fast
1	271	595	Ahlstrom 631	11	Medium/Fast
2	201	. . .	. . .	7–8	Medium
3	211	602	. . .	6–7	Medium/Slow
5	200	. . .	Ahlstrom 610	1–2.5	Slow

Quantitative Papers					
Whatman	S&S	Other	Hardened	Approximate Retention, μm	Speed
41	589 Black	. . .	No	20–25	Fast
54	. . .	. . .	Yes	20–25	Fast
541	. . .	. . .	Yes	20–25	Fast
43	. . .	. . .	No	16	Fast
. . .	. . .	Ahlstrom 15	Yes	15	Fast
. . .	. . .	Ahlstrom 10	Yes	10	Fast
40	589 White	. . .	No	8	Medium
540	. . .	. . .	Yes	8	Medium
52	. . .	. . .	No	7	Medium
44	. . .	. . .	No	3	Slow
542	. . .	. . .	Yes	2.7	Slow
50	. . .	. . .	No	2.7	Slow
42	589 Blue	. . .	No	2.5	Slow
. . .	. . .	Ahlstrom 2	Yes	2	Slow
. . .	. . .	Ahlstrom 1	Yes	1	Slow

through which a flat ground-glass funnel support has been passed. The glass fiber (or membrane) filter is placed on a sintered glass disk in the center of the support and a funnel with a ground glass base is mated to the support and secured with a clamp. This apparatus is commonly sold in two sizes—25 and 47 mm—the latter being the most generally useful.

Glass fiber filters have very high loading capacities and thus make excellent pre-filter pads for small-porosity membrane filtrations. Here, the membrane is placed down first, with the glass fiber next, and the "sandwich" is secured with the clamp. Glass fiber filters are used alone where carbon contamination must be avoided, such as in the combustion analysis of graphitic carbon in cast iron and where most other filter materials would succumb such as in filtering strong solutions of acids. Filtered residues can be weighed directly on the air-dried glass fiber filters. Alternately, filtered residues can be easily released because the filters dissolve readily in hydrofluoric acid and the silicon may be volatilized away. Table 2-10 shows some commercial glass fiber filters and their properties. The user should be aware that certain types of glass fiber filters contain an acrylic binder and thus are not suitable for certain uses. Always read the manufacturer's information before beginning.

TABLE 2-10—Glass fiber filters and their properties.

Whatman	Gelman	Millipore	Ahlstrom	Retention, μm	Speed
. . .	. . .	. . .	141	3.1	Fast
GF/D	. . .	4	. . .	2.7	Fast
GF/A	. . .	1	. . .	1.6	Fast
934-AH	. . .	. . .	. . .	1.5	Fast
GF/C	. . .	3	111	1.2	Medium
. . .	. . .	. . .	161	1.1	Medium
GF/B	A/E	2	121, 131	1.0	Slow
GF/F	TCLP	5	151	0.7	Slow
. . .	Metrigard	. . .	. . .	0.5	Slow

Membrane filters are a large subject, the fine details of which are of little concern in the metals analyst's work. However, these filters are sometimes indispensable, such as in certain wet chemical preconcentration schemes for X-ray fluorescence analysis and in certain classical procedures where very fine particles must be filtered. Thus it pays to be somewhat informed in this largely microbiological arena.

Cellulose acetate, *cellulose nitrate*, and mixtures of these esters are used to manufacture membranes with porosities ranging from 8 μm all the way down to 0.025 μm (small enough to filter certain viruses). They are hydrophilic and withstand dilute acids. They have been used to collect very minute inclusion particles isolated from steels. The filters can be dissolved in acetone, releasing the residues which they collected. Manufacturers include Millipore, Nalgene, Gelman, and Sartorius.

Polyvinylidene fluoride (Kynar) membranes can be prepared in hydrophilic and hydrophobic forms, although the former are of most use to the metals analyst. They are among the most resistant of membrane filters with significantly better acid tolerance than cellulose membranes. They are available in porosities from 5 to 0.1 μm (roughly this range represents an average size bacillus to an average size tobacco smoke particle). They are the most generally useful of the membrane filters for metals analysis work. They have been used to filter and collect rare earth fluorides, hydrous oxides of certain group IVB, VB, and VIB elements, and elemental selenium and tellurium, all for X-ray fluorescence measurement. Among the manufacturers are Millipore and Gelman.

Track-etched polycarbonate filters are manufactured by inserting a polycarbonate film in a nuclear reactor's collimated particle beam. Sensitized tracks left by the passage of nuclear particles are etched into cylindrical holes. In this process, pore size and density are under close control. These filters are ideal when the filtered particles are to be observed by light microscopy (as steel inclusions often are) because the filter background is a smooth surface. Manufacturers are Poretics (12 to 0.01 μm) and Millipore (5 to 0.2 μm).

Polytetrafluoroethylene membranes are sold in a hydrophilic form with a polyethylene or polypropylene backing to prevent curling. These membranes resist most chemicals, including strong acids, and are available in porosities from 3 to 0.2 μm from Millipore and from 5 to 0.2 μm from Gelman. *Pure silver* membranes (Millipore: 0.8 and 0.45-μm porosities) are useful for collecting fine particles of silica or carbon. Other membrane filters are manufactured from *nylon* (Gelman, Whatman, Nalgene), *polyvinyl chloride*, *polysulfone*, and *polypropylene* (Gelman).

Selecting the best material and porosity for a given job is at least partly a matter of experiment unless one is following the guidance of an established procedure. A membrane should only be handled with flat-tipped tweezers, must be carefully aligned on the wetted sintered glass support, and the glass funnel must be carefully placed so as not to move it. A few membranes have special handling characteristics—some have a "right" (up) and a "wrong" (down) side, and many are heat sensitive and so must be air-dried at room temperature.

Many manufacturers are producing plastic-unitized filtration devices that have a funnel compartment, a pre-mounted membrane, and a filtrate chamber with vacuum connection. Some of these are designed with a demountable membrane, and others have the membrane permanently embedded in the seal between the two chambers. The disposable nature of these devices may justify their cost if particularly "dirty" samples have to be handled—molybdenum disulfide or carbon black suspensions, for example.

While ignitable asbestos pad Gooch crucibles are no longer used, their place can be taken by porcelain crucibles with porous ceramic bottoms or by the platinum Monroe crucible (with a burnished platinum mat on the bottom). Glass frit crucibles are available in three porosities and are suitable for low-temperature precipitates that can be dried to constant weight in a drying oven. All these crucibles are used with a special rubber holder that fits in a vacuum filter flask.

There are a few other pieces of equipment associated with filtration in certain laboratories. A bell jar type of device (the Fisher filtrator) is an example. A volumetric flask (typically) or another container is placed inside the bell jar, which is fitted with a porcelain funnel through a rubber stopper. As the bell jar is evacuated, the filtrate is collected in the contained vessel. This device offers an advantage if the filtrate volume must be limited, avoiding the transfer washings and the danger of sample loss or contamination that would be associated with the transfer step. Labs involved in hazardous waste and leachate (TCLP) testing need a special pressure filtration apparatus made of stainless steel and coated inside with polytetrafluoroethylene. Labs that use ion chromatography will need disposable in-line filter units for the end of the sample injection syringe to prevent particle contamination of the columns.

HEATING AND DRYING EQUIPMENT

In gravimetric work and in many other laboratory operations, substances are heated in furnaces or ovens and kept dry in desiccators. A metals analysis lab can use at least two sizeable drying ovens (sometimes termed "air baths")—one kept at or just above 100°C and another set at about 130°C. The 100°C oven is ideal for drying low-temperature precipitates such as nickel and palladium dimethylglyoximates, for driving off adsorbed water from powdered samples or reagents, and even as a controlled temperature environment for reaction chemistry. Provided that vessels do not contact the oven walls, a 100°C drying oven can be an excellent substitute for a boiling water bath. The 130°C oven is better for higher-temperature precipitates such as aluminum 8-hydroxyquinolate, and it does an efficient job of drying many types of spent desiccants.

In general, the 100°C oven can be used when the temperature limit is the primary concern, and the 130°C oven can be used for the most efficient low-temperature drying. Drying ovens should be equipped with at least two adjustable shelves and an accurate temperature readout device—often this consists of an immersion thermometer protruding from a hole in the oven roof. Older units may have some associated asbestos hazard, particularly at the door seals, and should be replaced. New models may be digitally controlled or even programmable like a GC oven.

With muffle furnaces, internal volume is more important than high temperatures. Nearly all analytical operations can be conducted below 1200°C, making the high-temperature muffles (which can operate up to 1700°C) an unnecessary extravagance. A large internal volume, however, will be extremely useful for platinum or fused silica evaporating dishes or large silica trays full of crucibles. Choose a model that allows the introduction of a gaseous atmosphere in the event that that feature might prove useful. Install the muffle in a hood or under a canopy hood with good stack velocity and allow adequate very well-insulated surface space nearby (but away from the furnace controller) where hot materials can be placed to cool.

One should always allow an item to cool below red heat (550°C) before placing it in a desiccator. Store tongs, aluminized insulated gauntlet gloves, and silica trays in the immediate vicinity. When not in use, muffle furnaces should be idled at about 550°C; they should never be turned off, except for relining or repair, to avoid excessive stress on the heating elements. It is handy to keep a sign warning other workers that a muffle furnace is "In Use" since a puff of air from an open furnace door at an inopportune time has ruined many determinations. Thermocouples should be recalibrated by reference to a (NIST-traceable) primary standard thermocouple at least once a year. If the true control-point temperatures are found to deviate from the readout temperatures by more than an established amount, the problem should be corrected or a correction chart should be prominently posted.

Several sizes of desiccator will be needed with inside (support plate) diameters of 250, 200, and 150 mm. They should be glass with porcelain support plates, and the lids should have ground glass stopcocks. Aluminum and plastic desiccators are frequently regarded as impractical for use in the metals analysis lab for fairly obvious reasons—the former is opaque and the latter cannot tolerate heat. If the analyst ever needs to use a vacuum desiccator, a plastic shield designed as a safeguard against flying glass shards in the event of an implosion is a must.

The desiccator rim and the cover stopcock should be lightly greased with a high-quality laboratory grease (Apiezon L or M, Thomas Lubriseal, or Fisher Cello Seal, for example). Silicone high-vacuum grease should only be used on vacuum desiccators. The porcelain support plate can be either flat and perforated or footed with crucible holes, or both can be used simultaneously, the footed plate standing on the perforated plate. The desiccant chamber below should be charged with a high-quality desiccant. One good choice is a bed of activated alumina sprinkled with a top layer of indicating silica gel. When the silica gel begins to lose its deep blue color, the desiccants must be dried overnight in a 130°C drying oven.

Repacking a desiccator usually requires solvent cleaning and regreasing the rim and also a fresh charge of indicating silica gel on the alumina surface. When hot materials are placed in the desiccator, the stopcock on the lid must be open. When cool, the stopcock is closed. Before the lid of a desiccator containing cooled materials is removed, the stopcock must first be gently opened. These steps will prevent fine precipitates from being blown out of cooled vessels by the rush of incoming air.

There are a number of good desiccants, but not all are suitable for routine use in desiccators. Table 2–11 lists some common desiccants, their properties, and their applications. Indicating desiccants contain cobalt (II) chloride, which is blue in its anhydrous form and pink in its hydrated form. Desiccator cabinets may be useful to the metals analyst for storing samples and reagents affected by humidity and possibly for storing dried or ignited labware for later use. Long-term storage of low-alloy steel standards, for example, is one practical use for such a cabinet. There are several designs available ranging from stainless steel and glass to various plastics, some with an integral dial hygrometer.

Sometimes it is necessary or desirable to go to special lengths to ensure that just the right heating effects are achieved. Infrared lamps are one means for controlled evaporation. In a hood or under a canopy hood the lamps can be mounted on a ringstand or buret stand using special bulb sockets with integral screw clamps. Plug an array of lamps into a switched outlet strip and be sure that the lamp cords and the outlet strip are well out of the way of the infrared light paths. Such arrangements are ideal for overnight evaporation of aqueous solution samples that must be kept below the boiling point and also for the drying of filtered precipitates prior to ignition in a muffle.

Boiling water baths are used to maintain a 100°C temperature for precipitations or color development. They can be elaborate "steam-table" style troughs with concentric ring openings to hold vessels in place or simply a series of large beakers with boiling beads and glass rod sections to prevent bumping and with just enough water to evenly heat a small, partially submerged flask.

The sandbath is a useful means of moderating the heat of a gas or electric hotplate. They can be made in quantity by welding a stainless steel sheet into a 12-cm-wide trough that is as long as the hotplate width. The sides of the trough should be about 4 cm high. Fill the trough with fine sand and place it in the center of a hotplate. By this means polytetrafluoroethylene beakers can be safely heated without deformation, and platinum crucibles can be heated without danger of hotplate metal alloy contamination.

Microwave ovens have become an important item in many laboratories. Some labs make do with consumer-style ovens and replace them when acid fumes begin to take their toll. Others pay a premium to purchase a product designed for laboratory use. While open vessels *can* be used, the real advantage of this technology is in the closed vessel/pressurized mode. It is possible with pressure and temperature to dissolve certain alloys in types and quantities of acids that would not be possible in an open vessel on a hotplate.

Despite claims to the contrary, for labs that analyze many diverse samples there appears to be little advantage in speed over hotplate work. Also, the pressure/temperature regimes involved can be approached or exceeded with acid digestion bombs designed to be placed in a drying oven (albeit *without* the safety precaution of the pressure readout and the blowout plug that some laboratory microwaves provide). The real advantage of the microwave oven is for laboratories that analyze a great number of very similar samples that are normally slow to dissolve in acid or must be molten salt fused. A laboratory that normally uses dozens of different dissolution schemes is unlikely to find a microwave answer for all its work.

TABLE 2–11—Properties and application of desiccants.

Desiccant	Use	Mechanism	Approximate Residual Micrograms, H_2O/L air	Optimum Regeneration
$P_2O_5{}^a$	Special desiccator	Chemisorption^b	<0.02	None
$MgClO_4{}^c$	Inert gas train	Hydration	1	250°C + vacuum
$Al_2O_3{}^d$	Desiccator	Chemisorption/Adsorption	3	175°C
H_2SO_4	Inert gas train	Hydration	3	None
$CaSO_4{}^e$	Desiccator	Absorption	5	225°C
$SiO_2{}^f$	Desiccator	Adsorption	30	175°C
$CuSO_4$	Alcohols	Hydration	$(1400)^g$	250°C
Na_2SO_4	Nonpolar solvents	Hydration	$(12000)^g$	150°C

[a] Trade name of granular form: Granusic.

[b] H_3PO_4 is produced.

[c] Trade name: Anhydrone; may explode if exposed to organic solids, liquids, or vapors.

[d] Activated alumina (available in indicating form).

[e] Tradename: Drierite (available in indicating form).

[f] Silica gel (available in indicating form).

[g] Does not reflect the primary use of these desiccants, which is the removal of residual water from certain organic liquids.

MISCELLANEOUS EQUIPMENT, ELECTRICAL

The laboratory should have at least one explosion-proof refrigerator for the storage of purchased and prepared reagents that are heat sensitive. The optical emission laboratory may want to reserve some space for photographic plates as well, but food items must be strictly forbidden. An ice machine is a great asset because so many wet chemical procedures require an ice bath. A restaurant-style machine with a collection bin is ideal. The use of the ice for food or beverages must also be forbidden because of the possibility of inadvertent chemical contamination. A labware washer is a luxury that will serve little purpose in a metals analysis lab because vessel contamination removal is a complex and diverse art, unsuited to automation for the most part.

Most labs will need at least two pH meters and a sizeable collection of pH electrodes, saturated calomel reference electrodes (SCEs), and platinum, silver, or tungsten redox-indicating electrodes. Today, pH meters are compact with digital display readouts, although many older meter-readout instruments and even some battery-operated null point galvanometer instruments are still being used. Temperature-compensating probes can be useful when dealing with solutions still warm from the hotplate.

The most common problem with pH meters is a salt-clogged SCE. It is wise to drain and rinse the saturated KCl solution from SCEs that are not being constantly used since refilling them is a minor job. All common electrodes should be soaked in distilled water for several hours before use. Combination pH electrodes are convenient if much work is done with small vessels. If work with hot solutions is frequent, the Ross electrode is a good investment. If accurate measurements at high pH are required, a low sodium error electrode is called for. Among the redox-indicating electrodes, the platinum rod or wire electrode is usually the best choice. If specific ion electrodes are needed, read the manufacturer's instructions carefully since there are often interfering ions that will enhance their response.

Magnetic stirrers are an invaluable aid in titrations and for reagent preparation. Ceramic-topped units will stay clean, and some units have built-in heating elements that will facilitate some reagent prep work. Lighted stirrers are unquestionably the best approach for color change endpoint titrations. Keep a collection of polytetrafluoroethylene-coated stir bars of various sizes. A compartmentalized lucite storage box is an ideal way to keep the assortment organized. Stir bars tend to pick up iron from the laboratory environment and should be cleaned in hydrochloric acid before use in iron determinations.

A mercury cathode device, such as that manufactured by Eberbach, is an invaluable aid in separations of complex alloys. So long as the hazards associated with the use of mercury are clearly understood and proper operating protocols established, there should be no reason for any laboratory to shun this technology. Keep the instrument in a fume hood or under a good canopy hood, store fresh and spent mercury in sealed containers, and maintain spill control equipment specific for mercury in the immediate vicinity. The associated glassware is fairly complex and fragile, so it is prudent to contact a commercial laboratory glassblower for repairs if such talent is not available within the laboratory.

If the metals analysis laboratory is required to determine major levels of copper (and certain other metals), there may be a need to maintain an electrochemical plating apparatus. These require a small collection of platinum gauze electrodes—cathodes and anodes. An ordinary hairdryer (as opposed to a laboratory heatgun) is useful for a preliminary drying of the electrodes before they are placed in an airbath oven.

Some labs will find the need for automatic titrators persuasive. They save considerable time and can be at least as accurate as an experienced analyst's manual titration. Potentiometric endpoint models are quite sophisticated, and methods development is often a simple extrapolation from manual titration procedures.

MISCELLANEOUS EQUIPMENT, SAFETY

Safety equipment is a major concern of both the analyst and the organization that supports him or her. Rubber gloves should be available in both wrist length and gauntlet styles in sizes that fit all the workers who will need them. Textured fingers and palms will provide a more positive grip than smooth styles. Black rubber or latex will provide adequate protection from acids and bases, but neoprene will be needed for work with solvents. Glove thickness is a tradeoff between dexterity and protection, so at least two thicknesses should be available. Disposable latex gloves are a valuable aid for certain operations, but their use should be discouraged for some of the more hazardous manipulations. Aluminized insulated gauntlet gloves should be available for muffle furnace work.

Safety glasses must be provided to all personnel who work in or enter laboratory areas. Prescription lens safety glasses must be provided to all who need them. Contact lenses and conventional prescription glasses must never be worn in a laboratory. All safety glasses must have side shields. Face shields must be available for particularly hazardous operations. Lab coats and rubber aprons must be available. Personnel who work in laboratories must be trained in the operation of eyewash stations, emergency showers, fire extinguishers, and other emergency equipment. Protective shields must be provided for use in particularly dangerous operations, such as peroxide fusions, Schöniger flask combustions, and similar hazardous work. Such shields must be of a design proven to provide adequate protection in the event of a mishap. Spill control kits for acids, bases, solvents, mercury, and hydrofluoric acid must be located near areas where such spills are likely to occur. Safety signs must be prominently posted, and directions for safe operating procedures must be readily available.

OTHER MISCELLANEOUS EQUIPMENT

It is really impossible to enumerate all the other equipment that a metals analysis laboratory requires, but a few remaining major items can be listed. In the area of hardware, there is a host of "monkey-bar" equipment for glassware support:

stainless and nickel-aluminum bars, connectors, and clamps, ringstands, and buret stands. Specialized glassware includes condensers of various designs, Florence and round-bottom flasks, and numerous interjoint connecting pieces. Plastic and glass-weighing dishes, medicine droppers, bottle and buret brushes, a good detergent for glassware washing (like Alconox or Micro), and lint-free wipers (like Kimwipes) are all needed. Piezoelectric or flint gas lighters, weighing bottles, mechanical or electric timers, thermometers, and pH and litmus paper are necessary.

Teflon sleeves and Keck clips are ideal for interjoint glassware connections, and brass hose clamps will ensure a good seal for cooling water connections. Lab carts, stainless or fiberglass, are invaluable, and trays for beaker or flask transport and for use as ice baths should be either purchased or fabricated. Cooling troughs with running water and overflow drains are very useful. Ion exchange columns can be purchased in glass or fabricated in plastic, and a supply of test tubes is ideal for trying something new. A large-capacity centrifuge will also find use. There is much more, but there is little to be gained by going on. The metals analysis lab is an eclectic place, changing with the times and the needs. And the equipment it will contain will reflect the work required of it.

REFERENCES

Allcock, H. R. and Lampe, F. W., *Contemporary Polymer Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1981.

Barr, W. E. and Anhorn, V. J., *Scientific and Industrial Glass Blowing and Laboratory Techniques*, Instruments Publishing Co., Pittsburgh, PA, 1949.

The Condensed Chemical Dictionary, 10th ed., revised by G. G. Hawley, Van Nostrand Reinhold, New York, 1981.

Hammesfahr, J. E. and Strong, C. L., *Creative Glass Blowing*, W. H. Freeman & Co., San Francisco, 1968.

Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, John Wiley & Sons, New York, 1953.

Modern Plastics Encyclopedia 1984–1985, McGraw-Hill, New York, 1984.

Schroeder, E. E., "Rubber," *Riegel's Handbook of Industrial Chemistry*, 8th ed., J. A. Kent, Ed.,Van Nostrand Reinhold, New York, 1983.

Shand, E. B., *Glass Engineering Handbook*, 2nd ed., reissued, 1982, McGraw-Hill, New York, 1958.

Shugar, G. J., Shugar, R. A., and Bauman, L., *Chemical Technician's Ready Reference Handbook*, McGraw-Hill, New York, 1973.

Van Nostrand's Scientific Encyclopedia, 4th ed., D. Van Nostrand, Princeton, NJ, 1968.

Also, technical information in the literature and catalogs of the J. T. Baker, Berghof/America, B. J. Scientific Products, Corning, Fisher Scientific, GFS Chemicals, Kontes, Matthey Bishop, Millipore, Nalgene, Network Laboratory Products, Owens-Illinois, Quartz Scientific, Thomas Scientific, Whatman, and Wheaton companies.

TRADEMARKS

Alconox (Alconox, Inc.)
Alundum (The Norton Company)
Anhydrone (J. T. Baker Co.)
Apiezon (Shell Chemical Co., Apiezon Products, Ltd., London, UK)
Bakelite (Union Carbide Corp.)
Buna-N (Pittway Corp.)
Cello-Seal (Fisher Scientific Co.)
Corex (Corning Glass Works)
Dacron (E. I. duPont de Nemours Co.)
Drierite (W. A. Hammond Drierite Co.)
Granusic (J. T. Baker Co.)
Halar ECTFE (Allied Corp.)
Kel-F (3-M Co.)
Kimax (Owens-Illinois, Inc.)
Kimwipes (Kimberley-Clark Corp.)
Kynar (Pennwalt Corp.)
Lucite (E. I. duPont de Nemours Co.)
Lubriseal (Arthur H. Thomas Co.)
Micro (International Products Corp.)
Plexiglas (Rohm and Haas Co.)
Pyrex (Corning Glass Works)
Pyroceram (Corning, Inc.)
Ray Sorb (Owens-Illinois, Inc.)
Ross (Orion Research)
Teflon FEP (E. I. duPont de Nemours Co.)
Teflon PFA (E. I. duPont de Nemours Co.)
Teflon TFE (E. I. duPont de Nemours Co.)
Tefzel ETFE (E. I. duPont de Nemours Co.)
Tygon (The Norton Company)
Viton (E. I. duPont de Nemours Co.)
Vycor (Corning Glass Works)

3

Reagents

IF LABORATORY EQUIPMENT IS THE HAMMER and chisels of metals analysis, then reagents are the fine Carrara marble. Just as a sculptor chooses a starting piece for shape and grain and assesses surmountable versus fatal defects, all with an eye toward his final purpose, so the analyst must plot a route to *his* goal, selecting reagents for type and purity and weighing compatibilities and reaction rates.

To pick a number somewhat arbitrarily, about a thousand reagent chemicals may be involved in currently valid procedures for the analysis of metals and alloys. Of these about a hundred are used with sufficient frequency to warrant mention in this chapter; although experienced analysts who toil in certain industries may have valid objections that their "favorite reagent" was ignored.

The plan is to cover purchased reagents first by categories that either describe the compound or how it is commonly used. One problem with this approach is that certain reagents will fall into several categories. Thus ammonium hydroxide is a base, a precipitant, and a complexing agent. In each case of this sort, only the first occurrence will be listed (which, hopefully, will be the most commonly held and familiar category.) In the case of ammonium hydroxide, the category is "base." Later in the chapter, prepared reagents will be described. These are mostly standard titrant solutions and elemental standard calibration solutions that find use in a variety of different methods.

PURITY LEVELS

It would be gratifying to be able to say that reagent purity is no longer an issue in the laboratory and that any compound sold as an analytical reagent is going to be good enough. In fact, these days the analyst needs to be as vigilant as ever to ensure that a week's worth of work will not be ruined by selecting a contaminated reagent.

"ACS" on a reagent label is a claim by the manufacturer that the compound meets the specifications of the Committee on Analytical Reagents of the American Chemical Society (as set forth in *Reagent Chemicals, American Chemical Society Specifications*). It is *not* the final word in purity or a *nihil obstat* for all analytical work. For example, ACS grade nitric acid is often sold contaminated with titanium since that element is not specified. Reagent manufacturers chart a course through specifications and known needs, offering a dozen or more grades of purity, sometimes with precipitous price boundaries. In this hierarchy ACS grade has become the baseline with "CP" (Chemically Pure) grade just a step below and with "Practical" or "Technical" grades never employed for analytical work if any higher grade is available.

The first level of purity above ACS grade is variously termed "Electronic," "Trace Metal," or "Instrument" grade. It is usually accompanied by an extensive lot analysis, which may, however, omit key elements that are present in measurable quantities. The "ultra-purity" grades are sold at premium prices, often in special packaging, and are accompanied by an exhaustive lot analysis. If one is prepared to spend between two and ten times the unit cost of ACS grade, there is no better choice for tramp and trace work where high or inconsistent blank readings may otherwise constitute a problem. Some manufacturers also sell certain reagents in a "Primary Standard" grade. These can be used to prepare standard titrant solutions that do not themselves need to be standardized.

A completely separate argot of terms is being used for organic solvent grades. Once again, ACS grade is somewhat of a baseline level. At or slightly below this level of purity are solvents sold for high-performance liquid chromatographic use ("HPLC" grade). "Pesticide" grades are low-residue solvents, suitable where solvent evaporation concentration is needed. "Spectrophotometric" grades are very high purity, often sold with accompanying ultraviolet absorption curves for the lot. The highest level organic solvents are prepared for use in specific procedures, such as certain EPA methods. They can be five times the unit cost of ACS grade.

Gases are sold in purity level categories that are only a little less bewildering. "Extra Dry" (or sometimes "Bone Dry") is a common appellation for fixed gases at around 99.6% purity. "High Purity" usually means 99.99%, and "Zero Gas" refers to a very low total hydrocarbon content (less than 0.5 ppm). "Prepurified," "Ultra High Purity," and "Research" grades represent the final ascent into five "9's" and beyond. Rarely does the metals analyst need to climb those heights.

WATER

There is little need to remind a classical chemist that the quality of the water available for his use can have a profound effect on the analytical results he obtains. And as instruments have opened up the trace and ultratrace realms, analytical water quality has become even more of an issue. High-purity water is used almost everywhere and for almost everything—labware is rinsed with it, reagents and samples are diluted with it, sometimes instruments are "zeroed" with it, and detection limits are frequently based on measurement noise

TABLE 3-1—ASTM Standard Specifications for Reagent Water (Designation D 1193).

	Type I	Type II	Type III	Type IV
Total matter, mg/L	0.1	0.1	0.1	2.0
Electrical resistivity, minimum megaohm · cm at 25°C	16.67	1.0	1.0	0.2
pH at 25°C minimum color retention of $KMNO_4$, in minutes	NM[a], 60	NM[a], 60	6.2–7.5, 10	5.0–8.0, 10
Max, soluble SiO_2	ND[b]	ND[b]	10 ppb	NL[c]

[a] Not measured.
[b] Not detectable.
[c] No limit.

Preparation:

Type I: The distillation of feedwater having a minimum resistivity of 0.05 megohm-cm at 25°C, followed by polishing with a mixed bed of ion exchange materials and a 0.2-μm membrane filter.

Type II: Distillation using a still designed to produce a distillate having a resistivity of more than 1 megohm-cm at 25°C. (Ion exchange, distillation, or reverse osmosis may be required as a preliminary treatment prior to distillation.)

Type III: Distillation, ion exchange, reverse osmosis, or a combination thereof, followed by filtration with a 0.45-μm filter.

Type IV: Distillation, ion exchange, reverse osmosis, electrodialysis, or a combination thereof.

from it. It is essential not only that water of adequate quality be available but also that the quality remain consistent. A "surge" of, say, calcium contamination during a two-day calcium determination would create a problem from which there would be no recovery except to start over after the problem was corrected.

The American Society for Testing and Materials (ASTM) has published ASTM Specification for Reagent Water (D 1193), which covers four types, shown in Table 3–1. Types I through III are analytically useful and should be practically attainable in most laboratories. Compare Table 3–1 with Table 1–1, which was based on actual laboratory experience. The color retention test listed in Table 3–1 is a measure of oxidizable organic substances. To a mixture of 500 mL of reagent water combined with 1 mL of concentrated sulfuric acid, 0.2 mL of potassium permanganate solution (0.316 g/L) is added. The solution is mixed in a stoppered borosilicate glass bottle and allowed to stand. The water should not discharge the pink color within the indicated time intervals. Since water in contact with air will absorb atmospheric carbon dioxide and become slightly acidic with carbonic acid, boiled, cooled, and inert gas-sparged distilled water is always used for the most accurate pH and conductivity measurements.

Laboratories with solution-based multi-element spectrometric capabilities, like ICP-OES, should routinely monitor their distilled water taps, perhaps even plotting elemental trend charts. If one is alert to likely contaminants, a simple check by flame AA may be sufficient. Silicon, calcium, magnesium, copper, and iron commonly show up in certain problem situations, although others are possible depending on the lab's system configuration. Sometimes the cleanest water, inorganically speaking, is contaminated with organics from ion exchange columns. And so, if the laboratory does much organic analysis, particularly trace organic analysis, special water supplies may have to be provided. High-purity water in a variety of grades can be purchased for prices ranging from $15 to $70 or more per liter.

GASES

These days one thinks less frequently of gases as reagents, yet they still qualify even if only occasionally used as such. Here we will briefly review *all* the gases important to metals analysis, including those that do not function as reactants.

Reactant Gases

Acetylene (C_2H_2) is the standard flame atomic absorption fuel gas with bond energy to burn. It is sold dissolved in acetone or a similar solvent and should never be discharged at outlet pressures that exceed 15 psig (104 kPa). Some glassblowers use an oxyacetylene torch to work Vycor and fused silica. The characteristic garlic-like odor warns of a leak. Acetylene's flammable range with air is 2.5 to 82%, the broadest of any gas. Some analytical procedures use *air* sparged through solutions to augment the atmospheric oxidation of some analyte species; ferrous iron and stannous tin are two ready examples. Air is a major oxidant gas in flame AA work, and "zero air" is the oxidant gas for gas chromatographic flame ionization detectors.

Ammonia (NH_3) is sometimes used to prepare silica-free ammonium hydroxide by bubbling the gas through water in a hood. This practice is sometimes necessary because commercial ammonium hydroxide (except ultra-purity grade) is always sold in glass bottles and is heavily contaminated with silicon. Anhydrous ammonia should be treated with respect; it is a noxious, dangerous gas that will cause severe burns. Nearly 90 parts (by formula weight) will dissolve in 100 parts of water. Its flammability range with air is 16 to 25%.

Chlorine (Cl_2) is used to isolate oxide inclusions from steel by subliming away with heat the $FeCl_3$ formed from the matrix iron. Chlorine is a yellowish-green, highly toxic, and corrosive oxidizer that causes severe burns. Chlorine should be used only in closed systems in an efficient hood with the effluent bubbled through one or more traps of 50% (w/v) sodium hydroxide.

Hydrogen (H_2) has been used in pyrolysis methods for interstitial nitrogen in steel and to estimate certain readily reduced oxides on steel surfaces. In the former case NH_3 is measured, in the latter H_2O is measured. Hydrogen is also used occasionally in flame AA work with a special argon-entrained air-hydrogen burner. Such a flame is nearly invisible, thus suitable care must be taken with its use. More frequently, hydrogen is used as an argon additive in graphite furnace AA work. A low total hydrocarbon grade is usually used for GC flame ionization detectors. Sometimes hydrogen is used as a GC carrier gas. Vycor and fused silica glasses are commonly worked with an oxyhydrogen torch. Hydrogen gas has a broad flammable range of 4 to 75% with air.

Hydrogen/air mixtures have the highest maximum flame velocity of any fuel/air mixture (1.7 times that of acetylene/air). To prevent potentially catastrophic detonations, especially with "home-made" or improvised apparatus, great pains must be taken to ensure that air has been thoroughly purged from the system with a heavy gas like argon before any hydrogen is introduced. Effluent hydrogen should be "burned off" at a constricted exit tube to prevent buildup of hydrogen in the room. When the experiment is complete, the hydrogen should be immediately and thoroughly purged from the system with argon.

Hydrogen Chloride (HCl) is still sometimes used from a cylinder to volatilize chromium out of a fuming perchloric acid solution as chromyl chloride (CrO_2Cl_2). It remains one of the best techniques because it does not significantly cool the solution as dropwise hydrochloric acid does; it is less tricky to use than a boiling azeotrope generator; and it adds no sodium as solid sodium chloride does. As one might expect, gaseous hydrogen chloride is highly toxic and corrosive. It requires the same type of corrosion-resistant regulator as does chlorine gas; these are usually constructed of stainless steel or nickel alloys with seats and seals of fluorocarbon polymers.

Hydrogen sulfide (H_2S), a dangerous toxic gas with the smell of rotten eggs, was formerly used for many sulfide separations. Today it is frequently replaced with thioacetamide (unfortunately, a known carcinogen), which releases H_2S in situ in acid or basic solution. Those labs that still use hydrogen sulfide cylinders should install monitors and alarms since olfactory fatigue makes its pungent stench an unreliable indication of concentration levels in room air. This is especially important because of its highly toxic nature (a threshold limit value of 10 ppm). Hydrogen sulfide will burn in air over a concentration range of 4.3 to 46%.

Nitrous Oxide (N_2O) is used in flame atomic absorption as a higher temperature oxidant. A stoichiometric mixture of nitrous oxide and acetylene achieves a temperature of 2800°C, while air and acetylene reach only 2400°C. Nitrous oxide is an anesthetic gas with a sweet odor. Like carbon dioxide, it has a high enough critical temperature to be shipped as a liquid, but the work of expansion through regulators draws enough heat away to freeze the mechanism. For this reason, specially designed regulators are often used for both gases.

Oxygen (O_2) is used most commonly for carbon and sulfur determinations by the so-called "combustion" techniques. Sometimes an oxygen atmosphere is introduced into a muffle furnace to facilitate ignitions, especially when it is critical to remove all traces of carbon and sulfur. The "pre-burning" of combustion crucibles for trace carbon and sulfur analysis is an example. Oxygen is the prime oxidant used in glassblowing work. Organic microsamples are prepared for inorganic constituent analysis by Schöniger flask or bomb calorimeter combustions. In the former technique, a special glass flask is filled with oxygen at atmospheric pressure; in the latter, a stainless steel cylinder is pressurized with oxygen. At one time oxygen was widely used for oxyacetylene flame emission work, but that is rare today.

Sulfur dioxide (SO_2) can be used to economically prepare sulfurous acid by bubbling the gas through a dilute sulfuric acid solution in a hood. The gas itself has been employed to reduce vanadium, where sulfurous acid is ineffective due to contamination by other oxidizable sulfur compounds. Sulfur dioxide is highly toxic and nonflammable. It requires the same type of corrosion-resistant regulator as anhydrous ammonia and hydrogen sulfide, made of stainless steel and fluorocarbon polymers. Although sulfur dioxide has an irritating and pungent odor, many claim they can taste it before they smell it.

Inert Gases

Argon (Ar), like most gases in this category, is sold in a variety of grades with guaranteed low levels of oxygen, moisture, total hydrocarbons, and other contaminants. The liquid gas is also sold and, as described in Chapter 1, is one of the most economical and convenient ways to provide low-oxygen argon for ICP and other optical emission needs. Smaller volumes of argon are used for graphite furnace AA work and (rarely) as a sheath-gas for an air-hydrogen burner in FAA. Occasionally argon is used as a GC carrier gas for thermal conductivity detection despite generally poor sensitivity. An example of this use would be to measure the oxygen content of an argon sample since most molecular sieve columns do not resolve oxygen and argon. Argon is a good purge gas since it is heavy and will readily displace air and most other gases. But therein lies the danger of asphyxiation if argon gas is not properly vented. Once in the lungs argon is more difficult to expel with air or oxygen than other gases.

Carbon dioxide (CO_2) is sold as a liquid and is best dispensed with a freeze-free regulator. It is sometimes used to provide an oxygen-free inert blanket over tin or iron solutions. It is considered low toxicity, but can paralyze the respiratory response at high concentrations.

Helium (He) is used for the inert gas fusion determinations of oxygen, nitrogen, and argon. It is the most common carrier gas for gas chromatography and is occasionally used as an optics purge gas in optical emission and X-ray fluorescence. Although helium is an asphyxiant, the danger at low flow rates is small because it is lighter than air and will usually find its way out of a room or building before displacing a significant amount of air.

Nitrogen (N_2) is arguably not an inert gas since it can be made to undergo a host of reactions. The metals analyst, however, always employs it as a blanket, sparge, or purge gas to prevent the absorption of atmospheric carbon dioxide by a boiled aqueous solution, to control the atmospheric oxygen wave in polarography, or to eliminate the "water bucket" due to atmospheric water vapor in infrared absorption spectrophotometry. Sometimes it is used as a carrier gas in GC work. Flow rates are usually low, so there is little danger that room air will be significantly displaced.

Table 3–2 summarizes key information about the gases just discussed. CGA numbers refer to the standard cylinder outlets and connections specified by the Compressed Gas Association. Figure 3–1 depicts some frequently used CGA outlets and connections. Probably the only routinely purchased gas mixture will be "P-10" gas, which is 10% methane in argon. It is used in flow proportional counters in X-ray fluorescence spectrometers. There are also special mixtures for GC electron capture detectors and for other types of radiation and ionization detectors. If much gas analysis work is performed, especially by GC, a collection of custom-blended calibration and validation gas standard mixtures will be needed unless the analyst can satisfy his or her needs in the catalogs of the specialty gas companies or NIST. Such custom blends are available by arrangement with many specialty gas companies.

ACIDS

Even the simplest solution-based techniques in metals analysis require acids in quantity and variety. Virtually all metals, alloys, and industrially useful minerals, even the most resistant, are attacked to some degree by some combination of

TABLE 3-2—Miscellaneous gas data.

Gas	Molecular Weight	Specific Gravity[a], @ 21°C	Commonly Shipped as	TLV[b], ppm	Major Hazards[c]	CGA[d] Outlet and Connection
Acetylene, C_2H_2	26.04	0.9092	Gas in Solvent	...	F	510
Air	(28.96)	(1)	Gas	...	P	346
Ammonia, NH_3	17.03	0.5914	Liquid	25	I,C	660
Argon, Ar	39.95	1.378	Gas	...	P,A	580
Carbon dioxide, CO_2	44.01	1.519	Liquid	5000	P,I	320
Chlorine, Cl_2	70.91	2.475	Liquid	1	I,C	660
Helium, He	4.003	0.1382	Gas	...	P,A	580
Hydrogen, H_2	2.016	0.0696	Gas	...	F,P	350
Hydrogen chloride, HCl	36.46	1.226	Liquid	5C[e]	I,C	330
Hydrogen sulfide, H_2S	34.08	1.193	Liquid	10	I,F	330
Nitrogen, N_2	28.01	0.9685	Gas	...	P,A	580
Nitrous oxide, N_2O	44.01	1.536	Liquid	...	S	326
Oxygen, O_2	32.00	1.105	Gas	...	P,S	540
Sulfur dioxide, SO_2	64.06	2.265	Liquid	5	I	660

[a] Air is defined as 1.000.

[b] *Threshold limit value*: airborne concentration to which it is believed that nearly all workers may be repeatedly exposed without harm.

[c] Hazard Code: A—asphyxiation; C—bodily contact; F—fire; I—inhalation; P—high pressure; S—supports combustion.

[d] See Fig. 3-1.

[e] TLV Ceiling: the airborne concentration that should never be exceeded, even instantaneously.

acids. And so acids play a role in almost all dissolutions. Acids are also used to prepare reagent solutions, and they serve as standard titrants in volumetric work and as pickling agents to remove scale and corrosion from the surface of solid metal specimens. And, of course, they are used to adjust pH for reaction chemistry. While the modern definition of an acid (by Lewis) is an electron pair receptor and the older definition (by Lowry-Brønsted) is a proton donor, it is sufficient for our purposes here to define an acid as an electrolyte that furnishes hydrogen ions in aqueous solution. In this sense of the term, acids are classed as either "strong" or "weak" based on their degree of dissociation in the presence of water. These terms do not reflect, however, on the reactivity or the associated hazard. A more useful classification for metals analysis divides the "oxidizing" and "nonoxidizing" acids. Sometimes the term "mineral acids" is used to distinguish inorganic acids.

Hydrochloric acid (HCl) is probably the most widely used mineral acid. Reagent grade is a 37% (w/w) solution of the gas in water. It will dissolve a surprisingly large number of metals and alloys given enough time, although it frequently leaves important oxide inclusions untouched. Technical grade is commonly referred to as "muriatic acid" and is often contaminated with a significant amount of iron and other metals. The ACS reagent grade is usually good enough for most determinations down to analyte concentrations of about 0.01%. Below that level the analyst should become cautious, and at 0.001% the "electronic" grade is usually called for. At

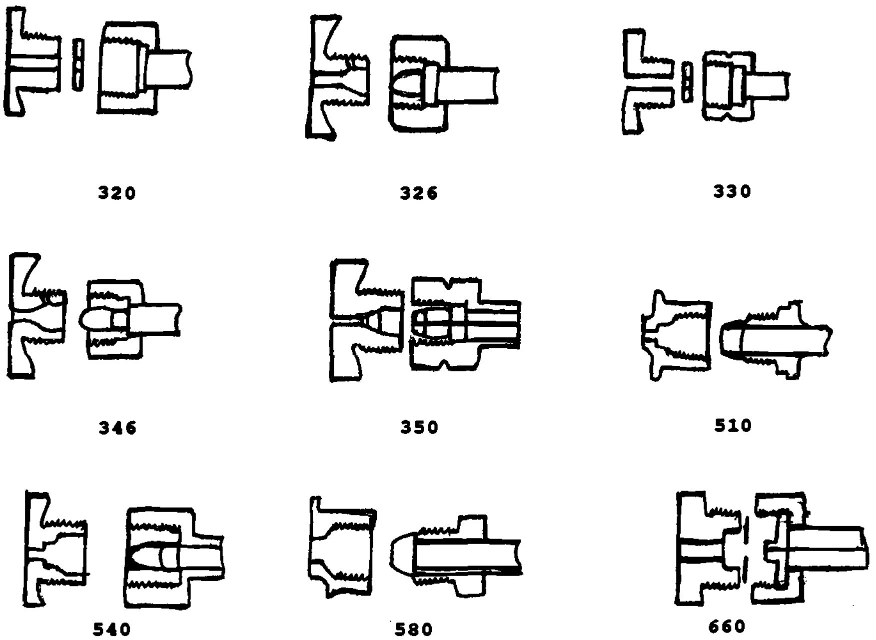


FIG. 3-1—CGA outlets and connections.

tramp levels, caution is again advised, and for certain determinations an ultra-purity grade, prepared by sub-boiling, may be necessary.

Hydrochloric is a nonoxidizing acid, but its use frequently results in soluble chloride complexes that become important in subsequent manipulations, including ion exchange work. Some elements, like silver, copper (I), mercury (I), and bismuth, form insoluble compounds. Other elements like phosphorus, arsenic, tin, antimony, selenium, tellurium, germanium, and boron form low boiling volatile chlorides that may be lost by heating. Like all gaseous acids, when a water solution of hydrochloric acid is boiled at atmospheric pressure the vapor will eventually reach a constant boiling azeotrope of HCl and water. This becomes important for methods where the analyte is distilled away from the matrix in a closed system. Inhalation and bodily contact are the primary hazards associated with work with hydrochloric acid. Gloves and a hood are called for down to a concentration of at least 6 molar.

Nitric acid (HNO_3) is a strong oxidant. Reagent grade is 70% (w/w). Alone or in dilute solution it readily dissolves certain metals and passivates others. The passivation results from the formation of an oxide on the surface of the metal particles and often is so refractory that subsequent treatment with other acids is ineffective. The oxidizing power of nitric acid is particularly evident with organic materials, and caution is always advised in these instances. A red fuming grade at 90% (w/w) is available but unneeded for metals work. Nitric acid is most effective for dissolutions in combinations with other acids such as hydrochloric or hydrofluoric, where volatile or unstable species are formed in solution.

Those few elements that form volatile oxides, like osmium and ruthenium, will be partially or completely lost from a boiling nitric acid solution. Many other elements at high concentrations will precipitate as hydrous oxides, in particular the so-called "earth acids"— titanium, zirconium, hafnium, niobium, tantalum, molybdenum, and tungsten. Always use ultra-purity grades for titanium determinations at levels below 0.1%.

Nitric acid is routinely used alone and in combination with perchloric and/or sulfuric acids to destroy organic matter. The process is fraught with hazards and always requires a good knowledge of both safe laboratory practices and the exact nature of the sample material. Even with inorganic samples it is always best to apply nitric acid only where the expected reaction and its rate are known since explosions with inorganic materials have also been reported. In general it is unwise to allow nitric acid to sit in contact with undissolved metals for days at a time.

Nitric acid attacks the skin, forming a characteristic brown stain, thus gloves must be worn at all times. Gloves should also be rinsed and examined after use because nitric acid attacks many glove materials. All work should be in an efficient fume hood not only because of the acid vapor but also because nitric acid reactions often produce highly toxic gaseous compounds. Discolored nitric acid has been contaminated and should be disposed of by a safe standard procedure.

Sulfuric acid (H_2SO_4) is generally regarded as a nonoxidizing acid, but at its fuming temperature (when heavy white vapors of its anhydride, SO_3 , begin to evolve) it becomes slightly oxidizing. Reagent grade is 96% (w/w). As dilute solutions are heated, a series of constant boiling azeotropes forms until all but 1.2% of the water has been expelled. This "anhydrous" acid boils at 335°C. "Fuming sulfuric acid" or "oleum" (a saturate of SO_3) is sold but finds no use today in metals analysis. Concentrated sulfuric acid is noted for its dehydrating power and its extremely high heat of hydration. Thus it is the most hazardous acid to dilute.

As with all acids, good laboratory practice prescribes always adding acid to water, never the reverse, while stirring cautiously and vigorously. With sulfuric acid a cooling bath is necessary since the heat may be generated rapidly enough to boil the solution or even crack a borosilicate vessel with disastrous results. Since dilutions of sulfuric acid and water when cooled to room temperature occupy less volume than the sum of the original volumes of the components, it is simplest to specify concentrations as "parts" to be added, such as "1:1 H_2SO_4:H_2O." Some metals dissolve in the concentrated acid, but many more require dilute sulfuric acid. And some metals are only partially attacked or untouched by any concentration.

Sulfuric acid is more broadly effective as a dissolution agent in combination with other acids. By bringing the mixed acid solution to fumes of sulfuric acid, it is often possible to expel the (potentially interfering) anions of the other acids. Mercury, rhenium, and selenium can be lost as volatiles by such a process, however. And lead, calcium, strontium, and barium will precipitate in the presence of sulfuric acid.

Concentrated sulfuric acid has a low coefficient of friction (and has even been used as a lubricant in special limited applications). This can cause a contaminated vessel to slip out of a gloved hand, so special caution is advised. Skin contact with sulfuric acid requires an immediate flush with a *large* excess of cold water since a small amount of water may result in a more serious burn from the heat of hydration. All dilutions of the concentrated acid and all fuming must be conducted in a hood. Gloves, a face shield, and a rubber apron are always a good idea.

Hydrofluoric acid (HF) is a unique, nonoxidizing, highly reactive complexing acid. Because of covalent bonding in the molecule, hydrofluoric acid is incompletely ionized in aqueous solution (a 0.1 molar solution is 15% dissociated). It is also one of the greatest hazards in the metals analysis laboratory. ACS reagent grade is 49% (w/w) and is usually adequate for all but certain trace level work. "Electronic" or "instrument" grade is about twice as expensive, and ultra-purity grade may be ten times as expensive at about the same concentration.

Alone, hydrofluoric acid will dissolve many metals and siliceous materials, but in combination with other mineral acids, it can be used to dissolve a great number of metals, alloys, ores, and other materials. Many metal ions, including those that precipitate as hydrous oxides in other acids, form soluble fluoride complexes even at low concentrations of hydrofluoric acid. Thus one or two drops are sometimes sufficient to hold a great deal of tungsten, niobium, or tantalum in solution. The rare earths *will* precipitate as fluorides, and use of that reaction is readily applied to their determination. Certain elements like silicon, boron, arsenic, and antimony will be lost as volatiles from heated solutions. In aqueous solution the anionic species HF_2^- results from the association of free fluoride ion with undissociated HF. It is this species that is responsible for many of the important reactions of this valuable reagent.

The only trouble with hydrofluoric acid is that it is very dangerous to work with. Any bodily contact with the reagent or its vapors requires immediate flushing with copious amounts of water because hydrofluoric acid penetrates the skin very readily, producing burns deep in tissue. Such burns, especially from dilute solutions of the reagent, may not be painful until many hours after contact. First aid treatment after flushing with copious water consists of soaking all affected skin areas with iced water solutions of the quaternary amine compounds HYAMINE 1622 benzethonium chloride (1 part to 500 parts of water) or ZEPHIRAN benzalkonium chloride (1 part to 750 parts of water).

All burns require the immediate attention of a physician who is familiar with hydrofluoric acid burn treatment. But the soaks with these solutions should not stop during any required transportation or delay. These solutions should not be used for burns of the eye, which must be flooded with water. In this case a physician, preferably an eye specialist familiar with proper procedures, is immediately required. For detailed information about hydrofluoric acid burns, write for information to the major manufacturers (such as Allied Chemical, P.O. Box 1053R, Morristown, NJ 07960, Attn: Marketing Manager—Hydrofluoric Acid).

Perchloric acid ($HClO_4$) is another unique acid. Its aqueous solutions are nonoxidizing at room temperature, but its hot, concentrated solutions are powerfully oxidizing. It is completely ionized in concentrated sulfuric acid solution, which indicates that it is the stronger acid of the two and which puts it among the strongest of the acids. Perchloric acid is essentially noncomplexing, a property that makes it valuable for certain ion exchange work and in numerous situations where complexes are to be left undisturbed by competing ligands. In hot, concentrated solution it is also a powerful dehydrating agent, which makes it valuable in gravimetric silicon determinations, where it converts the soluble polymeric silicates to insoluble silicic acid. The combination of the oxidizing and dehydrating power of the hot, concentrated solution makes perchloric acid invaluable for the destruction of organic matter. This "wet ashing" of organics must always be conducted in the presence of a large excess of nitric acid and in carefully controlled sample sizes to avoid a violent explosion. High-boiling organics are particularly dangerous to destroy in this manner, so special pretreatment approaches are sometimes necessary. Silver, bismuth, and antimony perchlorate salts are shock-sensitive explosives, and many other inorganic explosions have also been reported. The analyst should regard any metal perchlorate salt as a potential hazard.

The acid is sold commercially at two different concentrations: 60% (w/w) and 70% (w/w), the latter being close to the 72.4% (w/w) azeotrope with water, which boils safely at 203°C. The anhydrous acid distills out of sulfuric acid/perchloric acid mixtures, but the distillate from such mixtures must never be collected since it will detonate spontaneously. "Instrument" and ultra-purity grades are available at 70% (w/w).

Most perchlorates are very water soluble, but potassium (and rubidium and cesium) perchlorates are only slightly soluble. This causes problems, for example, when there is a need to combine the leach solution from a potassium pyrosulfate fusion with a solution that was fumed with perchloric acid. But it can also be used to advantage, as in the gravimetric determination of potassium (where the even lower solubility of $KClO_4$ in butyl alcohol is sometimes utilized).

Ammonium perchlorate is more soluble in water than the potassium salt, but still of limited solubility. This makes it impossible, for example, to fume the filtrate of an ammonia separation in perchloric acid—a fortunate impediment since the ammonium perchlorate would almost certainly explode. The only elements volatilized from fuming perchloric acid alone are osmium, ruthenium, and rhenium, which are lost as OsO_4, RuO_4, and ReO_7. Numerous elements are, of course, volatilized from perchloric acid mixtures with other acids.

Fuming with perchloric acid will cause high concentrations of the "earth acids" and tin and antimony to precipitate as hydrous oxides. Perchloric acid must be heated only in a hood designed for its use (see Chapter 1). An approved safety shield must be used when working with incompletely characterized samples. Never heat a material with perchloric acid near the fuming point unless a large excess of nitric acid has also been present. For more information, safety tips, and references, see the monograph *Perchloric Acid and Perchlorates* by A. A. Schilt (published by GFS Chemical Company, 867 McKinley Ave., Columbus, OH 43223). Perchloric acid is an invaluable reagent that has been used in quantity in metals analysis labs for over 60 years, almost since the pioneering efforts of G. Frederick Smith, himself. Treated with the respect it deserves, it can well serve the needs of today's and tomorrow's laboratories.

Phosphoric acid (H_3PO_4) is a nonoxidizing acid used chiefly for its complexing characteristics. It is sold as a 86% (w/w) solution that boils at 213°C. Anhydrous acid is a solid that melts at 42.3°C; it is sometimes referred to as "ortho-phosphoric acid." In combination with perchloric or sulfuric acids, phosphoric acid has good solvent properties and allows many elements to remain in solution that would otherwise precipitate as hydrous oxides. Zirconium, hafnium, and titanium will precipitate as insoluble phosphates, although the precipitation of titanium can be avoided by the addition of hydrogen peroxide. Phosphoric acid is often added to solutions for potentiometric titrations or color endpoint redox titrations. Here it serves to adjust the formal endpoint potential for ease of detection. One problem that occurs on strong fuming with phosphoric acid mixtures is the formation of a polymeric form of the acid that is nearly insoluble.

Acetic acid (CH_3COOH) is the most commonly used carboxylic acid. It is sold at close to 100% purity in a form known as "glacial" acetic acid. It is available in an array of grades that reflects both the inorganic and organic applications of the reagent—ACS grade, instrument grade, ultra-purity grade, HPLC grade, aldehyde-free grade, and others. Glacial acetic acid fumes slightly in air, has an irritating vinegar odor, and should only be used in a hood. Even though only partially dissociated in dilute solution, the concentrated acid will cause serious burns and should be handled with gloves. In the metals analysis laboratory it is used primarily in the preparation of organic reagent solutions, although it also finds use in certain types of group separation schemes. And its properties as a "weak" acid are sometimes used to selectively leach readily soluble components from a solid matrix and for the preparation of pH buffer solutions.

TABLE 3-3—Concentration data for reagent grade acids and ammonium hydroxide.

Acid	Formula Weight	% (w/w)	Molarity	Normality	Specific Gravity
Acetic glacial	60.053	99.8	17.4	17.4	1.06
Formic	46.026	90.0	23.6	23.6	1.20
Hydrobromic	80.91	48.0	8.87	8.87	1.50
Hydrochloric	36.461	37.2	12.1	12.1	1.18
Hydrofluoric	20.006	49.0	28.9	28.9	1.15
Nitric	63.013	70.4	15.9	15.9	1.14
Perchloric	100.459	70.5	11.7	11.7	1.66
Phosphoric	97.995	85.5	14.8	44.4	1.69
Sulfuric	98.079	96.0	18.0	36.0	1.84
Ammonium hydroxide	35.046	56.6	14.5	14.5	0.90

Other acids that may be used regularly in some metals analysis labs can be briefly mentioned. *Formic acid* (HCOOH) at around 90% (w/w) is used dropwise to destroy the last traces of nitric acid from solutions that must exclude it. *Hydrobromic acid* (HBr) at 48% (w/w) is used alone or in combination with bromine to dissolve lead alloys, including lead-based solders. It quickly dissolves copper alloys, unlike hydrochloric acid, which attacks them slowly. It is used alone or in combination with hydrochloric acid to volatilize tin away from other elements of interest or to distill and collect it for analysis. *Fluoboric acid* (HBF_4) is sold at a concentration of 49% (w/w). It finds application in special dissolution schemes. It dissolves silicate minerals but not quartz, and thus it can be used to determine quartz. It has also been used to dissolve tin-based alloys.

Some laboratories have found it worthwhile to prepare their own ultra-purity acids with a sub-boiling still. This is usually only practical for the gaseous acids (HCl, HNO_3, HF, etc.). Mattinson (see references to this chapter) described a very simple device consisting of two Teflon FEP bottles of 1000-mL capacity screwed into a Teflon TFE connector at a right angle to one another. The bottle containing the "feed" acid is heated by a 300-W heat lamp, and the collection bottle is cooled in a running water bath. Over 500 mL of distillate are collected per week. Little and Brooks (see references to this chapter) later showed that the design can produce a product reduced by two to ten times in trace metals. Table 3–3 lists concentration data for the common commercial reagent grade acids plus ammonium hydroxide.

BASES

The "caustics" or alkali compounds release hydroxyl ion in aqueous solution. According to our simplified definition, these are the bases. As with acids, the extent of dissociation determines if they are "strong" or "weak." Bases are used as dissolution agents in molten salt fusions; they are even used in aqueous solution to dissolve certain amphoteric metals like aluminum. They are used as standard solutions in acid-base titrimetry, and they aid in the preparation of some reagent solutions. Bases also serve as reagents themselves in precipitation and complexation reactions.

Ammonium hydroxide (NH_4OH) is a water solution of ammonia gas sold at a concentration of 29% (w/w) NH_3 [equivalent to 59.7% (w/w) NH_4OH]. "Instrument" and ultra-purity grades are available, the latter sometimes at a lower concentration. The solubility limit of ammonia gas in water at room temperature is about 48% (w/w).

Ammonium hydroxide is a weak base. Its degree of dissociation increases rapidly with dilution. Like all weak acids and bases, it obeys Ostwald's dilution law, which simplifies to: $x^2 = K_dV$, where x is the fraction dissociated, K_d is the dissociation constant, and V is the solution volume. Thus, ammonium hydroxide can be used to prepare buffer solutions that resist changes in pH.

It is also used as a precipitant for the "R_2O_3" group of elements (erroneously named for certain oxide forms that only *some* of them attain at ignition). The group includes iron, aluminum, titanium, the rare earths (including scandium and yttrium), beryllium, gallium, indium, zirconium, hafnium, niobium, tantalum, thorium, uranium, and chromium (III). Chromium (VI) does not precipitate, but it and many other elemental species can be occluded in the "R_2O_3" group.

Ammonium hydroxide also serves as a complexing agent, forming stable, soluble complexes with nickel, cobalt, copper, zinc, silver, cadmium, and other metals. Ammonium hydroxide is infrequently employed as a dissolution medium, although molybdenum trioxide dissolves readily in it, and copper and molybdenum metal will dissolve in a mixture of ammonium hydroxide and hydrogen peroxide. Like the strong bases, ammonium hydroxide feels slippery because it readily decomposes the skin; thus, such contact must be avoided. The vapors are very pungent and will burn skin and eyes, so bottles should be opened and all work conducted in a hood.

Sodium hydroxide (NaOH) is a solid at room temperature (m.p. 328°C). ACS grade is sold in the form of pellets, lower grades as pellets, flakes, or sticks. Look for labels that say "low in carbonate," for others will not usually produce clear solutions upon dissolution in water and must be filtered through hardened filter paper. For convenience, solutions at various concentrations are also sold, including standard solutions for alkalimetric titrations.

Sodium hydroxide is a strong base with many uses. It dissolves aluminum and its alloys with the formation of sodium aluminate ($NaAlO_2$). The reaction is generally quite vigorous and exothermic ($2Al^0 + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$). Frequently the solid is valuable as a flux in molten salt fusions. Solid sodium hydroxide is delinquescent and cannot be weighed accurately in air. It also absorbs carbon dioxide, and this property is used to protect solutions from atmospheric CO_2 by using a sodium hydroxide trap. It is also used to gravimetrically determine carbon dioxide.

For these applications, the compound is adsorbed onto the surface of an inert substrate (formerly asbestos, now a clay mineral) that does not clog as a trap of the pure compound would do. Sodium hydroxide solutions will precipitate many metals, including iron, nickel, cobalt, copper, manganese, silver, cadmium, indium, thallium, magnesium, titanium, zirconium, hafnium, scandium, yttrium, lanthanum, and the lanthanides, thorium, and uranium. Many metals are incompletely precipitated, such as niobium, tantalum, lead, bismuth, mercury, ruthenium, rubidium, osmium, and others. Thus sodium hydroxide separations are best applied after at least one separation by other means.

The dissolution of sodium hydroxide in water is exothermic, accompanied by the generation of an aerosol, and is best conducted in a cooling bath in a hood. Excessive cooling, however, will cause the solid to stick to the bottom of the vessel, so vigorous stirring is called for. Sodium hydroxide solutions readily leach silicon, aluminum, and boron from borosilicate glass vessels, so solutions that are to be used for the determination of these (and other elements that are constituents of this type of labware) should be prepared, stored, and used in plastic vessels. In general, it is wise to store all sodium hydroxide solutions in plastic and certainly any concentrations above 1 mol. Always wear gloves since the slippery feel of sodium hydroxide solutions is your own skin dissolving. Flush any contact with a great deal of cold water.

Other bases include *potassium hydroxide* (KOH), which is also sold as pellets and as solutions of various concentrations. This reagent finds more applications in organic analysis, although it is sometimes used as a molten salt flux. The same is true of *lithium hydroxide* (LiOH), which is sometimes specified for molten salt fusions. The anhydrous form of this reagent may be difficult to find, although it is more suitable for fusions than the monohydrate.

MOLTEN SALT FLUXES

We have already discussed hydroxides as molten salt fluxes for metals, ores, and other materials, but there are many more compounds that find application for treating samples that are refractory to acids. Here we will briefly review some of the commonly used fluxes.

Sodium carbonate (Na_2CO_3) is one of the most widely applied compounds in this category. As an anhydrous powder or anhydrous granules, it will fuse most siliceous materials. Since its melting point (851°C) is quite high, sodium carbonate fusions are performed in a platinum crucible with a lid, either over a burner or in a muffle furnace. Without a lid to contain the heat, the melting point will not be attained with a Meker burner. The ACS grade is good enough for most applications, although an ultra-purity grade is available at about twice the cost. Sodium carbonate fusions have the advantage of not adding anions to the sample since carbonate is lost as gaseous CO_2 when the cooled, leached melt is acidified.

Potassium carbonate (K_2CO_3) is specified for certain fusions. Its solvent properties as a molten salt flux are frequently enhanced by mixture with sodium carbonate. Alone, it melts at 891°C. In a 50-50 (w/w) mixture with sodium carbonate, the eutectic melts at 715°C.

Lithium carbonate (Li_2CO_3) is the lowest melting of this series (618°C). It is also the most corrosive to the platinum crucibles used for carbonate fusions. Because of the strong attack on the vessel materials, porcelain, Vycor, and fused silica crucibles are unsuitable for any carbonate fusion.

Boric acid (H_3BO_3) and *boron trioxide* (B_2O_3) are an acid and its anhydride ($2H_3BO_3 \rightarrow B_2O_3 + 3H_2O$). Both are available, although the acid is more accessible in high-purity form. At 300°C the acid decomposes to the trioxide, which melts at 460°C. Since the loss of water does not cause spattering, the acid can be used effectively as a molten salt flux. These are acidic flux materials, suitable for a wide range of dissolutions. Boric acid is also useful to eliminate the interference of fluoride ion in many determinations.

The borates include *sodium tetraborate* or *borax* ($Na_2B_4O_7$), *lithium tetraborate* ($Li_2B_4O_7$), and *lithium metaborate* ($LiBO_2$). They are all available in anhydrous form and find use in the dissolution of high-alumina materials by molten salt techniques. Combinations of carbonates and borates are sometimes recommended as "universal" fluxes for handling a variety of silica/alumina sample materials.

Potassium pyrosulfate ($K_2S_2O_7$) is perhaps the most important of the acidic fluxes. Manufacturers are reluctant to assign the above formula to their product since the commercial reagent is a mixture with potassium bisulfate, from which it is formed ($2KHSO_4 \rightarrow K_2S_2O_7 + H_2O$). A more correct way to refer to it is *potassium bisulfate, fused* . This flux will dissolve most forms of alumina (including corundum, ruby, and sapphire) and most metals and alloys. Potassium pyrosulfate is also used to clean platinum crucibles. Since its attack on silica is limited, fusions can be conducted in Vycor, fused silica, and even porcelain crucibles.

Sodium bisulfate, fused ($NaHSO_4$) is valuable when perchloric acid is to be used since sodium perchlorate is much more soluble than potassium perchlorate. Thus, fusions in this medium will not cause salting problems when leached in a perchloric acid solution. This flux tends to spatter more than potassium pyrosulfate fusions, but this effect can be ameliorated by the addition of a few drops of concentrated sulfuric acid.

Sodium peroxide (Na_2O_2) will dissolve some of the most refractory materials by molten salt fusion in a zirconium crucible (chromite ore, for example). For the metals analyst it comes as close as anything to the universal solvent, but it is usually relied upon only when necessary because of the hazard and difficulties associated with its use. It is also used as a reagent to provide oxidation in caustic separations. When used as a flux, extreme caution is necessary since sodium peroxide may react with pyrotechnic violence with certain samples. An approved shield is always advised. The cooled melt reacts vigorously with water to produce a strong sodium hydroxide solution. The oxidizing power of sodium peroxide can be moderated by adding anhydrous sodium carbonate to the crucible before applying heat. Flush spilled reagent with a great deal of water and never use cloth, paper, or anything organic to clean up a spill until the area has been flooded with water.

OXIDIZING AGENTS

Reagents are frequently used for their oxidizing properties in solution chemistry. Sometimes these effects are selective and even surprising. Here we will summarize some facts about the more commonly used oxidizing reagents.

Potassium permanganate ($KMnO_4$) is sold as dark purple or black crystals that dissolve in water. When used for volumetric work, the solution is allowed to stand in the dark for two weeks and then filtered. It must then be standardized before use by titration of a weighed portion of either oxalic acid or sodium oxalate, the latter being preferred since it is not associated with waters of hydration. Since the reaction is slow, the solution must be heated near the endpoint. Once standardized, potassium permanganate solutions can be used to titrate the reduced form of many elements, most notably iron (II). Today potassium permanganate has fallen from favor except where it is irreplaceable (as in the Lingane-Karplus titration for manganese) because of its need for daily standardization. Solutions of potassium permanganate are also used for their oxidizing power in other types of methods and to test reagents for the presence of reducing substances.

Potassium dichromate ($K_2Cr_2O_7$), unlike the above, is a primary standard when purchased in a sufficiently pure grade. Primary standard grade potassium dichromate is prepared by repeated crystallizations from aqueous solutions and may be obtained from reagent chemical manufacturers or standardizing bodies such as NIST. These products can usually be weighed without drying because they are not hygroscopic. The weighed crystals dissolve readily in water, and the resultant solutions require no further standardization. Protected from evaporative losses, potassium dichromate solutions keep a stable titer for many weeks or even months. They are employed in the redox titration of iron, tin, tellurium, and tungsten, and as back-titrants for chromium and other analytes reduced by iron (II). Unlike potassium permanganate, which is self-indicating in all but the most dilute concentrations, potassium dichromate requires an indicator (frequently one of the diphenylamines) for visual endpoint work.

Ceric sulfate ($Ce(SO_4)_2$) should not be purchased as such when it is to be employed as a redox titrant. The commercial product is usually impure and difficult to dissolve. The analyst should obtain primary standard grade *ceric ammonium nitrate* ($(NH_4)_2Ce(NO_3)_6$), dry it at 85°C, and, after cooling in a desiccator, weigh an appropriate amount into a large beaker [54.83 g for a 0.1 *N* $Ce(SO_4)_2$ solution]. Concentrated sulfuric acid is then added (56 mL for a solution that is to be 1M H_2SO_4), and the crystals are stirred for a time. Then (in violation of the acid-water rule) very small increments of water are very cautiously added, while the solution is continuously stirred until the heat of reaction has dissolved all of the solid reagent. This process takes some time. When cool, the solution is transferred to a 1-L volumetric flask, diluted almost to the mark, mixed, cooled to room temperature again, diluted to the mark and mixed. Standardization is not needed for a solution prepared in this way, and the titer is stable for months.

Cerium (IV) sulfate undergoes most of the same reactions as potassium permanganate. Its formal redox potentials are higher, however, and show marked variation in different acid media. The reason for this may be that instead of the simple Ce^{4+}/Ce^{3+} couple, complex ions like $Ce(SO_4)_3^{2-}/(Ce^{3+})(SO_4^{2-})_3$ may be involved. As with potassium dichromate, endpoints are determined either potentiometrically, or visually with an internal indicator (often ferroin, which is the ferrous complex of o-phenanthroline), and sometimes an osmium tetroxide catalyst is employed.

Iodine (I_2) is a very useful oxidizing titrant, but its solutions must be standardized by means of a primary standard material such as arsenious oxide. The best grade of iodine available is sublimed and recrystallized. Never put iodine in a drying oven; it is a low-temperature, high-vapor pressure material that would quickly corrode the inside of an oven. If moisture is ever suspected, place the crystals in an ungreased desiccator for several days (ungreased because even trace organic contamination must be avoided). In aqueous solution, the reacting species is actually always triiodide ion (I_3^-).

While I_2 is volatile and has very low solubility in water, I_3^- tends to be less volatile and is very soluble in water. Thus a 0.1 *N* iodine standard solution is prepared by weighing 12.7 g of iodine into a beaker, then weighing 40 g of potassium iodide into the same beaker. About 10 mL of water are added, and the solution is alternately swirled and allowed to stand until all is dissolved (swirling rather than stirring lessens volatile loss of iodine). The solution is transferred to a 1-L volumetric flask, diluted to the mark, and mixed. It is then transferred to an amber or low-actinic glass bottle with a glass stopper for storage in a cool, dark location. The analyst must always remain aware that iodine has significant volatility; thus, solutions should be removed from storage vessels by pipet, not poured, and storage bottles must be kept stoppered. Iodine standard solutions are almost always used with a soluble starch indicator (best prepared by dissolving a water paste of potato starch in boiling water). Many elements are determined iodimetrically, notably tin, arsenic, and antimony. A disadvantage with iodine titrations is that most reaction rates are very sensitive to pH and temperature.

Potassium iodate (KIO_3) provides a more convenient way of performing iodimetric work. It is a primary standard that will generate triiodide in the presence of iodide ion and acid ($IO_3^- + 8I^- + 6H^+ \rightarrow 3I_3^- + 3H_2O$). The potassium iodate should be dried at about 170°C for 1 h. To prepare a 0.1 *N* solution, combine 3.5667 g of potassium iodate with 10 g of potassium iodide and 1 g of sodium hydroxide, dissolve in water, and dilute to 1 L. The reactant species (I_3^- is instantly generated upon addition to the acid sample solution. Potassium iodate is also sometimes used to precipitate thorium, especially to remove it from the rare earths.

Potassium bromate ($KBrO_3$) is also available in a primary standard grade. It should be dried at 150°C. It is sometimes used to standardize sodium thiosulfate solutions. Usually in this procedure an exact volume of 0.1 *N* potassium bromate is allowed to react with potassium iodide in the presence of hydrochloric acid. After 5 min the liberated iodine is titrated with sodium thiosulfate solution (near 0.1 *N*). Arsenic (III), antimony (III), and iron (II), among others, can be titrated directly with sodium bromate. In these reactions bromate is reduced to bromide ($BrO_3^- + 6H^+ \rightarrow Br^- + 3H_2O$), and at the endpoint the slight excess of bromate generates bromine ($BrO_3^- + Br^- + 6H^+ \rightarrow Br_2 + 3H_2O$), which is easy to detect with the proper indicator. A mixture of potassium bromate and potassium bromide is sometimes useful for generating free bromine in solution. Such a mixture can also be used in the precipitation of bismuth oxybromide (BiOBr).

Bromine (Br_2) is a useful oxidizing agent in many procedures. The pure halogen is a noxious, corrosive, dark-brown liquid (b.p. 58.76°C) in equilibrium with the heavy, reddish-brown fumes of its vapor phase. Except for bromine-methanol or bromine-methyl acetate inclusion isolations and the bromine-hydrobromic acid dissolution of lead alloys, most applications of bromine utilize a saturated water solution ("bromine water"). Elemental bromine and its vapors are extremely hazardous, and all work must be conducted with gloves in an efficient hood. One advantage to oxidation with bromine water is that excess reagent can be readily removed by boiling the solution. Bromine will oxidize sulfur to sulfate and is often employed for this purpose in gravimetric sulfur procedures. Bromine water is also employed to prevent any reduction of molybdenum in its precipitation with alpha-benzoinoxime.

Hydrogen peroxide (H_2O_2) serves as both an oxidizing and a reducing agent. Adding it during the acid dissolution of metals creates oxidizing conditions, but does not passivate metal surfaces (as nitric acid often does). A brief boil converts it to oxygen and water, so it is easily removed from the solution. Hydrogen peroxide is most useful as the 30% (w/w) ACS grade reagent that is stabilized with sodium stannate (Na_2SnO_3); an ultra-purity grade at about the same concentration is also available. It readily oxidizes ferrous iron, but, interestingly, it *reduces* permanganate and dichromate. These reactions take different paths; thus, iron (II) is oxidized as follows: $2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$, and permanganate is reduced by this means: $2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$.

With dichromate, a deep blue flash of color when hydrogen peroxide is first added shows that a brief excursion to a very high, unstable oxidation state (perchromate ion) precedes reduction to Cr^{3+}. Hydrogen peroxide at 30% concentration will produce white stinging burns on the skin that persist for 5 to 15 min, even if flushed with water. Thus, gloves should be worn when working with this reagent. Some labs extend the shelf life of hydrogen peroxide by storing the reagent in a refrigerator. Discard any reagent that has become contaminated by flushing it down a drain with a large amount of water.

Ammonium persulfate ($(NH_4)_2S_2O_8$), also known as *ammonium peroxydisulfate*, is a very powerful oxidizing agent, especially in the presence of a silver ion, which serves as a catalyst in the oxidation of Cr^{3+} to dichromate, Mn^{2+} to permanganate, and VO^{2+} to VO_2^+ (in boiling dilute sulfuric acid). Advantage is often taken of these reactions in the volumetric determination of chromium, manganese, and vanadium. The reagent is also sometimes used to oxidize chromium when the use of perchloric acid is precluded.

Obviously, there are many other oxidizing agents used in the analysis of metals, some with narrow or specific uses—*potassium metaperiodate* (KIO_4) or *periodic acid* (H_5IO_6) to oxidize manganese to permanganate for its spectrophotometric determination; *potassium ferrocyanide* ($K_3Fe(CN)_6 \cdot 3H_2O$) to oxidize cobalt (II) to cobalt (III) in its potentiometric titration. These are but two examples.

REDUCING AGENTS

As with oxidizing agents, there is no clear line between reducing agents used as standard solutions in redox volumetric work and reducing agents used in general reaction chemistry.

Ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$), also known as *ammonium iron (II) sulfate, hexahydrate*, or *Mohr's salt*, is a widely used reducing titrant. Properly classed as a secondary standard, its exact normality can be established easily by titration with standard potassium dichromate. The normality or titer will change daily due to some air oxidation, but the variation is much less dramatic than for *ferrous sulfate* ($FeSO_4 \cdot 7H_2O$). The reducing power of ferrous sulfate is best utilized when it is added to a solution as a weighed salt. Ferrous ammonium sulfate solutions, on the other hand, are easily prepared and reasonably stable. It is important, however, that ferrous salts not be placed in a drying oven before weighing, as they will oxidize. Ferrous ammonium sulfate is used in the redox titration of chromium and vanadium and in numerous methods as a back-titrant for excess additions of permanganate, dichromate, or cerium (IV).

Sodium oxalate ($Na_2C_2O_4$) and *oxalic acid* ($H_2C_2O_4 \cdot 2H_2O$) can both be used to standardize potassium permanganate since both can be primary reductimetric standards. Sodium oxalate is the material of choice, however, since it is not a hydrate (many hydrates, including oxalic acid, show some variation in the degree of hydration). Even so, sodium oxalate must be dried at 100°C before use. The titration of either reagent with permanganate involves an inherently slow reaction, so it is important to warm the solution a few millilitres short of the final endpoint.

Arsenious oxide (As_2O_3) and *sodium meta-arsenite* ($NaAsO_2$) are even better reductimetric standards than the above, although both are highly toxic. Arsenious oxide is generally available in a purer form than the water-soluble sodium arsenite, but it must be dissolved in dilute sodium hydroxide solution and the solution neutralized with acid before dilution. These reagents are used in the redox titration of permanganate, cerium (IV), bromine, and iodine, and frequently in the back-titration of excess additions of permanganate and cerium (IV). It is extremely important not to dry these compounds in a drying oven before weighing since toxic vapors would be generated.

Sodium thiosulfate ($Na_2S_2O_3$) is available in anhydrous form and as a 5-hydrate (photographic "hypo"). As with all materials for standard solution preparation, the water-free form, if available, is usually preferred because hydrates can effloresce when exposed to moist air, producing a substance of indefinite composition. Sodium thiosulfate is not a primary standard. Also, its solutions are subject to deterioration by the presence of a *thiobacillus* microorganism. But, nevertheless, it is a valuable reductimetric titrant, especially for iodine. Various sterilizing additives have been suggested to prevent the growth of sulfur bacteria in the solution, including sodium carbonate, sodium borate, di-basic sodium phosphate, and chloroform. At the very least the standard solution should be prepared with freshly boiled and cooled distilled water. Just prior to each use, the sodium thiosulfate solution should be standardized by titration against standard potassium permanganate or standard iodine solutions. If the solution becomes turbid or if sulfur coats the glass storage vessel walls, the solution must be discarded and the vessel sterilized by soaking in chromic acid before it is reused.

Stannous chloride ($SnCl_2 \cdot 2H_2O$) is an important reducing agent in solution chemistry. It dissolves in hydrochloric acid and will remain a clear solution down to about 1:1 $HCl:H_2O$. To prevent hydrolysis of stannous oxide at lower hydrochloric acid concentrations, a few tin shot pellets are usually added to the solution. However, the solution must not be stored in a tightly sealed container since pressure may develop from the formation of hydrogen gas. Stannous chloride is commonly used to reduce iron for its subsequent volumetric de-

TABLE 3–4—Half-cell potentials for selected redox species.

Ion/Compound	Half-Cell Reaction	E^0_{redox}, V
Persulfate	$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	2.01
	$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82
Hydrogen Peroxide	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.77
	Ce (IV) + e^- → Ce (III) (1 *M* $HClO_4$)	1.61
Permanganate	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51
Dichromate	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow Cr^{3+} + 7H_2O$	1.33
	$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00
	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.771
Hydrogen Peroxide	$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$	0.682
Iodine	$I_3^- + 2e^- \rightarrow 3I^-$	0.545
Ferrocyanide	$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$	0.36
	$Cu^{2+} + 2e^- \rightarrow Cu^0$	0.337
Saturated Calomel Electrode	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg^0 + 2Cl^-$	0.244
Sulfurous Acid	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow SO_2(aq.) + 2H_2O$	0.17
	$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	0.154
Thiosulfate	$S_4O_6^{2-} + 2e^- \rightarrow 2S_2O_3^{2-}$	0.08
	$2H^+ + 2e^- \rightarrow H_2O$	0.000
Hydrazinium	$N_2 + 5H^+ + 4e^- \rightarrow H_2NNH_3^+$	−0.23
	$Ni^{2+} + 2e^- \rightarrow Ni^0$	−0.246
Oxalic Acid	$2CO_2 + 2H^+ + 2e^- \rightarrow H_2C_2O_4$	−0.49
Hypophosphorous Acid	$H_3PO_3 + 2H^+ + 2e^- \rightarrow H_3PO_2 + H_2O$	−0.50

termination and to reduce molybdenum prior to its spectrophotometric determination. It will also reduce selenium, tellurium, and arsenic to the elemental state.

Sulfurous acid (H_3SO_3) is sold as an 8% (w/w) solution of SO_2 gas in water. It reduces vanadium (V), iron (III), and antimony (V) to vanadium (IV), iron (II), and antimony (III), respectively. It reduces selenium and tellurium to elemental form. And it causes the "earth acids" to precipitate as hydrous oxides. It is sometimes useful to redissolve MnO_2, which may precipitate from solutions of high-manganese alloys. It also reduces chromium to the trivalent state in the presence of hydrochloric acid. Sulfurous acid that has been stored for some time loses strength due to outgassing and the formation of sulfur compounds (which adversely affect its reducing power). The bottle should be opened cautiously in a hood since pressure may develop, and all operations with sulfurous acid must be similarly conducted in a hood. Sulfurous acid has the advantage that any excess may be completely expelled from an acidic sample solution with 5 or 6 min of boiling.

Hydrazine sulfate ($H_2NNH_2 \cdot H_2SO_4$) is a powerful reducing agent, which, like hydrazine and its dihydrate, is very toxic, It is, however, much more stable than those two compounds. Hydrazine sulfate is a solid that dissolves in water. Such solutions should always be prepared fresh on the day of use. One important application is in the reduction of heteropolymolybdate complexes to their intensely colored forms, as in the spectrophotometric determination of phosphorus. The hydrazinium ion, in turn, decomposes into hydrogen ion and N_2 (which leaves the solution).

Hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) is a comparatively mild reducing agent that works best in very dilute acid solution. Thus it finds use wherever large amounts of acid are not required to keep alloy components in solution. It has been used to reduce iron prior to the gravimetric determination of barium in barium ferrite magnet materials and to reduce manganese and cerium in magnesium alloy solutions. It is added either as a freshly prepared solution or directly as solid crystals. The reaction products are N_2, H^+, and H_2O.

A few other reducing agents bear brief mention. *Hypophosphorous acid* (H_3PO_2) is sold as a 50% (w/w) solution. It is the strongest reducing agent in common use and will reduce certain metal ions to the elemental state. *Titanous chloride* ($TiCl_3$), sold as a 20% (w/w) solution, can be used to titrate iron (III) (when used as a 1% solution protected by a blanket of carbon dioxide). *Sodium nitrite* ($NaNO_2$) is convenient (as a fresh aqueous solution) for destroying the permanganate color after its spectrophotometric measurement (so that the sample background color can be measured). *Sodium sulfite* (Na_2SO_3), *sodium bisulfite* ($NaHSO_3$), and *sodium dithionite* ($Na_2S_2O_4$) have all been used for their reducing power in the analysis of metals. *Ascorbic acid* ($C_6H_8O_6$) can be used as a reductimetric titrant, but it is principally used as a reducing agent in procedures like the TOPO/iodide/MIBK extraction of trace tin and other metals.

A related area might be more properly termed "reducing techniques." Thus *nascent hydrogen* formed in solution by the action of acid on some pure reactive metal has been used to reduce metal ions. The *Jones reductor* and the *silver reductor* are reducing systems confined in glass columns through which an acid solution of the sample is passed. The Jones reductor is filled with a zinc-mercury amalgam (1 to 5% mercury) of 20 to 30 mesh (850 to 600 μm) and will reduce iron, chromium, vanadium, molybdenum, titanium, and other elements introduced in dilute hydrochloric or sulfuric acid solution. The silver reductor is filled with metallic silver (precipitated by ionic displacement with pure copper from a silver nitrate solution). Iron, molybdenum, vanadium, and other elements are reduced by the silver reductor, but titanium is not. Table 3–4 shows some half-cell reactions and potentials for selected redox reactants. Table 3–5 illustrates the preparation of certain redox standard solutions.

PRECIPITANTS

We have already discussed several important precipitants in previous categories— ammonium and sodium hydroxides,

TABLE 3-5—Preparation for selected redox standard solutions (0.1*N*). (In all cases dilute to 1 L.)

Compound	Weight, g	Procedure	Standardization	Shelf Life
Ceric sulfate, $Ce(SO_4)_2$	54.83 (ceric ammonium nitrate, dried at 85°C)	Add 56 mL conc. H_2SO_4, stir, then cautiously add H_2O in small increments with stirring until dissolved, then dilute	Primary standard	Stable
Potassium permanganate, $KMnO_4$	3.2	Add 1 L H_2O and stir. Heat below 90°C for 1 h. Cool, store in dark two weeks, then filter.	Dry primary standard grade sodium oxalate and accurately weight 0.3 g into 600 mL beaker. Add 250 mL H_2SO_4 (5 + 95), which has been boiled and cooled. Stir to dissolve. Add 40 mL $KMnO_4$ by buret and stir until color is gone. Heat to 60°C and carefully finish titration to first permanent pink.	Standardize for each use. (Store in dark.)
Potassium dichromate, $K_2Cr_2O_7$	4.903 (dried at 100°C)	Dissolve in H_2O and dilute.	Primary standard	Stable
Iodine, I_2	12.7	Add 40 g KI to the weighed I_2 in a 50 mL beaker. Add 20 mL H_2O and swirl gently until dissolved, then dilute.	Accurately weigh 0.3 g primary standard grade As_2O_3 into a 250 mL Erlenmeyer flask; add 10 mL 1 *N* NaOH and stir to dissolve. Add 15 mL 1 *N* H_2SO_4, stir, then add 50 mL $NaHCO_3$ solution (40g/L). Add 5mL 0.5% starch solution and titrate with I_2 to first blue color.	Standardize for each use. (Store in dark.)
Sodium thiosulfate, $Na_2S_2O_3$	25. (5-hydrate)	Dissolve with 0.1 g Na_2CO_3 in 1 L of freshly boiled, cooled H_2O.	Add 10 g KI to each of two 250 mL Erlenmeyer flasks. Add 100 mL boiled and cooled H_2O and 2 mL HCl to each. To one flask add 40 mL standard $KMnO_4$ by buret. Stopper both and let stand 10 min in the dark. Add 2 mL 0.5% starch solution to both flasks and titrate both with thiosulfate to first blue color. Subtract the blank.	Standardize for each use. (Discard if turbidity or deposits appear.)

hydrogen sulfide, sulfur dioxide, stannous chloride, and others. Here we will examine a few more.

Dimethylglyoxime ($CH_2C(:NOH)C(:NOH)CH_2$) is a white powder soluble in methanol or in sodium hydroxide solution. It is a specific precipitant for nickel and palladium. Nickel precipitates as a bright red voluminous compound from ammoniacal solutions, while palladium comes down as a yellow compound from dilute hydrochloric acid solutions. These precipitates are dried and weighed as stoichiometric compounds.

alpha-Benzoinoxime ($C_6H_5CHOHC(:NOH)C_6H_5$) or *benzoin anti-oxime* is a methanol-soluble white powder that is a specific precipitant for molybdenum. The precipitate is not stoichiometric and must be ignited at low temperature (<525°C) to MoO_3. Tungsten is coprecipitated quantitatively in the presence of excess molybdenum, but its precipitation is otherwise incomplete.

Cupferron ($C_6H_5N(NO)ONH_4$) is the *ammonium salt of N-nitroso-N-phenylhydroxylamine*. It is a crystalline material usually sold with cloth pouches of ammonium carbonate in the bottle to maintain a slight ammonia atmosphere to prevent decomposition. Cupferron dissolves in water, but must be filtered before use. A 6% (w/v) solution is stable for a week under refrigeration. It is a nonspecific precipitant that is seldom applied without some preliminary separation or other treatment. Ferric iron forms a dark brown precipitate, and copper (II) forms a gray precipitate, but these elements are most frequently removed before cupferron is used. The "earth acid" elements (groups IVB, VB, and VIB minus Cr) all precipitate. Significantly, aluminum, chromium, cobalt, and nickel do not precipitate. Cupferron precipitates are either "wet ashed" or ignited to oxides. The reagent is listed as a carcinogen and should be handled with gloves in an efficient hood; drying, charring, and igniting the precipitates must likewise be conducted in an efficient hood.

8-Hydroxyquinoline ($HOC_6H_3N:CHCH:CH$) or *8-quinolinol* is a white powder with a characteristic odor that dissolves in acetic acid solution. It is a nonspecific precipitant that has found use in the precipitation of aluminum as a yellow compound after that element has been isolated by preliminary separations. It will not precipitate beryllium, which is otherwise difficult to separate from aluminum. 8-hydroxyquinoline has also been used to precipitate zinc from acetic acid solution and magnesium from ammoniacal solution (with the reagent added as an alcohol solution). Sometimes these precipitates are dissolved in hydrochloric acid, and the released 8-hydroxyquinoline is reacted with excess bromine (standard bromate plus bromide) and the excess back-titrated with standard sodium thiosulfate. More commonly, they are dried and weighed or sometimes ignited to the oxide and weighed.

TABLE 3–6—Solubility of selected metal compounds.

	Br^-	CO_3^{2-}	Cl^-	CrO_4^{2-}	CN^-	F^-	OH^-	I^-	$C_2O_4^{2-}$	PO_4^{3-}	SO_4^{2-}	S^{2-}	SO_3^{2-}	$C_4H_4O_6^{2-}$	SCN^-
Al	S	...	S	...	...	S	A	S	A	A	S	D	...	A	...
Sb	D	...	S	...	...	S	...	D	...	...	A	A	...	S	...
As	D	...	D	...	..	S	...	D	...	...	...	I	...	...	...
Ba	S	A	S	A	S	A	S	S	A	A	I	D	S	A	S
Be	S	S	S	...	...	S	...	D	S	S	S	A	...	...	...
Bi	D	...	D	...	A	S	A	A	A	A	D	A	...	A	...
Cd	S	A	S	A	S	S	A	S	A	A	S	A	A	A	...
Ca	S	A	S	S	S	A	S	S	A	A	A	A	A	A	S
Cr	B	S	B	...	A	A	A	B	S	A	B	D	...	A	...
Co	S	A	S	A	A	S	A	S	A	A	S	A	A	A	S
Cu	S	...	S	...	A	A	A	A	A	A	S	A	A	A	D
Au	B	...	B	...	B	...	B	I	...	...	...	I	...	...	...
Fe	S	A	S	A	A	A	A	S	B	A	B	A	A	B	S
Pb	S	A	S	A	A	A	A	A	A	A	A	A	A	A	A
Mg	S	A	S	S	S	A	A	S	A	A	S	D	S	A	S
Mn	S	A	S	...	...	A	A	S	A	A	S	A	...	A	S
Hg	B	A	B	A	B	D	A	A	A	A	A	I	...	I	A
Ni	S	A	S	A	A	A	A	S	A	A	S	A	A	A	...
Pt	A	...	S	...	I	S	A	I	...	...	S	I	...	...	...
RE	S	A	S	...	...	I	A	S	A	...	S	D	...	...	...
Ag	A	A	A	A	A	S	...	I	A	A	A	A	A	A	I
Sr	S	A	S	A	S	A	S	S	A	A	A	S	A	A	S
Sn	S	...	S	B	...	S	A	S	A	A	S	A	...	S	...
Zn	S	A	S	A	A	A	A	S	A	A	S	A	A	A	S

NOTE:
S = Soluble in water.
B = One form is soluble in water and one is insoluble in water.
D = Decomposes in water.
A = Insoluble in water or slightly soluble in water, but soluble in acids.
I = Insoluble in water and insoluble in acids.

para-Bromomandelic acid ($BrC_6H_5CHOHCOOH$) is the most useful of a series of substitution products of mandelic acid. It is a selective precipitant for zirconium and hafnium from hot hydrochloric acid solution. It works best when added as the solid crystals to the acidified sample, which is then digested in a boiling water bath. This reagent is expensive to use since it is only available as a "fine chemical" from specialty chemical companies.

Cinchonine ($C_{19}H_{22}N_2O$) is a white powder soluble in 1:1 hydrochloric acid:water. It is a specific precipitant for tungsten always used in combination with conditions that favor the hydrolysis of tungsten trioxide. The resultant precipitate is always contaminated, so the ignited, weighed residue is treated to dissolve the WO_3, and the impurities are weighed as a correction.

Thioacetamide (CH_3CSNH_2) is the principal agent for performing sulfide separations by homogenous phase generation of hydrogen sulfide. The reaction ($CH_3CSNH_2 + H_2O \rightarrow CH_3CONH_2 + H_2S$) proceeds under mildly acidic, neutral, or mildly basic conditions. The reagent is a known carcinogen, and H_2S is highly toxic, thus gloves and a hood are essential. There is a long list of elements that precipitate as sulfides, forming subgroups based on the solution's hydrogen ion concentration. Detailed separation schemes founded principally on sulfide separations have been devised, but are not much used today. The technique is still valuable as a single-step separation, however.

There are, of course, many other organic precipitants that find use from time to time. *Ammonium oxalate* ($(NH_4)_2C_2O_4 \cdot H_2O$) is sometimes used for calcium, strontium, and the rare earths. Hillebrand et al. in *Applied Inorganic Analysis* describe the use of *sodium acetate* (CH_3COONa) in the "basic acetate method" and *sodium succinate* ($C_4H_4O_4Na_2 \cdot 6H_2O$) for separating iron, but these approaches are little used today. *Nitron* ($C_{20}H_{16}N_4$) will precipitate rhenium as the perrhenate.

Among the inorganic precipitants, *hydrochloric acid* is used for silver, mercury (I), and thallium (I); *sulfuric acid* is used for barium, lead, and strontium. *Dibasic ammonium phosphate* ($(NH_4)_2HPO_4$) has been applied to precipitate aluminum, bismuth, cadmium, zinc, zirconium, and hafnium. *Potassium chromate* (K_2CrO_4) is useful for barium, lead, and thallium. *Potassium fluoride* (KF), *ammonium fluoride* (NH_4F), and *hydrofluoric acid* have been variously applied to precipitate calcium, thorium, scandium, yttrium, and the lanthanides. *Silver nitrate* ($AgNO_3$) has been used for chlorine (as in titanium metal), and *barium chloride* ($BaCl_2$) has been used for sulfur (after oxidation to sulfate). Table 3–6 summarizes the solubilities of a selection of metal compounds.

COMPLEXING AGENTS

In this category we will review some of the commonly used substances that form stable, soluble complexes with metal ions in solution. These reagents are used in two major ways—as titrants in complexometric titrations and as masking agents to prevent a precipitation or other reaction from occurring.

EDTA ($C_{10}H_{16}N_2O_8$) or *(ethylenedinitrilo)tetraacetic acid* is certainly the most important substance in this category. Since the acid form is difficult to dissolve even with heating, the

TABLE 3-7—Stable soluble complexes.

	NH_3	Br^-	Cl^-	CN^-	F^-	I^-	Acetate	Citrate	Oxalate	Tartrate	EDTA
Al					X			X			X
Ba							X	X			X
Be					X			X	X		X
Bi		X	X								X
Cd	X	X	X	X		X	X	X			X
Ca							X	X			X
Cr							X				X
Co	X						X	X			X
Cu	X	X	X				X	X			X
Au		X	X	X							
Fe	X		X				X	X	X	X	X
Pb		X	X				X	X			X
Mg							X	X			X
Mn	X						X	X			X
Hg	X	X	X				X				X
Ni	X						X	X			X
Pt	X	X	X								X
RE							X	X			X
Ag	X						X	X			X
Sr							X	X			X
Sn		X	X		X						X
Ti					X						
Zn	X						X	X			X
Zr			X		X						X

disodium salt (a dihydrate) is most frequently used. Some fine chemical houses market an ammonium salt that finds application in GFAA work. EDTA is by far the most widely used chelating agent; either direct or indirect titration methods have been published for nearly every metallic element. Most of this work employs visual endpoints with added indicators, each of which in some way responds to an excess of EDTA. In the metals analysis laboratory, EDTA titrations are used for cobalt, nickel, zinc and aluminum, among other elements. EDTA is also added to samples in the ferrocyanide titration of cobalt to prevent the interference of diverse ions. In this application cobalt undergoes oxidation by ferrocyanide ion while held in the "grip" of the chelate. While there are many related chelating compounds of this class (generically, aminopolycarboxylic acids or "complexanes"), surprisingly few are used in analytical procedures.

Potassium cyanide (KCN) has been used as both a titrant and a masking agent for decades, but its use has fallen out of favor because of disposal and other toxic hazard problems. Acidification generates deadly hydrogen cyanide gas and must be avoided at all costs. Gloves and an efficient hood are absolutely essential for all work with this compound. All waste solutions must be stored in closed containers for proper disposal. At one time a potassium cyanide titration was one of the principal methods for high levels of nickel. Today it finds restricted use for its ability to mask certain reactions in gravimetry and spectrophotometry.

Sodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$) forms a wine-red, stable, soluble complex with manganese, which is used as the basis of a clever and accurate titration of that element with standard permanganate solution. In the Lingane-Karplus titration, both sample manganese and titrant manganese end up in the same complexed state.

Some other complexing substances are best described by the anionic species involved since they are applied in a variety of forms. *Phosphate* and *citrate* compounds are widely used to complex iron; *fluoride*, *tartrate*, and *oxalate* are used to hold the easily hydrolyzable earth acids in solution. *Peroxide* holds titanium and vanadium as peroxy complexes. *Thiocyanate* has been used for molybdenum and copper. And *ammonia* complexes hold nickel, cobalt, silver, and copper in solution. Each of these anions complexes with many other cations, and the list of complexing anions could go on, but even then we would have only scratched the surface of this rich field of aqueous chemistry. See Table 3–7 for a selection of stable, soluble complexes.

SPECTROPHOTOMETRIC REAGENTS

The inclusion of this category was debatable because of the impossibility of doing justice in a few paragraphs to an area that multi-volume tracts have been written about. However, it was decided to include a few words about some compounds with a known track record in metals analysis labs.

Acetylacetone ($(CH_3CO)_2CH_2$) or *2,4-pentanedione* is both a solvent extractant and a chromophore. It is reasonably sensitive for iron and, since the color is bleached by hydrofluoric acid, has become the basis of one of the procedures for HF in pickling baths.

Dithizone ($C_6H_5NHNHCSN{:}NC_6H_5$) or *1,5-diphenylthiocarbazone* is soluble in chloroform and carbon tetrachloride. It forms colored complexes with trace levels of lead, bismuth, and zinc.

Silver diethyldithiocarbamate ($(C_2H_5)_2NCSSAg$) dissolved in pyridine is used to collect evolved arsine gas (AsH_3) from the sample. The colored complex that forms is then measured spectrophotometrically.

Nitroso R acid, disodium salt ($C_{10}H_5NO_8S_2Na_2$) is an excellent color reagent for cobalt. With steel samples the iron matrix is first removed by means of a zinc oxide separation.

Pyrogallol ($1,2,3\text{-}(HO)_3C_6H_3$) reacts with tantalum in the presence of ammonium oxalate to produce a yellow complex.

Hydroquinone ($1,4\text{-}(HO)_2C_6H_4$) is a light-sensitive compound that dissolves in concentrated sulfuric acid. It forms colored complexes with tungsten, titanium, and niobium and allows combinations of these analytes to be determined by measurement of the developed color at two different wavelengths.

Dianthrimide ($C_{28}H_{15}O_4$) or *1,1'-iminodianthraquinone* was formerly used (in concentrated sulfuric acid solution) for the direct determination of trace boron. It is one of the few spectrophotometric compounds for boron that does not require isolation of the analyte.

Curcumin ($C_{21}H_{22}O_6$) is widely used for the spectrophotometric determination of boron following its isolation by distillation as the methyl borate ester.

Diantipyrylmethane ($C_{23}H_{24}N_4O_2 \cdot H_2O$) forms a colored complex with titanium in aqueous solution that is used for the spectrophotometric measurement of that element.

Brilliant green ($C_{35}H_{34}O_4N_2S$) is the basis for a colorimetric method for antimony.

Neocuproine ($C_{14}H_{12}N_2$) or *2,9-dimethyl-1,10-phenanthroline* is the most widely used of a series of related reagents for the spectrophotometric measurement of low levels of copper. It is used in a chloroform solution.

Trioctylphosphine oxide ($(CH_3(CH_2)_7)_3PO$) is not a spectrophotometric reagent *per se* , but rather a valuable extractant for lead, bismuth, tin thallium, and silver in trace amounts. The extraction takes place in the presence of iodide with methylisobutylketone as the solvent. Measurement is commonly performed by flame atomic absorption. The same reagent is used to extract zirconium into cyclohexane, in this case for spectrophotometric measurement with pyrocatechol violet (see below).

Diphenylcarbazide ($C_6H_5NHNHCONHNHC_6H_5$) or *1,5-diphenylcarbohydrazide* is frequently used for the spectrophotometric determination of low levels of chromium.

1,10-Phenanthroline ($C_{12}H_8N_2 \cdot H_2O$) or *o-phenanthroline* is a sensitive spectrophotometric reagent for traces of iron.

Sodium thiocyanate ($NaSCN$) is a useful reagent in spectrophotometric methods for molybdenum in the presence of reducing conditions. The molybdenum color formation requires the presence of iron. The colored complex tends toward instability, and measures are often taken to ensure reproducible readings.

Dithiol ($C_7H_8S_2$) has been frequently employed for traces of tungsten. Molybdenum interferes, but can be removed by solvent extraction.

Sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$) and *ammonium molybdate* ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) are both used for spectrophotometric methods that produce the heteropolyacids—phosphomolybdate or molybdivanadophosphate for phosphorus; arsenomolybdate for arsenic; or molybdisilicate for silicon.

Pyrocatechol violet ($C_{19}H_{14}O_7S$) has been used in the spectrophotometric determination of zirconium and tin, among other metals.

Already mentioned, *hydrogen peroxide* forms colored complexes with titanium, vanadium, and (in sulfuric acid) niobium—each is used for spectrophotometric measurement. *8-hydroxyquinoline*, as well as being an important precipitant, provides a very good spectrophotometric method for traces of aluminum. Similarly, *dimethylglyoxime* not only precipitates nickel and palladium, but also forms soluble colored complexes with both elements.

ORGANIC SOLVENTS

The metals analysis laboratory must keep a supply of solvents, both for sample preparation and for chemistry. Since nearly all of these are either flammable or toxic, it is essential that they be properly stored, used, and disposed of. An approved, grounded solvent cabinet should be the repository for most of these chemicals when not in use. Flammable solvent storage drums and cans must always be grounded. A few labs have attempted to redistill their own solvents for reuse, but this practice is inherently hazardous since perchlorates and other potentially explosive residues may contaminate the laboratory waste. Waste solvents should be stored in approved containers for disposal by approved techniques. Often it is appropriate to segregate polar and nonpolar waste solvents, and in some cases each solvent compound should be separately stored. The analyst should be aware that acid residues that accompany many waste solvents may attack steel solvent storage cans.

Alcohols are essential in the metals analysis lab. A general solvent grade of *methanol* (CH_3OH) should be available for degreasing and for removing organic residues from glassware. HPLC grade or higher is needed for methyl borate distillations. Methanol is a systemic poison and should be kept in bottles with appropriate warning labels. Both denatured and absolute *ethanol* (C_2H_5OH) are usually necessary; the latter is often stored with other precious commodities in the laboratory safe. Both *1-propanol* ($CH_3CH_2CH_2OH$) (or *N-propanol)* and *2-propanol* ($CH_3CHOHCH_3$) (or *isopropanol*) are often required. Similarly, *1-butanol* ($CH_3CH_2CH_2CH2OH$) (or *N-butanol*) and *2-methyl-1-propanol* ($(CH_3)_2CHCH_2OH$) (or *isobutyl alcohol*) are frequently needed for solvent extraction work. Little else beyond this is usually necessary.

Ketones are even more restricted in use. Generally only *acetone* (CH_3COCH_3), *methylisobutylketone* ($CH_3COCH_2CH(CH_3)_2$) (or *MIBK*) and perhaps *methylethylketone* ($CH_3COCH_2CH_3$) (or *2-butanone*) are necessary.

Esters are required by some metals analysis work. *Methyl acetate* (CH_3COOCH_3), used with bromine, is the basis for most ester-halogen steel inclusion isolations. *Butyl acetate* ($(CH_3COO(CH_2)_3(CH_3)$) is used in certain solvent extraction procedures.

Chlorinated hydrocarbons are a major category of important solvents. *Methylene chloride* (CH_2Cl_2) (or *dichloromethane*) is the simplest and least toxic. Despite recent hazard warnings that implicate it with the other members of this category, it remains a valuable general purpose solvent. It is flammable and has carcinogenic properties. It should be used in a hood (electric hotplate only) with gloves. Many labs use methylene chloride for sample degreasing. *Chloroform* ($CHCl_3$) at one time served this purpose, but today, because of the hazard associated with its use, it should be restricted to solvent extraction work conducted with gloves in a hood. *Carbon tetrachloride* (CCl_4) is so hazardous that some labs restrict its use, although there are methods where it is analytically a better choice than chloroform. Similar bans on the use of *trichloroethylene* ($ClCH{:}CCl_2$) and *1,1,1,-trichloroethane* (CH_3CCl_3), both of which are specified in some older methods, are in place in some organizations.

Aromatics are even more of a dilemma. *Benzene* (C_6H_6) is now outlawed in most labs as a known carcinogen. *Toluene* ($C_6H_5CH_3$) and *xylene* ($C_6H_4(CH_3)_2$) are not far behind. It is best to forego methods that require these solvents.

Of the *aldehydes*, only *formaldehyde* (HCHO) is used and that mostly in a rarely used method for trace sulfur. The pararosaniline method is a sensitive means to quantify very low sulfur levels, but the hazard of formaldehyde suggests that modern trace methods will prevail.

Unsubstituted *hydrocarbons* are rarely used, although they sometimes are indispensable for certain (especially organic analyte) extractions. *Hexanes* (C_6H_{14}) is a practical solvent in this area for general use. The flammability hazard is, of course, a major concern.

Some labs forbid the use of *ethers* because of flammability hazards. They *are* important reagents in metals analysis, but should be purchased in small quantities that will be used up relatively quickly. This is to avoid the explosion hazard associated with peroxide buildup in long storage. Only *diethyl ether* ($C_2H_5OC_2H_5$) is necessary for most work, although *isopropyl ether* ($(CH_3)_2CHOCH(CH_3)_2$) is sometimes needed for certain extractions.

ELEMENTAL STANDARDS

This last category represents one of the biggest challenges to the metals analyst. Until the advent of the ICP-OES technology, most chemists believed they knew how to prepare standard solutions of pure elements. But the remorseless stability of this new excitation source began to suggest that some of the older procedures and measures of accuracy were not good enough. A standard cobalt solution that yielded, say, perfectly good results at the 0.5% level may not be quite adequate to calibrate an ICP-OES instrument at the 10% level. Perhaps there was some surface oxide on the cobalt metal. Perhaps the solution was still a few degrees above ambient temperature when the volumetric flask was diluted to the mark. Maybe there was a clinging microdrop in a transfer pipet. For purposes of discussion, let us assume that these effects amount to a cumulative error of 2.6% (relative). At the 0.5% cobalt level the error is invisible for routine work (say we find 0.51% Co on a standard certified at 0.50% Co), but the same error at the 10% cobalt level (say, 9.79% on a 10.05% Co standard) begins to wave a red flag at us. While the classical wet analyst is used to striving for relative standard deviations of 0.1% or lower, until the advent of the ICP-OES it was seldom within the framework of pure element standards that work of this caliber was required.

Thus, extreme attention to detail and the best laboratory practice are the order of the day if modern labs are to get the best work out of modern instruments. Pipets and burets must be cleaned regularly with concentrated sulfuric acid to remove residues that lead to drainage errors. Dilutions to the mark and aliquot transfers should be performed on room temperature solutions as close to the time of final measurement as possible. Only the best water, acids, and elemental standard materials should be used. Fine metal powders and sponges are easy to weigh but are often contaminated with massive amounts of surface oxygen that does not show up on accompanying certificates of purity. Wire or thin rod are usually better because of much lower surface area. Elemental oxide powders can be ideal starting materials if they are stoichiometric and readily dissolvable, but some are neither.

Some easily dissolved salts of acid-resistant metals are hygroscopic ($ZrOCl_2 \cdot 8H_2O$ and $HfOCl_2 \cdot 8H_2O$ are examples), and solutions prepared from them should always be standardized using classical methods. It may be stylistically satisfying to prepare integral concentrations of all elemental standards, but a tremendous amount of time can be wasted trying to subdivide a chromium pellet to produce, say, a 1.0000-mg Cr/mL solution, when a 1.0239-mg Cr/mL solution will work just as well.

The analyst or lab manager should keep an orderly file of all certificates of purity for elemental standard materials (as well as for all primary standard compounds), adding new certificates for each new lot purchased. Prepared elemental standard solutions (with few exceptions) are best stored in plastic bottles. These should be prominently marked with the element, its concentration, the solution medium, and the date and initials of the preparer. If the preparation involves significant detail, a code on the bottle should reference the preparation procedure in a central file. The bottle caps should be kept tightly closed and the solutions thoroughly shaken before use. A valuable reference is ASTM Practice for Preparation of Calibration Solutions for Spectrophotometric and for Spectroscopic Atomic Analysis (E 452) (*Annual Book of ASTM Standards*, Vol. 03.06, American Society for Testing and Materials, Philadelphia, 1993).

Table 3–8 lists some suggested elemental standard preparations; the tabulation is not meant to be either exhaustive or definitive. The weights listed in the table are based on 1987 atomic weights. For the most accurate work with elements (like boron and lithium) that have two or more stable, naturally occurring isotopes, the analyst should assure himself that the standard material has not been enriched or depleted isotopically before sale. In these cases the vendor should certify the atomic weight of the element of interest.

In ICP-OES work it is often very desirable to calibrate with the minimum number of mixed elemental standards. The solution matrix often limits compatibilities, however, and it is seldom possible to set up a large array of even two-point calibrations without using five or more mixed element solutions. Table 3–9 illustrates some compatibilities and incompatibilities. It should be noted that it is sometimes possible to escape some of these solubility rules for sample solutions, especially at high dilutions and when measurements are made soon after dissolution. However, it is always a mistake to violate these rules in the preparation of standard calibration solutions, which are expected to be used repeatedly and upon which the measurement process accuracy must stand or fall. Advantage *can* be taken of alternate preparation schemes, however, when compatibility is an issue. Thus if one needs to calibrate for barium and titanium, he or she can combine solutions only if the titanium is prepared in hydrochloric acid (which ordinarily would be a less desirable medium for that element).

Today many laboratories purchase elemental standard solutions rather than preparing their own. Because of a large

TABLE 3–8—Suggested preparation of elemental standard solutions (1000 µg/mL).
Note: Correct weights for assay, if necessary. Dilute to 1 L with water and store in plastic bottles (unless indicated).

Element	Preparation
Aluminum	1.0000 g Al wire + 50 mL HCl (1 + 1) + one small drop of Hg.
Antimony (1)	1.0000 g Sb + 10 mL HNO_3, then 5 mL HCl.
Antimony (2)	2.7427 g $K(SbO)C_4H_4O_6 \cdot 1/2H_2O$ (potassium antimony tartrate hemihydrate) + H_2O.
Arsenic	In a plastic vessel: 1.3203 g primary standard As_2O_3 + 2 g NaOH + 20 mL H_2O; dilute to 200 mL, neutralize with 20% (v/v) H_2SO_4 (phenolphthalein).
Barium	1.4370 g $BaCO_3$ + 300 mL H_2O, add 10 mL HCl slowly with stirring.
Beryllium	1.0000 g Be + 25 mL HCl (1 + 4) (*Warning*: Be & its solutions are very toxic!).
Bismuth	1.0000 g Bi + 10 mL H_2O + 5 mL HNO_3; boil to expel NO_x.
Boron	5.7190 g NIST SRM 951 (H_3BO_3) or equiv.; dissolve in H_2O.
Bromine	1.2877 g NaBr; dissolve in H_2O.
Cadmium	1.0000 g Cd + 20 mL H_2O + 5mL HCl.
Calcium	2.4973 g $CaCO_3$ + 300 mL H_2O, add 10 mL HCl slowly with stirring.
Cerium	Dry $(NH_4)_2Ce(NO_3)_6$ at 85°C. Weigh 3.9127 g; dissolve in H_2O.
Cesium	1.2668 g CsCl; dissolve in H_2O.
Chlorine	1.6485 g NaCl; dissolve in H_2O.
Chromium (1)	1.0000 g Cr + 10mL HCl, then 5mL HNO_3.
Chromium (2)	2.8289 g NIST SRM 136e ($K_2Cr_2O_7$) or equiv.; dissolve in H_2O.
Cobalt	1.0000 g Co + 20 mL H_2O + 10 mL HNO_3; boil to expel NO_x.
Copper	1.0000 g Cu + 20 mL H_2O + 10 mL HNO_3; boil to expel NO_x.
Dysprosium	1.1477 g Dy_2O_3 + 20 mL H_2O + 20 mL HCl.
Erbium	1.1436 g Er_2O_3 +20 mL H_2O + 20 mL HCl.
Europium	1.1579 g Eu_2O_3 + 20 mL H_2O + 20 mL HCl.
Fluorine	2.2101 g NaF; dissolve in H_2O in a plastic vessel. Dilute in a plastic volumetric flask.
Gadolinium	1.1526 g Gd_2O_3 + 20 mL H_2O + 20 mL HCl.
Gallium	1.0000 g Ga + 10 mL HCl + 5 mL HNO_3.
Germanium	In an 800-mL Teflon beaker: 1.0000 g Ge + 20 mL HF, add HNO_3 dropwise until complete. Dilute in a plastic volumetric flask.
Gold	1.0000 g Au + 10 mL HCl, add HNO_3 dropwise while heating; boil to expel NO_x. Store in dark.
Hafnium	In an 800-mL Teflon beaker: 1.0000 g Hf + 10 mL HF, add HNO_3 dropwise until dissolved. Dilute in plastic volumetric flask.
Holmium	1.1455 g Ho_2O_3 + 20 mL H_2O + 20 mL HCl.
Indium	1.0000 g In wire + 10 mL HCl + 5 mL HNO_3. Warm gently until dissolved.
Iodine	1.3081 g KI; dissolve in H_2O.
Iridium	2.3882 g $(NH_4)_3IrCl_6$; dissolve in 100 mL 1% (v/v) HCl; dilute with same.
Iron	1.0000 g Fe wire + 50 mL HCl (1 + 1).
Lanthanum	1.1728 g La_2O_3 + 20 mL H_2O + 20 mL HCl.
Lead	1.0000 g Pb + 10 mL HNO_3.
Lithium	5.3228 g Li_2CO_3 + 300 mL H_2O; add 15 mL HCl with stirring.
Lutetium	1.1372 g Lu_2O_3 + 20 mL H_2O + 20 mL HCl.
Magnesium	1.0000 g Mg + 50 mL H_2O, then 5 mL HCl.
Manganese (1)	1.0000 g Mn + 15 mL HCl + 5 mL HNO_3.
Manganese (2)	1.5825 g MnO_2 + 15 mL HCl + 5 mL HNO_3.
Mercury	1.0000 g Hg + 10 mL H_2O + 5 mL HNO_3.
Molybdenum	1.5003 g MoO_3 + 15 mL NH_4OH + 15 mL H_2O.
Neodymium	1.1664 g Nd_2O_3 + 20 mL H_2O + 20 mL HCl.
Nickel	1.0000 g Ni + 20 mL H_2O + 20 mL HNO_3; boil to expel NO_x.
Niobium	In an 800-mL Teflon beaker: 1.0000 g Nb + 15 mL HF; add HNO_3 dropwise. Dilute in a plastic volumetric flask.
Nitrogen	3.81890 g NH_4Cl; dissolve in H_2O.
Osmium	Purhcase 0.01 M OsO_4 solution (= 1.902 mg/mL). Transfer 25 mL by pipet to a 50-mL volumetric flask; dilute to mark with 1% (v/v) H_2SO_4 and mix. This solution is 951 µg Os/mL. (*Warning*: Os in solution is very toxic and volatile!) Store in glass.
Palladium	1.0000 g Pd wire + 10 mL HNO_3; heat and add HCl dropwise until dissolved.
Phosphorus	4.2635 g $(NH_4)_2HPO_4$; dissolve in H_2O.
Platinum	1.0000 g Pt + 30 mL HCl + 10 mL HNO_3; evaporate to 1 mL; add 10 mL HCl.
Potassium	1.9068 g KCl; dissolve in H_2O.
Praeseodymium	1.1703 g Pr_2O_3 + 20 mL H_2O + 20 mL HCl.
Rhenium	1.4406 g NH_4ReO_4; dissolve in 200 mL H_2O. Dilute with 1% (v/v) H_2SO_4.
Rhodium	3.7680 g $(NH_4)_3RhCl_6 \cdot H_2O$; dissolve and dilute with HCl (1 + 9).
Rubidium	1.4148 g RbCl; dissolve in H_2O.
Ruthenium	2.0523 g $RuCl_3$; dissolve and dilute with HCl (1 + 4).
Samarium	1.1596 g Sm_2O_3 + 20 mL H_2O + 20 mL HCl.
Scandium	1.5338 g Sc_2O_3 + 20 mL H_2O + 20 mL HCl.
Selenium	1.0000 g Se + 5 mL HNO_3.
Silicon	Fuse 2.1393 g SiO_2 with 5 g Na_2CO_3 in a platinum crucible with a lid. Cool and leach in H_2O (plastic beaker). Dilute in a plastic volumetric flask.
Silver	1.5748 g $AgNO_3$; dissolve in H_2O.
Sodium	2.5421 g NaCl; dissolve in H_2O.
Strontium	1.6849 g $SrCO_3$ + 300 mL H_2O; add 10 mL HCl slowly with stirring.
Sulfur	4.1209 g $(NH_4)_2SO_4$; dissolve in H_2O.

TABLE 3–8—*(continued)*

Element	Preparation
Tantalum	In an 800-mL Teflon beaker: 1.0000 g Ta + 15 mL HF; add HNO_3 dropwise. Dilute in a plastic volumetric flask.
Tellurium	1.0000 g Te + dropwise HNO_3 to dissolve. Add 50 mL H_2O, stir, add HCl to clear solution. Dilute with 1% (v/v) HCl.
Terbium	1.1762 g Tb_4O_7 + 20 mL H_2O + 20 mL HCl.
Thallium	1.3034 g $TlNO_3$; dissolve in H_2O.
Thorium	2.3794 g $Th(NO_3)_4 \cdot 4H_2O$; dissolve in 50 mL H_2O, add 5 mL HNO_3.
Thulium	1.1421 g Tm_2O_3 + 20 mL H_2O + 20 mL HCl.
Tin	1.0000 g Sn + 100 mL HCl.
Titanium (1)	1.0000 g Ti + 100 mL HCl (1 + 1); dilute with same.
Titanium (2)	In a large flask: 1.0000 g Ti + 100 mL H_2SO_4. Very cautiously add 300 mL H_2O in small increments, mixing well. Keep warm until dissolved. Add three drops HNO_3.
Tungsten (1)	Fuse 1.2611 g WO_3 with 5 g Na_2CO_3 in a platinum crucible with a lid. Leach in 100 mL H_2O + 100 mL 10% (w/v) NaOH.
Tungsten (2)	1.7942 g $Na_2WO_4 \cdot 2H_2O$; dissolve in H_2O, add 100 mL 10% (w/v) NaOH.
Uranium	2.1095 g $UO_2(NO_3)_2 \cdot 6H_2O$; dissolve in H_2O.
Vanadium	2.2963 g NH_4VO_3 + 100 mL H_2O + 10 mL HNO_3; heat, cool, add 10 mL additional HNO_3. Heat and cool alternately until dissolved.
Ytterbium	1.1387 g Yb_2O_3 + 20 mL H_2O + 20 mL HCl.
Yttrium	1.2699 g Y_2O_3 + 20 mL H_2O + 20 mL HCl.
Zinc	1.0000 g Zn + 10ml HCl.
Zirconium	In an 800-mL Teflon beaker: 1.0000 g Zr wire + 20 mL H_2O + 20 mL HF. Dilute in a plastic volumetric flask.

potential demand, especially from environmental analysis laboratories, suppliers have proliferated. In fact, anyone with an analytical balance and a small hood may set themselves up as a supplier of certified calibration solutions. The danger of abuse is obvious. Therefore, it behooves the analyst to critically evaluate suppliers by comparison with both in-house prepared solutions and with nationally certified reference materials before such solutions are used for routine work. As with elemental standard materials, all purchased calibration solution certificates should be filed by element and lot number. Solutions that have exceeded their expiration dates should either be discarded or clearly marked, "For matrix synthesis only—not for calibration."

OTHER MATTERS

In this chapter we have discussed some of the uses and properties of a number of reagents commonly employed in metals analysis laboratories, but we have barely scratched the surface of the variety of chemicals that a classical analyst will need to use in a career. Each of these reagents will have associated handling, storage, and waste disposal requirements, and each will have an associated array of hazards.

TABLE 3–9—Elemental standard solution compatibilities. (All other elements *may* be in the category listed unless stated otherwise.)

Matrix	Must Be Here, If Needed	Must NOT Be Here
	ACID	
$Cl^- + NO_3^-$		Hg, Ag
Cl^- only	Sn, Ti	Hg, Ag
NO_3^- only	Hg, Ag	Hf, Mo, Nb, Ta, Ti, W, Zr
$F^- + NO_3^-$	Hf, Mo, Nb, Ta, Ti, W, Zr	Ba, Ca, Cr, Cu, Fe, Pb, Mg, Ni, RE, Sr, Zn
SO_4^{2-}	Ti	Sb, Ba, Ca, Pb, Hg, Ag, Sr
	BASIC	
NH_4OH	Mo	Al, Bi, Cd, Cr, Au, Fe, Pb, Mg, Mn, RE, Sr, Sn, most others
NaOH	Si, Mo, W	Most others

When a reagent shipment is received, any packaging dates or expiration dates should be noted, and the date of receipt should be marked on each bottle. Even without an expiration date from the manufacturer, the analyst must be aware of those reagents with limited shelf life and of those that present a hazard when old. Discolored, off-color, or contaminated reagents should be properly disposed of. Old containers of ether may have developed explosive peroxides. Chlorate and perchlorate salts become explosive when contaminated, as does sodium azide if exposed to metals. Such reagents must be disposed of by an approved procedure.

Many materials will build up explosive pressure in sealed containers if exposed to moisture before sealing—aluminum chloride, alkali metals, calcium metal, sodium borohydride, sodium peroxide, calcium carbide, and others fall into this group. Contaminated 30% hydrogen peroxide may decompose with violence. Some materials lose their usefulness upon repeated exposure to room air—delinquescent salts turn to slush, absolute alcohol loses its "absoluteness," and titanous chloride loses its reducing strength. Even water becomes slightly acid by absorbing CO_2 from the air.

Storage is a key issue for many reagents. Some prepared solutions—bases and basic solutions, fluoride and hydrofluoric acid solutions, and solutions of EDTA and other chelates—must be stored in plastic bottles. The best storage vessels for most elemental standards are made of Teflon PFA. If these are too expensive, high-density polyethylene will usually do. Despite the hazard associated with possible breakage, borosilicate glass is still the best substitute for Teflon PFA for chlorinated hydrocarbon solutions. Some solutions, like silver, gold, or mercury standards, hydroquinone, potassium ferrocyanide, iodine, or potassium permanganate must be kept in the dark to prevent photochemical changes. Low actinic or amber glass are usually called for, although opaque plastics are sometimes used. Standard base in automatic pipets should be protected from CO_2 pickup with traps on air intakes.

Since sodium hydroxide dispersed on a clay mineral is the standard trapping material, careful packing is required to prevent clogging or contamination of the titrant. Similarly, titanous chloride must be protected from air oxidation with a CO_2 or Ar blanket over the solution in a sealed bottle. Some prepared reagents, like cupferron solutions, need to be refrigerated, and certain purchased reagents like hydrogen peroxide keep for longer periods if refrigerated. The practice of refrigerating all organic reagents is unnecessary, however, and may even lead to deterioration if cold bottles are opened in moist air since water will condense on the reagent.

As discussed previously, good safety practice makes it imperative that purchased reagents and prepared solutions be stored separately by labeled categories: acids, bases, oxidizers, reducers, neutral salts, flammable solvents, and other organic compounds. Highly toxic or carcinogenic compounds should be kept only in small quantities and should be prominently labeled. All other reagents, purchased or prepared, should bear appropriate, prominent warnings. Reagents should be arranged alphabetically within each storage category, and regular inventories of all locations should be recorded and also reported to the designated chemical hygiene officer.

The hazards associated with the use of reagents in metals analysis represents a broad spectrum. A few are relatively innocuous, but most reagents can hurt you in some way. As with all safety considerations, the more you know about a hazard, the safer you will be. Laboratories in the United States are required to provide employees access to Material Safety Data Sheets (MSDSs) and other available information on hazardous chemicals (OSHA 1910.1450—*Occupational Exposure to Hazardous Chemicals in Laboratories*). One good source of information is *Dangerous Properties of Industrial Materials*, 5th ed. by N. I. Sax (Van Nostrand-Rienhold, New York, 1979). There are many other similar reference books.

Explosion, fire, and acid and caustic burn hazards have been discussed and are probably better understood in most situations than toxic hazards. The toxic effects of exposure to a reagent are usually classed as acute or chronic. Among reagents that present acute toxic hazards, the most dangerous are those that provide the least degree of warning. Thus, while it is unlikely that a worker would willingly remain in an area where high levels of ammonia gas were present, carbon monoxide gas provides no corresponding warning odor and represents the greater danger. Chronic effects are insidious, sometimes requiring many months or years of exposure to reveal themselves. Between 1000 and 2000 compounds are classed as known or suspected cancer-causing agents. And women of child-bearing potential should be aware of embryotoxic agents as well. In addition, allergic reactions to certain chemicals can occur.

In the United States, the Occupational Safety and Health Administration (OSHA) sets permissible exposure limits (PELs) for about 500 substances. For the most part these represent the exposure limit for an 8-h working day. The Environmental Protection Agency (EPA) is the regulatory body for chemicals in the environment and controls waste disposal through the Resource Conservation and Recovery Act of 1976 (RCRA). The Department of Transportation (DOT) controls the transport of chemicals.

With proper knowledge and attention to detail there is little to fear in the metals analysis laboratory. Following approved safety practices, a chemical analyst will not jeopardize his life or his health. But it is always wise to remember that with reagents, as with all hazards, it is mostly what you don't know that can hurt you.

REFERENCES

Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer Corp., Norwalk, CT, 1976.

Annual Book of ASTM Standards, Vol. 03.05, American Society for Testing and Materials, Philadelphia, 1992.

Annual Book of ASTM Standards, Vol. 11.01, American Society for Testing and Materials, Philadelphia, 1992.

Cheng, K. L., Ueno, K., and Imamura, T., *CRC Handbook of Organic Analytical Reagents*, CRC Press, Boca Raton, FL, 1982.

Cotton, F. A. and Wilkinson, G., *Basic Inorganic Chemistry*, John Wiley & Sons, New York, 1976.

Gregory, E. and, Stevenson, W. W., *Chemical Analysis of Metals and Alloys*, 2nd ed., Blackie & Son, London, 1942.

Handbook of Analytical Chemistry, L. Meites, Ed., McGraw-Hill, New York, 1963.

Handbook of Chemistry and Physics, 42nd ed., C. D. Hodgman, Editor-in-Chief, Chemical Rubber Publishing, Cleveland, 1960.

Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953.

Lange's Handbook of Chemistry, 11th ed., J. A. Dean, Ed., McGraw-Hill, New York, 1973.

Little, K. and Brooks, J. D., *Analytical Chemistry*, Vol. 44, No. 9, 1972, pp. 1343–1345.

Lundell, G. E. F. and Hoffman, J. I., *Outlines of Methods of Chemical Analysis*, John Wiley & Sons, New York, 1938.

Mattinson, J. M., *Analytical Chemistry*, Vol. 44, No. 9, 1972, pp. 1715–1716.

The Merck Index of Chemicals and Drugs, Merck & Co., Rahway, NJ, 1960.

Moody, J. R., Greenberg, R. R., Pratt, K. W., and Rains, T. C., *Analytical Chemistry*, Vol. 21, No. 1, 1988, pp. 1203A–1218A.

Occupational Exposure to Hazardous Chemicals in Laboratories, 1910.1450, Occupational Safety and Health Administration, Washington, DC (effective date, 1 May 1990).

Organic Reagents for Metals and Other Reagent Monographs, W. C. Johnson, Ed., Chemical Publishing Co., New York, 1955.

Prudent Practices for Disposal of Chemicals from Laboratories, Committee on Hazardous Substances in the Laboratory, Assembly of Mathematical and Physical Sciences, National Research Council, National Academy Press, Washington, DC, 1983.

Prudent Practices for Handling Hazardous Chemicals in Laboratories, Committee on Hazardous Substances in the Laboratory, Assembly of Mathematical and Physical Sciences, National Research Council, National Academy Press, Washington, DC, 1981.

Reagent Chemicals, 6th ed., American Chemical Society, Washington, DC, 1981.

Sax, N. I., *Dangerous Properties of Industrial Materials*, 5th ed., Van Nostrand-Reinhold, New York, 1979.

Schilt, A. A., *Perchloric Acid and Perchlorates*, GFS Chemical Co., Columbus, OH, 1979.

Schilt, A. A. and McBride, L., *Standard Substances and Solutions*, GFS Chemical Co., Columbus, OH, 1983.

Shugar, G. J., Shugar, R. A., and Bauman, L. *Chemical Technician's Ready Reference Handbook*, McGraw-Hill, New York, 1973.

Standard Methods of Chemical Analysis, Vol. 2, Part A, 6th ed., F. J. Welcher, Ed., D. Van Nostrand, Princeton, NJ, 1963.

Strickman, R., "Redox Titrations," *Encyclopedia of Industrial Chemical Analysis*, F. D. Snell and C. L. Hilton, Eds., Interscience, New York, 1966.

Van Nostrand's Scientific Encyclopedia, 4th ed., D. Van Nostrand, Princeton, NJ, 1968.

Welcher, F. J., *The Analytical Uses of Ethylenediamine Tetraacetic Acid*, D. Van Nostrand Co., Princeton, NJ, 1958.

Also, technical information in the literature and catalogs of Allied Chemical Co., J. T. Baker Co., Eastman Kodak Co., Linde Division of Union Carbide Co., and Matheson Gas Products Co.

Part II: Samples

"He could distinguish and divide
A hair 'twixt south and southwest side,
On either which he would dispute,
Confute, change hands, and still confute."

—Samuel Butler
Hudibras (1663)

"By a small sample we may judge of the whole piece."

—Miguel de Cervantes
Don Quixote de la Mancha (1604)

4

Sampling

SAMPLING IS LIKE THE WEATHER—everybody talks about it, but nobody does anything to change it. Well, almost. Nearly everyone who thinks about the subject of sampling agrees it is critically important. After all, a metals analysis can be no better than the sample portion on which it has been performed. And yet, there are a variety of unproductive or misguided attitudes that prevail in the workplace, especially among analytical chemists.

The first of these I call "the fatalist." This individual says, "I analyze only what they give me." He washes his hands of the sampling process and places responsibility for sampling on others. Such an attitude is not only unprofessional, it is ultimately self-defeating since his work will be judged not by how well it represents the lab sample, but by how useful the information is to customers or production personnel.

The second I call "the empiricist." This person says, "I don't know anything about sampling, but I know what I like." This individual makes his judgment about the quality of a sampling operation by the precision achieved in the analytical results. Even assuming that the expected analytical error is well characterized and can be effectively subtracted out, the variability in the sample is an incorrect measure of how *representative* the sample is. It is entirely possible—even common—that a homogeneous sample incorrectly characterizes the lot or process being tested.

Finally we have "the realist," who provides intelligent feedback to the process sampler. This individual wants to know how well the lab values represent the lot or the process. Do the compositional values correspond to the process variables? To the physical testing results? To the observed condition of the product? And if not, why not? Perhaps a change in the sampling practice will bring the expected and achieved results in line. Or perhaps the compositional values are really saying that something new and unanticipated has occurred. Of course, this scenario requires a dialogue that must usually extend beyond the laboratory. Samplers, process engineers, and management must be receptive, and the metals analyst must not be timid. Open discussion is called for.

Sampling is an enormous subject that deserves to be a separate discipline of study. Unfortunately, this has not been fully recognized, perhaps because no generally accepted theory of sampling has yet been formulated. The most comprehensive treatment to date is that of Pierre Gy, who has tackled the problem from its most difficult direction—that of geological and mineralogical sampling. Additional important work has been published by J. Visman, A. A. Benadetti-Pichler, C. O. Ingamells, P. Switzer, and others. Much of this work is very theoretical and is unlikely to capture the attention of engineers and technicians engaged in practical day-to-day endeavors. And yet there is a core of useful information in these treatments that requires dissemination. A good practical text is the two-volume *Pierre Gy's Sampling Theory and Sampling Practice* (by F. F. Pitard, CRC Press, Boca Raton, FL, 1989).

We should begin our discussion with a simple question, which has a (sometimes) surprisingly difficult answer: What are we trying to accomplish?

One common answer is the following. The process of sampling is an attempt to represent the distribution of the analyte in the test portion in the same proportion as it exists in the lot or other macrocosm being tested. This representation is never perfect, and the degree to which it fails is the *sampling error*. The *sampling plan* is the scheme by which one attempts to achieve this goal, that is, to make the sampling error as small as possible and, ideally, to make it a negligible part of the total measurement error.

There *are* other valid answers to our basic question, however. For example, we may be attempting to characterize the instantaneous concentration of the analyte in a changing process. Here a primary concern is that samples are taken in the same manner over increments of time so that meaningful analyte monitoring can be achieved. Often in this kind of testing absolute representation of the analyte's average *spatial* distribution is sacrificed, and an empirical measure is allowed to stand for it. There are also situations where in situ measurements are called for. Here there is no sample *per se* except that portion of the batch which is instantaneously measured. In both of these cases, it is sometimes necessary to ascertain how the empirical data relate to some finished lot or other final state of the process.

In reading some of the theoretical treatments of sampling, one begins to feel that no sampling plan is ever adequate. This feeling derives partly from the geological perspective that is the source of most of these studies. It is evident that the more heterogeneous the lot, the more planning that must go into the sampling plan. Clearly, metals are more homogeneous than ores, and commercial ores are more homogeneous than geological formations. While Pierre Gy's theoretical treatment transcends these distinctions, it nevertheless includes many variables that must be regarded as negligible in dealing with the much more uniform metals and alloys. In a related approach, the International Union of Pure and Applied Chemistry (IUPAC) has developed a "Nomenclature for Sampling in Analytical Chemistry" in which many relevant and useful terms are defined. While there are differences in some terms, the basic glossary appears generally compatible with Gy's.

The following brief list is extracted from both sources:

Consignment—a quantity of material transferred on one occasion covered by one set of shipping documents. It may consist of one or more lots.

Batch—an amount of material with well-defined boundaries known or assumed to be produced under uniform conditions. (*May* be synonymous with "lot.")

Lot—(1) a quantity of material assumed to be a single entity; (2) a batch of material from which samples are taken.

Sample—a part of a lot meant to represent the lot. It may consist of one or more increments. (The unmodified term "sample" should be reserved for the initial sampling stage.)

Increment—a portion of material collected by a single operation of a sampling device.

Defining terms is endemic to sampling theory at its current stage, so the reader must forgive these indulgences where they occur. It is entirely possible that quite different definitions will "shake out" of some future formal theory of sampling. And yet, without a set of defined terms, we will be most certainly lost. We have already spoken of:

Sampling plan—the scheme whereby, through a series of selection, withdrawal, and preparation stages, a test portion is obtained that is suitable for the estimation of one or more attributes of a lot.

Sampling error—the error associated with extrapolating from a smaller portion to a larger portion or to the whole. At its limit, sampling error is determined by constitution heterogeneity.

This leads us to Gy's concept of *heterogeneity* as a scalar quantity, with perfect homogeneity as its inaccessible limit. We must be aware that the term "heterogeneity" can have quantitative meaning only with respect to some measured attribute, such as an analyte concentration. It is entirely possible for different attributes (different elements, for example) to have quite different levels of heterogeneity in the same lot. In sampling particulate lots, *constitution heterogeneity* is the heterogeneity inherent to each particle, while *distribution heterogeneity* is the heterogeneity that derives from the manner in which distinct particles are physically arrayed within the lot. Total heterogeneity, then, is the sum of the constitution and distribution heterogeneities. A moment's reflection suggests that grinding or pulverizing operations (*comminution* to reduce particle size) are an attempt to lower constitution heterogeneity, while mixing or blending operations are an attempt to lower distribution heterogeneity. We will return to these concepts in the next chapter, where laboratory sample preparation operations will be discussed.

The sampling plan is crucial to every sampling operation, and considerable thought must be given to its design. Once we know just what it is we are trying to represent, we must answer several pointed questions: Relatively speaking, how heterogeneous is the lot? Tests may have to be conducted to determine an answer. Then we can address the next series of questions: How many increments are necessary to represent the lot and how practical are they? What are the best techniques and the best locations for removing the increments and how practical are they? What variations in the production process will affect the representativeness of the sampling plan and how can they be accommodated? How do we know when the sampling plan becomes inadequate and must be modified?

At this point, some additional terms require definition:

Gross sample—one increment meant to represent the lot.

Composite sample—a mixture of increments meant to represent the lot.

Subsample—a portion of a gross or composite sample obtained by selection or division.

Laboratory sample—the gross, composite, or subsample that is delivered to the lab.

Test sample—a sample suitable for testing prepared from the laboratory sample by comminution, mixing, selection, division, and/or other operations.

Test portion—the quantity of the test sample used to determine the concentration of an analyte or to measure some other attribute of the lot.

Selection—choosing a sample or an increment.

Division—a reduction of the sample in unit size, as by coning and quartering or by riffling (see Chapter 5).

Specimen—(1) the result of purposive sampling (sampling founded on the choice of the sampler without regard to a sampling plan)—thus, a specimen must never be used to represent the lot (Gy); (2) in the dynamic sampling of bodily fluids, a synonym for the increment removed (IUPAC). (Note that this term plays no significant role in either approach to sampling.)

Segregation—a synonym for distribution heterogeneity.

There is some slight overlap between this chapter and the next, but the intention here is to discuss sampling activities generally performed outside of the laboratory, up to and including the preparation of the laboratory sample. In the next chapter we will describe how the laboratory sample is converted to the test sample and how the test portion is selected. Some may object that all this formalism is at its core fairly basic stuff and that a little thought and common sense applied to an empirical approach will lead to perfectly representative samples. Perhaps. But there *are* nonintuitive features to the sampling process, and the need for a systematized approach becomes increasingly evident as lots tend toward greater heterogeneity.

SAMPLING MOLTEN METAL

Since the early days of steel testing laboratories, "prelim" and "ladle" tests have been taken of the molten bath, and other metals industries were quick to recognize that compositional adjustments could be made based on tests performed before an ingot was cast. The task of sampling molten metal is inherently difficult and dangerous. The metal is not only very hot, but often highly reactive. It is generally covered with a layer of slag and may be undergoing violent stirring by currents of gas or electromagnetic fields.

The sampling process must remove a minuscule fraction of this cauldron's metal portion (perhaps, *one-millionth* of the total mass) that must stand for its complete elemental composition. Usually there is no time to select multiple regions even if they were accessible; one gross sample derived from one sampling increment must serve as a "snapshot" of the

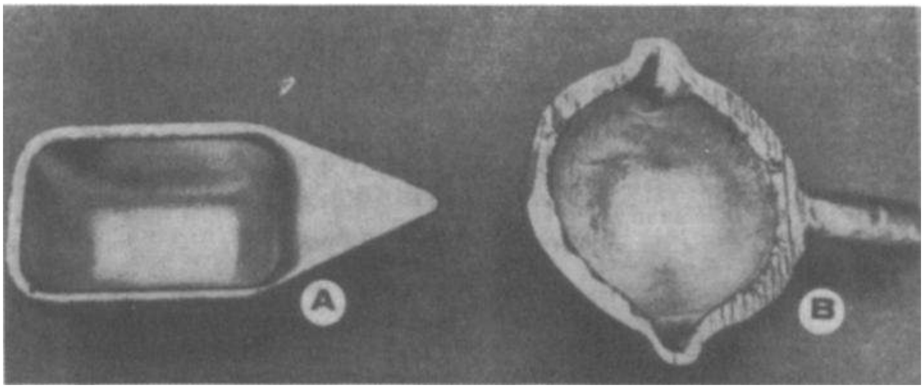


FIG. 4–1—Spoons for sampling molten steel.

molten bath, at least for the prelim test. As we discussed earlier, this sort of sampling under dynamic conditions requires a very reproducible technique because an empirical bias is likely to be encountered.

In two-stage sampling, a prepared spoon or ladle is used to remove metal from the furnace, which is then poured into sample molds. Sampling spoons (Fig. 4–1) are often "homemade" designs fabricated from steel or cast iron, often of about 500-mL capacity, attached to a metal handle 2 to 5 m long. High-purity nonferrous metals, especially those with significant iron solubility, are sampled with a graphite or ceramic spoon.

One common type of mold filled from a spoon is known as a "book mold" (Fig. 4–2) because its hinged design opens like a book. Split steel molds are similar but require a yoke and back-up blocks to hold the two halves of the mold together. Such molds can be used to cast pin samples or vertically or horizontally cast disks. Segregation associated with solidification effects is sometimes noted with both disk forms, and the region near the area where the "sprue" or "riser" was cut off (and its antipode) are avoided for optical emission excitation. Spoon and mold preparation may sometimes involve special coatings and preheating. Both must be completely free of moisture to avoid a dangerous explosion.

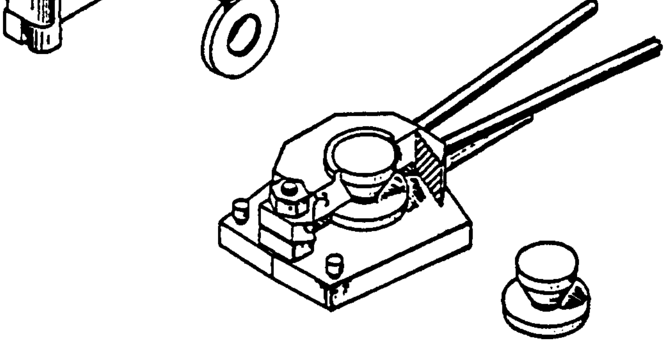


FIG. 4–2—Book molds for molten metal sampling.

In sampling slag-forming metals, the spoon is sometimes purposely coated with slag before plunging it into the lower metal layer. The spoon is then quickly withdrawn and may be skimmed of slag before the mold is filled. Much larger ladle test molds are commonly used in many steel-making plants. One design produces a 1½-in. (3.81-cm)-thick by 5⅛-in. (13.02-cm)-long, square cross-sectional specimen. "Rimgrade" and other active steels require the addition of a small piece of aluminum (or silicon, titanium, or zirconium) to the spoon or the mold to prevent gas holes in the solidified sample (known as a "blowy" test).

Fully killed (deoxidized) steels may still produce "pipe" due to center shrinkage. For this reason, all steel sampling molds incorporate a sizeable "sink head" region at the top of the mold, which can be cut or broken off and discarded. "Preliminary" or "prelim" tests are usually taken when the steel is near its maximum temperature so that sample mold filling is usually not a problem. But "final" or "ladle" tests, taken as the steel is being poured into ingots, may be much cooler, and difficulties are sometimes experienced due to incompletely filled sample molds as the frozen metal blocks the riser channel.

Properly deoxidizing the sample is somewhat of an art. Usually a small piece of light gauge aluminum wire is weighed out with an aim for between 0.125 and 0.250% aluminum in the solidified sample. Too much and areas of undispersed aluminum will affect spectrometric results; too little will result in a "blowy" specimen. If aluminum must be determined, smaller amounts of titanium or zirconium may be used to deoxidize the sample; silicon may also be used. Cast samples are released from the mold and either are allowed to air cool or are water quenched. Often identifying numbers are stamped in while the sample is still hot. In general, air-cooled steel is softer and more easily drilled, while water-quenched steel is harder and has a metallurgical structure more suitable for X-ray fluorescence and optical emission spectrometry.

It is possible to produce both types of structure from a single special center-pour book mold consisting of a copper bottom (which produces the chill cast spectrometric disk sample) and a steel upper half with a sand shell mold insert (which produces an easily drilled sample). (See W. R. Kennedy, *Suggested Methods for Analysis of Metals, Ores, and Related Materials*, Method E-2 SM 9-26, ASTM, Philadelphia, 1992.) Spoon sampling is also sometimes used to sample molten slag . Since some slags are rapidly changing in chemical composition, obtaining a meaningful sample is problematic. Some samplers stir the slag thoroughly with a long iron bar before taking a sample with a long-handled spoon. The slag is poured on a 2-foot-square clean iron plate to cool.

Single-stage sampling of molten metal is now more common than two-stage sampling, although sometimes the techniques are combined. Sampling tubes, sampling guns, dip molds, and immersion samplers are single-stage sampling devices in that one action with them generates the sample. Sampling tubes are made of heat-resistant glass, usually 5.6 mm in inside diameter. Open tubes are used with a one-way valved aspirator bulb or a suction gun (Fig. 4–3) to produce a partial vacuum for withdrawing a long pin sample. Evacuated and sealed tubes are held in special tongs and plunged into the molten metal. All tube samples are dropped into a bucket of water to shatter the glass and release the sample. These devices may be used at shallow troughs and furnace runners, but are more typically used in combination with spoon sampling. Thus the tubes are inserted into the deoxidized and slag-skimmed sample in the bowl of the spoon (held on a spoon rest).

A dip mold consists of a small steel or cast iron sample mold attached to a handle at least 3 m long. In one design the sample produced is a 30-mm-diameter cylinder that is 70 mm long. The dry, clean, coated mold is first covered at the top with two layers of aluminum reflective tape; then it is plunged into the molten metal beneath the slag layer. The tape, which prevents slag contamination, burns off in a few seconds and the mold fills. The mold is withdrawn and the sample is knocked out after a minute's cooling. It may then be water quenched.

Modern immersion samplers are sold in a variety of designs, some of which produce both disk and pin samples from the same mold (Fig. 4–4). They may be purchased empty or precharged with aluminum or other deoxidants and may incorporate a premixing chamber before the mold channels. The filler openings are capped with an ablatable material to prevent slag contamination upon immersion. Such samplers are attached to a probe arm that may have a vent hole. These devices lend themselves to being mechanically lowered and raised by a robot or remote-operated arm, which may allow safe and reproducible sampling of the molten bath's center of mass. Such an approach is applicable to sampling the tundish of a continuous caster as well.

Upon rapid retrieval of the device, the surrounding ceramic and mold is broken away. When cooled to dull red, the sample is water quenched. Special total hydrogen and diffusible hydrogen immersion samplers are also sold, some designed for use with a specific model hydrogen determinator. Samples for hydrogen determination always require special handling, especially in iron-based systems, where at room temperature the analyte diffuses readily through the lattice structure of the matrix. This subject will be discussed again later in this chapter.

The number and type of molten metal samples taken depends upon the degree of representativeness needed and the time constraints of the processing. The sampling plan must

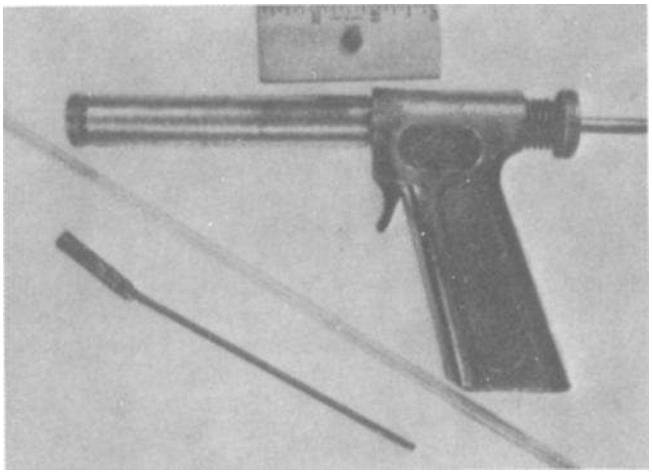
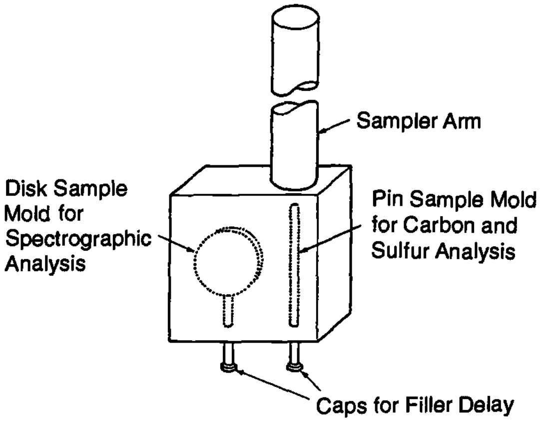
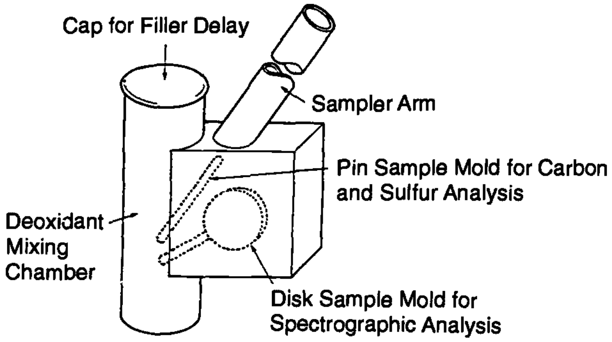


FIG. 4–3—Gun and glass tube for sampling molten steel.



Sampler Without Deoxidant (Type A)



Sampler With Deoxidant (Type B)

FIG. 4–4—Immersion samplers for molten steel.

incorporate a sampling error tolerance and an efficiency factor. The "prelim" test is almost always based on a single sample, although there may be several prelim tests as the results on these samples are used to feed back information and as changes and additions are made to trim and fine-tune the molten bath composition. These "dip" or immersion tests are often taken from a shallow region within the top one fifth of the vessel volume due to practical constraints. The results may, therefore, have some degree of empirical relativity associated with them. Nevertheless, experienced operators can use the lab results to bring the heat within specification.

When the molten metal is cast, from one to five "final" or "ladle" test samples are taken based on the size of the furnace. These tests are taken from the same tap-hole used to teem the ingots (with the flow rate throttled back). In steel-making it is common to test at one third and two thirds into the cast, or at the beginning, middle, and end of the pour. Other patterns are also employed at times. The results from these samples generally correlate well with finished product compositions. In fact, for certain plain carbon and low-alloy grades the ladle test results may represent the heat better than results taken from any finished products.

One must remain mindful, however, that molten metal is rarely at chemical equilibrium, and errors in sampling technique can produce unwanted reactions that drive the sample away from representing the lot. For example, in steel sampling, failure to exclude slag from the extracted metal may result in low phosphorus and manganese values, and failure to properly deoxidize the sample may lower the levels of carbon and manganese. Both oversights are also likely to result in an unsound laboratory sample.

SAMPLING SOLID METAL

In keeping with our intention to remain out of the laboratory in this chapter, we will confine this discussion to sampling billets, blooms, castings, and large finished forms. This is certainly not a trivial exercise since it is rare that some significant compositional heterogeneity has not been imparted during solidification and incompletely removed in subsequent processing. The convective currents that form as castings cool produce a refining action that carries impurities such as oxides toward the core of the form. Later heat treatments may produce depletions and enrichments of elements on and near the outer surface of the shape. Thus conventional wisdom dictates that the most representative samples are obtained at mid-radius, that is, halfway between the center and the outer edge. Of course, forging and remelt refining are designed to smooth out anisotropic patterns and homogenize the product, but mid-radius generally remains the area of choice for sampling all large forms. Unfortunately, it is not always the most practical, technically or economically.

Heat-affected zones, such as regions that have been flame cut, hot sheared, or welded, must be avoided in sampling operations, leaving also a comfortable buffer zone where extended heat effects are uncertain. Billets are often small enough to be routinely sampled by taking full cross-sectional slices. Thus, taking drillings or cutting out spectrometric solids at mid-radius is usually fairly routine.

Large castings and blooms are another matter. These forms may be enormous in size and sampling them is a difficult procedure, usually mandated by either critical specification requirements or a suspicion that something may have gone awry. Blooms are sometimes drilled on their end face about one half the distance from the center to the edge in a direction parallel to their main axis. The drillings from the first two centimeters of penetration should always be discarded, and if the drilled face has been hot sheared or flame cut, at least double that depth should be discarded. It is best to use the largest practical drill bit for this sampling—1, ¾, and ½-in. bits are common. Flat beaded or twist drills have been used. If it is impractical to drill into the end face of a bloom, it can be drilled from one of the long sides, but all drillings must be discarded until the drill bit nears the mid-radius location (Fig. 4–5). Slabs are treated in the same manner as blooms.

Often with large mill forms, tensile test specimens must be cut out at specified locations (say, quarter sections or half sections). Spectrometric samples may be cut out at the same time and millings taken. Alternatively, after testing, the tensile specimens may be milled into chips or melted into disks for compositional testing. Large castings may be sampled in a manner and location agreed upon between vendor and customer since sample holes in certain places may ruin the end use of the product. An exception is a cracked or failed cast, where a full-scale metallurgical investigation usually involves extensive sampling.

Sampling hollow forms presents special problems. Thick-wall bored forgings are sampled by drilling from the end midway between the inner and outer wall. Thinner wall pipe is best sampled by milling across the entire end, although sometimes it is more practical to drill into the side, completely through the pipe wall. Thin, welded tubing should be sectioned and the weld cut out and discarded. The remainder is then flattened and milled. Sheets rolled longitudinally must be sampled by cutting out a section across the entire width of the sheet perpendicular to the rolling direction. Transversely rolled sheet is sampled by cutting out a section midway between the middle and end. For detailed directions in sampling steel sheet forms, see ASTM Practice for Sampling Steel and Iron for Determination of Chemical Composition (E 59) (*Annual Book of ASTM Standards*, Vol. 03.05, ASTM, Philadelphia, 1992).

Sampling for gaseous element determination, especially for oxygen and hydrogen, requires special treatment. It is essential that oxygen and hydrogen samples, both of which must be solids, be extracted in a manner that produces no heating. The oxygen sample is subject to severe contamination since the sample is machined out, usually from a reactive matrix, in an atmosphere of air. The sample for hydrogen determi-

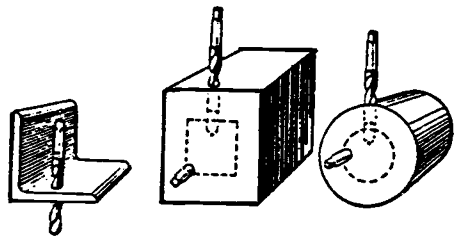


FIG. 4–5—Sampling large steel sections.

nation may have even more severe constraints on it because hydrogen is free to move in many metallic lattice structures (iron, for example). Thus, to remove a solid sample from a large steel specimen for hydrogen determination, the sampling location is packed with dry ice before and during slow drilling with a trepanning tool. The center pin sample is then broken off and stored in liquid nitrogen for transport to the laboratory. Several samples may be stored in the same liquid nitrogen dewar flask by attaching strings to them and labeling the strings with appropriate tags.

The mobility of hydrogen in metal alloys has been the subject of much discussion, but it is generally recognized to be freely mobile in low and medium alloy steels, where the utmost precautions in sampling are strongly advised. Austenitic stainless steel alloys and titanium alloys, on the other hand, appear to retain their hydrogen content without such heroic measures. However, it is always wise to avoid excessive heating even in these instances. There is some evidence that the most useful hydrogen values are obtained by systems that monitor the hydrogen content of the molten bath at the furnace side.

It is impossible to describe a suggested sampling plan for all the finished forms that might require sampling. With highly segregated materials like pig iron, it is best to select three or more pigs from the lot and submit them to the laboratory. In the case of wire, portions from the beginning, middle, and end of a spool should be submitted separately. Manufactured products require responsible personnel to select sampling locations based on requirements and practical concerns. It should be evident that the laboratory sample must be properly coded so that the data obtained are meaningful. Sometimes the size of the laboratory sample is a concern, as with the highly segregated ferroalloys. In general, it is important to submit larger laboratory samples when the material is known to be highly heterogeneous.

SAMPLING SCRAP

No metal sampling operation is more challenging than scrap sampling due to the wide variety of shapes and compositions that may end up in the scrap pile. In general, the use of scrap as a furnace charge material becomes more feasible and likely with high-volume metal commodities produced in electric furnaces. In the steel industry, so-called heavy melting scrap is still used but has been displaced to a large degree by the selected scrap required by electric furnaces. Making brass alloys is still largely the art of buying and blending the right kinds of scrap. And even in the realm of nickel-base high-temperature alloys, sorted scrap is sold in sealed barrels, with accompanying certificates of analysis.

"Scrap," then, is a word with different meanings, even within one metals industry. It may range from a hodgepodge of shapes, sizes, and alloy compositions to uniform machine shop dross from a single alloy. Shearings and punchings from light gauge sheet are frequently compacted into dense bundles in a hydraulic bailing press. So-called "prompt industrial scrap" is the dross generated by customers, which is returned for remelt. "Revert" or "home scrap" is generated by the alloy producer itself. It consists of the cropped ends of blooms and billets, rejected ingots, and the like. In the steel industry, worn-out manufactured goods (i.e., junk) are referred to as "dormant scrap." This requires sorting by a scrap dealer before it can be purchased and used by a steel company.

Sampling a shipment of low grade ferrous scrap requires a practiced eye and a familiarity with the types of alloys that are likely to appear in the blend. High-sulfur and high-phosphorus materials are particularly troublesome. If the shipment has been sold to a steel company as "alloy scrap" with a guaranteed alloy content, the frequency and distribution of manufactured shapes or their remnants may offer important guidance for the sampling plan.

Cast iron is easily identified by its characteristic appearance, and it should be completely absent. Gears, axles, and other forged parts are likely to be high in alloy content, while I-beams, channels, angles, and other structural forms are likely to be low in alloy content. One serious concern that has developed in recent times is the possibility of radioactive materials accompanying the scrap shipment (thoriated tungsten scrap mixed with tungsten scrap is one example in the high-alloy industry). There have been several such occurrences in this country and elsewhere. In some cases steel was melted with a measurable activity level and had to be disposed of, and the furnace had to be decontaminated at great cost. The exposure of workers to the radioactive hazard in such instances presents an incalculable concern.

To help prevent such disasters, many alloy producers have installed sensitive radiation monitors in their scrap-handling facilities. These will likely catch any "naked" source, but danger remains from encapsulated radioactive material, so melting facilities should be monitored as well. Radiation monitors will not detect low to medium intensity radioactive scrap shipped in closed drums, so each must be opened and checked before such material is used. A well-developed action plan in the event of a problem should be in place.

Old hands at sampling scrap have developed a feel for the nature of the product provided by the various dealers that supply their plant. Clearly, it is not in the interest of the scrap dealer to sell a product that others turn into poor quality, out-of-specification alloys. If the problem is traced to misrepresented scrap, he will certainly lose that business. Nevertheless, most alloy producers regularly sample and analyze the scrap they use, even from the most impeccable sources. In some cases, especially with very expensive sorted scrap, a cast spectrometric disk may be provided by the scrap dealer with each lot shipped.

Some customers may prefer to sample and cast their own disk instead, but seldom are they equipped for much more than combining several opportunistic "grab" samples. On the other hand, some scrap dealers use cross-stream cutters on conveyer belts to divert a percentage of the lot into a bin for melting into the sample button. Gy recognizes such an approach, if correctly implemented, as one of the valid ways to sample heterogeneous lots.

"Grab" sampling scrap can and should be a bit more than the random process the name implies. In low-grade scrap shipments consisting of recognizable objects or parts of recognizable objects, it makes sense to select three or four of each type from different parts of the lot. If one of these types assays to a grossly out-of-specification composition, the lot should be resampled at twice the original sample size. If a significant portion of these separately analyzed pieces are out of specification, there are grounds for the rejection of the shipment. In case of doubt, the lot may have to be sampled as many as four separate times.

At one time the primary concern with purchased scrap was alloy content, that is, minimum values of the major elements with perhaps a close eye to assure that carbon, sulfur, and phosphorus were at acceptably low levels. Today there is a major emphasis on trace element content. Elements like tin, selenium, tellurium, lead, bismuth, thallium, and others are closely monitored. With very expensive scrap, such as that used for melting nickel-base high-temperature alloys, both the supplier and consumer employ graphite furnace atomic absorption techniques or even inorganic mass spectrometry to monitor tramp levels down to sub-ppm concentrations.

Sometimes a laboratory-sized vacuum induction furnace employed with a low-pressure argon atmosphere is used to cast a small ingot that retains all tramp elements from the scrap. Such efforts are justified by the stringent requirements for the finished alloy and the economic loss associated with a contaminated heat. For less expensive commodities, optical emission or X-ray fluorescence analysis of melted button samples may be sufficient. Carbon and sulfur are typically checked by combustion tests on drillings. Some ferrous industries still rely on spark testing, in which the color and shape of the sparks produced when a piece of steel is abrasively ground are used to identify the grade. The technique is fast and well suited to scrap testing, but requires some expertise (which is rapidly being lost as the experts retire). Two comprehensive texts on the subject have been published (*Spark Atlas of Steels* by G. Tschorn, MacMillan, New York, 1963 and *Spark Testing* by W.M. Gladwin, United Steel Co., Sheffield, UK). Chemical spot tests, thermoelectric comparators (based on current flow between metal junctions at different temperatures), and simple magnet tests are also used.

It is usually outside the responsibility of the analytical chemist to keep track of the scrap supply, but he or she should appreciate the critical nature of this often daunting task. In most alloy-producing operations, it is necessary to classify and store scrap by both its physical size and its chemical composition. For example, in some modern steel-making facilities that employ electric arc furnaces, virtually the entire charge burden consists of scrap. A layer of light scrap (shearings, punchings, etc.) or medium scrap is used to line the furnace bottom. Then heavy scrap is placed just below the electrodes in the center of the furnace. This must be aligned in such a way that it will not shift and damage the electrodes as it melts. Finally, light or medium scrap is piled around the sides to protect the furnace walls and roof from the arc. All of this material must be composed of just the right composition alloys to produce a heat of steel within specification.

A specialty alloy plant may produce over 400 standard grades. Unlike low-alloy operations, here extensive use of virgin metals is often required, but still much of the margin of profit rests in maximizing the use of the right kind of scrap. A large part of the art and science of melting metallurgy consists of storing and selecting from a large collection of well-characterized scrap piles.

SAMPLING PARTICULATES

This category is the starting point for most theoretical treatments of the sampling process. Conclusions derived from the study of particulate systems can be simplified to accommodate other categories, like monolithic solids, liquids, and gases, which are inherently simpler. Particulates of interest to metals industries include metal powders, ores, ferroalloys, limestone, fluorspar, and crushed refractories, among others.

We have seen how the total heterogeneity of a lot is the sum of the heterogeneity associated with each particle (constitution heterogeneity) and that associated with the spatial relation of the particles (distribution heterogeneity). Metal powders, such as those produced in atomization vessels, are usually fairly uniform in composition (except, perhaps, in surface oxygen), and thus they have both low-constitution heterogeneity and low-distribution heterogeneity. Ores, on the other hand, are made up of mineralogical phases, and there is a maximum particle size at which the analyte is fully released from its matrix (the liberation size). Only then can a mixing operation minimize the analyte's distribution heterogeneity.

But perfectly mixed particulate samples are an idealized goal, not a reality. There are a number of causes of particulate segregation; most are related to the density, size, and shape of the particles. Density differences between particles affect the momentum they achieve when accelerated by gravity. Thus heavy particles follow more of a ballistic path as they drop onto a pile from, say, a moving conveyer belt. Light particles tend to drop straight down and accumulate immediately below the drop point. Size differences between particles affect both momentum and air resistance. Fines also tend to sift their way inside of a pile of mixed sizes. Shape differences between particles will result in effects due to friction and the angle of repose. For example, angular particles dropped from a vertical height sometimes end up in the center of a pile while accompanying rounded particles form the outside of the pile. External factors can also have a profound effect on particulate segregation—air turbulence, vibration, magnetic, or electrostatic fields are all possibilities.

The complexity of some sampling operations may be illustrated with a few examples. Native gold in quartz demonstrates the effect of particle density and optimum particle size and sample size. At the top of Fig. 4–6 is a hypothetical piece of rock removed from a geological site; its selection need not concern us. We begin to crush the rock and note that at Size I the (dark) gold particles have not been liberated from the (light) quartz matrix. At this size it is difficult to remove a portion of the whole, no matter how well mixed it is, and expect it to represent the whole. We then continue to crush the rock.

At Size II we find that a representative sample *can* be relatively easily removed even though the gold particles have not been completely liberated. If we continue crushing instead, we eventually liberate the gold from the quartz matrix (Size III). Here, if we could perfectly mix this size, we could readily select a smaller sample to represent the whole than we needed at Size II. But if the gold particles and the quartz matrix particles have different properties (density, shape, etc.), they may be difficult to mix well.

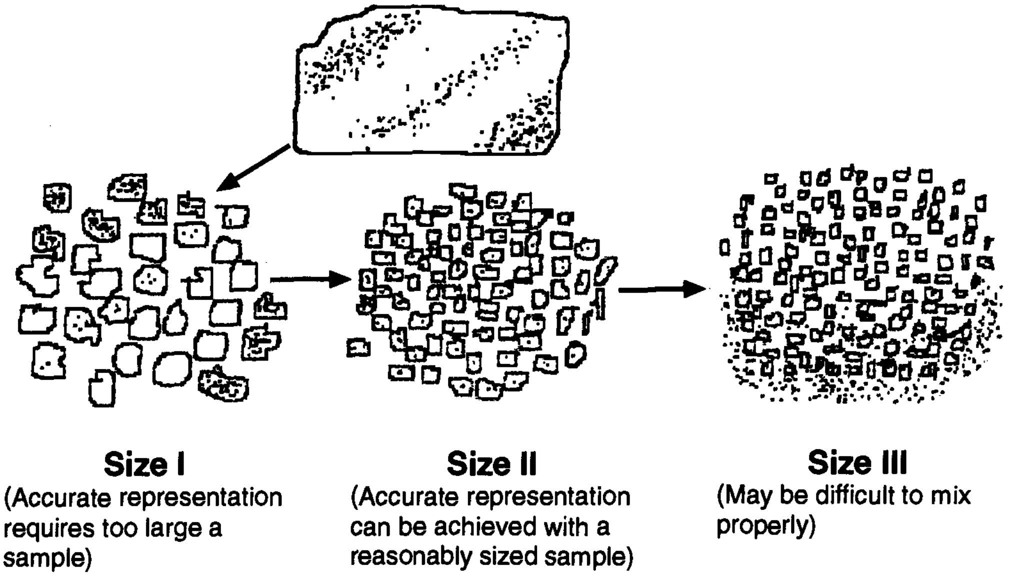


FIG. 4-6—Sampling gold in quartz.

Since gold is malleable, the particles may be flattened or rolled into tubes, and some may imbed in the crushing apparatus. We might have been better off taking our sample at Size II, at least for purposes of generating the laboratory sample. In this example the analyte (gold) forms its own separate minor phase in the sample, but similar situations may prevail when other analytes are primarily associated with a distinct minor phase in the lot. One important point is that trace or near-trace components associated with a phase require large samples to be taken. This will be discussed further in Chapter 5.

It is well known that certain ferroalloys are very prone to segregation. When ferrosilicon, for example, is cast into molds, a silicon-rich phase rises to the top of the casting and an iron-rich phase sinks to the bottom. There is also a pronounced edge effect, especially at the top of the casting. Most ferroalloys are sampled as crushed pieces less than 2 in. (50.8 mm) in size or as lumps (above 2 in.). ASTM Practices for Sampling Ferroalloys and Steel Additives for Determination of Chemical Composition (E 32) (*Annual Book of ASTM Standards*, Vol. 03.05, ASTM, Philadelphia, 1992) describes detailed procedures for sampling most ferroalloys.

In some cases every fifth container is dumped, and samples are selected to give a combined (composite) mass amounting to approximately 0.5% of the total lot. In other cases all the containers are dumped to form a cone-shaped pile, and one shovelful out of every four is reserved for the composite sample. The composite sample is then piled into a cone and divided similarly until the sample size has been reduced to one ton (0.9 Mg) for 2.5-in. (64-mm) pieces or 100 lb (46 kg) for ¼-in. (6.4-mm) pieces. This sounds like a rigorously derived series of sampling plans for dealing with large lots of highly heterogeneous particulate materials. But how does anyone really know that a hundred pounds, one ton, or even five tons adequately represents the lot?

In ASTM Practice for Sampling and Sample Preparation of Iron Ores and Related Materials (E 877) (*Annual Book of ASTM Standards*, Vol. 03.06, ASTM, Philadelphia, 1992), the number of sampling increments (one operation of a sampling device) is specified and a simple empirical formula is given for calculating the minimum weight of the increment (based on nominal particle size and specific gravity). But is the formula broad enough to include the most heterogeneous ores? And, if so, doesn't it represent wasted effort on the least heterogeneous ores? There is no final *practical* answer to these questions in the sense that no theory can currently displace such empirically derived rules of thumb. But Gy's sampling theory at least demonstrates all the parameters that go into the problem.

Gy defines a term called the *sampling constant, C*, which is central to the problem of how small a sample can be and still adequately represent the lot.

$$C = M(s_r)^2/d^3 \qquad (1)$$

where

M = minimum sample weight,
$(s_r)^2$ = relative sampling variance, and
d = linear dimension of the largest particles.

Also

$$C = fglm \qquad (2)$$

where

f = shape factor (a measure of how different the average particle shape is from an ideal cube, $f = 1$),
g = particle-size distribution factor,
l = liberation factor (at ideal homogeneity, $l = 0$; at ideal heterogeneity, $l = 1$), and
m = mineralogical factor (a measure of the maximum heterogeneity of the analyte in the lot).

In theory, at least, one calculates C from Eq 2, then selects a tolerable variance and solves for M in Eq 1. In fact, finding the best estimates for the terms in Eq 2 may be difficult. We always know d, and we can usually estimate a practical liberation size, L. Then from the ratio (d/L) the liberation factor, l is derived from a table. For the usual case when $d > L$, $l = (L/d)^{1/2}$. If the analyte-rich phase and the matrix phase are well characterized, a value for the mineralogical factor, m, can be calculated from the equation

$$m = (l - a)(r - ar + at)/a$$

where

r = density of the analyte-rich phase,
t = density of the matrix phase, and
a = average percent of the analyte-rich phase.

Estimates for the shape factor, f, and the particle size distribution factor, g, can be derived from Gy's sampling slide rule (see D. J. Ottley, *World Mining*, Vol. 19, No. 9, 1966, p. 40). There is also a good practical discussion of all four parameters by P. Minkkinen in *Analytica Chimica Acta*, Vol. 196, 1987, pp. 237–245). The shape factor, f, is estimated at 0.5 for most materials except those like gold and mica, which form flakes. The particle-size distribution factor for ground, unsieved material is estimated at 0.25. Using these equations in one worked example (see C. O. Ingamells, *Talanta*, Vol. 21, 1974, pp. 141–155), it was shown that to obtain a relative standard deviation of 3% (i.e., 6.6 ± 0.2%) with 95% confidence from a zinc sulfide ore with a "top size" (d) of 2 cm (0.8 in.), a 10-kg sample was sufficient. But to obtain the same result with a top size of 10 cm (3.9 in.), two tons of ore would be required. All the material in both cases must, of course, be properly processed and reduced before it can be in fact analyzed.

Particulate materials may be continuously sampled as they are produced or loaded for shipment. This often involves some type of stream cutter that diverts a percentage of material to the sample. Manually removing increments of finely divided materials from storage or shipment vessels may involve devices known as "thief probes." Both of these approaches and others are treated in great detail in Pitard's book, referred to earlier (see also under the references to this chapter). Even a casual perusal should put sampling personnel on guard, for there are many incorrect ways to sample. Unfortunately, many of them are in common use.

SAMPLING LIQUIDS AND GASES

Before proceeding to the next chapter where the "other shoe" of sampling (sample preparation) will drop, it is appropriate to say a few words about sampling liquids and gases since many metals labs are involved with these kinds of samples as well.

Among the liquids sampled, pickling acids, plating baths, solvents, lubricants, fuel oil, process rinse waters, and treatment plant effluents are common. Liquids may be sampled manually using a dipper for streams flowing from a tap. Tanks and drums are usually sampled by lowering a special sampling thief into the vessel. A sampling thief for liquids may consist of a device with valved openings at the top and bottom. One type is lowered into the vessel with both valves open. When it strikes the bottom, both valves seal automatically, trapping a sample.

A second type for sampling only the bottom of a vessel is designed to be lowered into a tank with both valves closed. When it strikes the bottom, both valves open, allowing the thief to fill. When lifted from the bottom of the tank, both valves again seal. Similar devices with separate cords for lowering the thief and for controlling the valves can be used to take samples at any depth.

Sampling from pipes of flowing liquid may be manually or automatically valved. If the operation of the valve is automatic, it may be on a fixed intermittent time cycle or its time cycle may be proportionately adjusted to the flow rate in the pipe. A few designs may employ non-valved automatic systems where a fixed percentage of the total flow is continuously diverted. These are usually proportional sampling systems. Pitard's book warns that probes in pipes, no matter how thoughtfully designed, always assume no correlation between the analyte concentration and the fixed portion of the stream being sampled. This may not be the case.

Suspended particles in liquids and settled solids at the bottom of tanks present special sampling problems that cannot always be solved by simple mixing. Sometimes an elaborate sampling plan is required.

The sampling of gases may involve furnace atmospheres in annealing operations, inert gases used for metal atomization or hot isostatic pressing, fuel gases, workplace atmospheres, and stack emissions, among others. At one time atmospheric pressure samples were taken by displacement of mercury from glass sampling bulbs. Today samples are frequently pumped into collapsed Tedlar (polyvinyl fluoride) or Teflon FEP gas sampling bags with a battery-operated personnel monitoring pump. Flammable gases at near-atmospheric pressure may be withdrawn using a large, sealable valved syringe which is then transported to the laboratory. Alternatively, such a syringe can be used to fill a gas sampling bag.

High-pressure gases are sampled with either single- or double-valved stainless steel sampling cylinders. The former must be evacuated, while the latter can be purged with the sample gas. The purging approach is generally better but often inappropriate, as in the case of flammable, toxic, or corrosive gases. Great caution must be exercised using both types. The sampler must always be aware of what sort of outlet pressure he is dealing with, and, if excessive, have it stepped down before a sample is taken. Both single- and double-valved stainless steel sampling cylinders must be equipped with appropriate rupture disks and, preferably, also with their own pressure gauges. When sampling flammable, toxic, or corrosive gases, the area of the sampling and the sample cylinder should be prominently marked with appropriate hazard warnings. And appropriate safety equipment must be worn.

REFERENCES

ASTM Publications

Annual Book of ASTM Standards, Vol. 03.05, ASTM, Philadelphia, 1992. Standards E32, E34, E55, E59, E88, and E255.

Annual Book of ASTM Standards, Vol. 03.06, ASTM, Philadelphia, 1992. Standards E634, E716, E877, and E1087.

Suggested Methods for Analysis of Metals, Ores, and Related Materials, 9th ed., ASTM, Philadelphia, 1992. See Suggested Methods Number E-2 SM9-26 (Kennedy, W. R.) and Number E-2 SM9-31 (Linde, T. R.).

Sampling, Standards, and Homogeneity, STP 540, ASTM, Philadelphia, 1973. See Jenkins, C. B. and Soth, G. C., "Sampling and Analysis for an Oxygen Steel Shop," pp. 110–122), and Cline, J. C., "Problems in Sampling Ferroalloys with Emphasis on Ferrosilicon," pp. 88–96.

Other Publications

Anderson, W. W., "Sampling of Solids," *Standard Methods of Chemical Analysis*, 6th ed., Vol. II, Part A, F. J. Welcher, Ed., D. Van Nostrand, Princeton, NJ, 1963, pp. 28–38.

Cropper, W. V., "Sampling of Liquids," *Standard Methods of Chemical Analysis*, 6th ed., Vol. II, Part A, F. J. Welcher, Ed., D. Van Nostrand, Princeton, NJ, 1963, pp. 39–51.

Gladwin, W. M., *Spark Testing*, United Steel Co., Sheffield, UK.

Horwitz, W., *Pure and Applied Chemistry*, Vol. 62, 1990, pp. 1193–1208.

Ingamells, C. O., *Talanta*, Vol. 21, 1974, pp. 141–55.

Majors, R. E., *LC-GC*, Vol. 10, No. 7, 1992, pp. 500–506.

The Making, Shaping and Treating of Steel, 9th ed., H. E. McGannon, Ed., USX Corp., Pittsburgh, PA, 1971.

Minkkinen, P., *Analytica Chimica Acta*, Vol. 196, 1987, pp. 237–245.

Ottley, D. J., *World Mining*, Vol. 19, No. 9, 1966, p. 40.

Pitard, F. F., *Pierre Gy's Sampling Theory and Sampling Practice*, Vol. I, *Heterogeneity and Sampling*, Vol. II, *Sampling Correctness and Sampling Practice*, CRC Press, Boca Raton, FL, 1989.

Sampling and Analysis of Carbon and Alloy Steels (USX Corp.), Reinhold, New York, 1938, pp. 19–32.

Shephard, O. C. and Dietrich, W. F., *Fire Assaying*, McGraw-Hill, New York, 1940, pp. 14–38.

Sisco, F. T., *Technical Analysis of Steel and Steel Works Materials*, McGraw-Hill, New York, 1923, pp. 115–147.

Tschorn, G., *Spark Atlas of Steels*, MacMillan, New York, 1963.

Wilson, A. D., *Analyst*, Vol. 89, 1964, pp. 18–19.

Wilson, C. W., "Fuel Gases and Related Products," *Standard Methods of Chemical Analysis*, 6th ed., Vol. II, Part B, F. J. Welcher, Ed., D. Van Nostrand, Princeton, NJ, 1963, pp. 1507–1513.

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5

Sample Preparation

In the last chapter we took the sample to the laboratory door; now it is our purpose to prepare it for analysis. Actually, in many high-speed metal-refining operations no one carries samples to the laboratory; they arrive by pneumatic tube from the furnace-side station where they were taken. What happens next is likely to be just as complicated and to involve just as many decisions as what has gone before. What we must formulate now is the final phase of the sampling plan. To this point our primary concern has been the representativeness of the sample, which, of course, must continue to be the prime objective of the sampling plan. In this phase, our aim is to represent the laboratory sample in the test portion.

On rare occasions the laboratory sample *is* the test portion. An example of this may be a filter disk from a personnel airborne dust sampler or a small impinger sample from a stack monitoring study. On other occasions, the laboratory sample may be a ton of ore that must be reduced to, say, a 30-g test sample from which a 1-g test portion may be selected. Usually the task lies between these extremes, but some labs find they must be prepared to deal with whatever is dropped at their doorstep.

As discussed in Chapter One, most metals analysis facilities prefer to keep control of and responsibility for the preparations performed on the lab sample. A few have delegated responsibility to a central machine shop where heavy milling and grinding equipment may be installed. The argument against this option goes beyond a simple case for "packing your own parachute." Machine shops can be busy, dirty places where sample preparation work for the analytical chemistry lab has to be squeezed in between machining tensile tests or a hundred other jobs requested by different departments. Even the best intentioned machinist is likely to contaminate a sample now and then under the pressure of work schedules. And certain jobs, like pickling before and degreasing after the machining, will still have to be done by chemistry lab personnel.

We have defined a number of terms in the last chapter, but the manipulations performed at this stage of the sampling plan will require a few more. And several key definitions bear repeating.

Laboratory sample— the gross, composite, or subsample delivered to the lab.

Test sample—a sample suitable for testing prepared from the laboratory sample by comminution, mixing, selection, division, and other operations.

Test portion—the quantity of the test sample used to determine the concentration of an analyte or to measure some other attribute of the lot.

Aliquot—a fractional part of the *dissolved* test portion. (An older and now largely obsolete usage reserved this term for use when the fraction was rational—½, ¼, etc. When the fraction was irrational—⅓, ⅙, etc.—the term *aliquant* was used.) These terms play no part in the formal sampling plan.

Comminution—crushing, grinding, or pulverizing to diminish particle size.

Liberation size—the particle size in a comminution at which the analyte is released from its matrix.

Preparation error—the sum of the errors introduced by contamination, loss, chemical or physical changes, mistakes, and fraud.

Selection error—the error due to taking the wrong sample.

Total sampling error—the sum of the preparation error and the selection error at all sampling stages.

Minimum sampling weight—the smallest weight of sample needed to adequately represent the analyte at each stage of the sampling process.

The reader may note that the general definition of "sampling error" in Chapter Four has here been replaced with an operational definition for "total sampling error." Gy stresses the distinction between the selection and preparation components of the sampling error, and that contrast ties in well with this two-chapter approach to the subject. As in Chapter Four, all the terms we have chosen to employ are derived from Gy and IUPAC.

PREPARING SOLID METAL LABORATORY SAMPLES

Except for raw material laboratories and other specialized facilities, the majority of samples delivered to the lab will be pieces of metal. These may range from samples as small as the pieces from an immersion sampler to large billet slices. Unless the lab is equipped with a small overhead crane or other equipment to handle them, samples larger than about 25 lb (11.25 kg) should be discouraged.

The first job is to verify that the material has been properly identified. It should be stamped or otherwise marked with an identifying code and accompanied by the appropriate paperwork. Some operations have adopted a computer system in which a network "handshake" is required. In other words, a

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central tracking system requires the submitter to enter a code signifying that the laboratory sample has been sent to the lab. The laboratory personnel then enter a second code signifying that the material has been received. This prevents mix-ups in busy facilities, such as lab samples being left on loading docks or diverted to the wrong location.

Many facilities make effective use of bar codes (such as those now common in supermarkets) to track both samples and paperwork. If the laboratory is equipped with its own LIMS (laboratory information management system), the lab sample may receive a new identifying code at this time which links it to all the other relevant information that has accompanied it up to this point. Each company will have its own needs, but typically lab samples are accompanied by one or more requestor names and phone and mail locations, heat number, order number, perhaps some type of ingot location code (top, middle, bottom, etc.), customer name, projected shipping date, grade or stock number, product category, and priority information.

The lab sample should be examined for scale, cracks, holes, and visible inclusions. Serious defects that would jeopardize the quality of the analysis should be immediately reported. In some cases the lab sample is rejected and a resampling requested. In other cases a resampling may be impossible, and the work must proceed as a "best effort." Often a minor problem with the lab sample can be accommodated by a proper approach at this stage of the sampling plan.

In a control laboratory, time is always of the essence. Typically immersion tests are trimmed of any riser material and ground to clean metal on a swing grinding machine. After a light polish on a belt or disk sander, the disk samples are ready for spectrometric analysis. Pin samples for carbon and sulfur determination are cut to size and analyzed. Twin-bladed cut-off wheels are useful to get a pin sample to an appropriate size. Some labs regard the pin sample as an expediency and will always revert to drilled chips for carbon and sulfur determination if time allows. Nitrogen alone is typically determined on chips; nitrogen and oxygen together are always determined using a small polished (sometimes hand-filed) solid. The hydrogen determination sample may arrive at the lab as the total test portion, in some cases as a sealed immersion sampler inserted directly in the determinator for the measurement of mobile and total hydrogen.

When chips must be taken, as in final certification testing, R & D, and (as time permits) in the control lab environment, it is essential to carefully select a tailored approach. For many metals a drill press is the best tool to use. One should avoid a technique that heats the sample excessively or that produces long, curled, "bed-spring"-type drillings (which are difficult to weigh and take long to dissolve). A large-diameter [¾-in. (19 mm) or even 1 in. (25.4 mm)] drill bit and a slow drilling speed are usually best.

Some would argue that only two drill speeds are needed: "slow" for soft materials, and "very slow" for hard materials. Since most labs deal with materials that vary widely in hardness, it is better and safer to use a manual rather than an automatic feed. Many labs use a high-speed steel flat-beaded track bit with nicked cutting edges to prevent long, curled drillings. The nick breaks off each curl as it begins to form. Smaller-sized drill bits—usually twist drills, ½ in. (12.7 mm) or ¼ in. (6.4 mm)—will be needed for obtaining chips from smaller lab samples. Drill bits smaller than ¼ in. (6.4 mm) should not be used (except when sampling very expensive commodities such as precious metals or when samples are diminutive or of intricate shapes).

A grinding wheel should be available for honing the cutting edges on sample preparation tools (and for cutting the nicks on the flat-beaded drill bits). A hard center punch is a good idea to mark the drilling locations and to provide a start point for the drill bit. While a drill press will produce a small amount of chips very quickly with a minimal amount of set-up time, it is not ideal for producing large amounts of chips and is totally impractical for certain kinds of lab samples. When a drill press is inadequate, the sampling operation can usually be handled by a milling machine, which is often used to produce highly representative chips from a full cross section of the lab sample. With these devices, the sample and the rotary cutting tool are usually horizontally mounted.

With both drill presses and milling machines, ordinarily no lubricants should be used. Also, some means of collecting all the chips must be provided. Some labs have had stainless steel sheeting fabricated into chip pans, while others make due with clean sheets of glazed paper. The sampling equipment must be kept clean and free of metal debris. A high-pressure oil-free air line with a trigger release mechanism can aid in dislodging chips from crevasses. Safety glasses with high-impact lenses and wire mesh side shields must be required for anyone in the room, not just the operators of the machines. Gloves and loose clothing must not be worn near metal working or other sampling equipment. Loose neckties are especially dangerous. In pickling operations goggles should be worn over safety glasses since wire mesh side shields are inadequate protection for splashed acids.

Typically, large sample casts are cropped of the shrinkage region known as "pipe" using an abrasive cut-off wheel. The surface of the remainder is examined for porosity and inclusions. If any are visible, additional material may be cut off and discarded. Spectrometric slices are then taken, stamped with an identifying number, and the opposite surface polished on either alumina or silicon carbide disks or belts. The abrasive cut-off machine should be equipped with cooling water and a ducted exhaust, as well as a safety shield. Sample polishing equipment may be manual, semi-automatic, or automatic, but all should have some provision for dust removal. If dust removal is not adequate, it is essential that operators and others in the room wear respirators.

The remaining section of the large sample cast may be chucked into a drill press vise and drilled at several places along the mid-radius of the freshly cut surface. The drill bit should not approach or penetrate the bottom of the cast. All drillings are collected. They should not be sieved unless there is a sound technical reason for doing so. In the past some labs have made a practice of sieving drillings and discarding coarse and fine fractions. While one can sometimes emerge unscathed by such a practice, it is likely to result in erroneous data and cannot be condoned. An acceptable alternative (rarely used) involves weighing the sieved fractions and selecting proportional weights of each for the test portion. Sometimes discarding fines produces a more homogeneous material that lends itself more readily to development as a chip reference standard; however, this is outside the scope of the current discussion.

It may be necessary to degrease the drillings, which is done by placing them in a clean beaker and covering them with a low-residue solvent in an efficient hood. Methylene chloride or acetone are possible choices. After stirring or agitation, the solvent is decanted off and the excess evaporated from the drillings at low heat on an electric hotplate in the hood. The room must be posted as a "No Smoking" as well as a safety glasses area. Lengthy or excessive heating must be avoided with readily oxidized materials like low-alloy steel. Nonmagnetic drillings are sometimes screened with a magnet to ensure that no particles of the iron-base tool bits end up in the sample. The worker must be sure, however, that a minor magnetic phase is not a part of the sample or else the test sample will be ruined by this treatment.

Preliminary acid cleaning of the lab sample is called for to remove corrosion, rust, or scale if heavy swing-grinding equipment is not available or impractical to use because the sample is too small or odd-shaped. Sometimes grit or shot-blasting equipment can provide another useful option. In acid cleaning, the "pickling" acids must be carefully matched to the alloy since the cleaning action should be no more vigorous than needed. In rare instances organic inhibiters can be added to prevent excessive undercutting of the base metal. A borosilicate glass tray of the appropriate pickling acid, gently warmed on an electric hotplate in a hood, is one convenient approach. Sample pieces can be added and removed with tongs, then plunged into a distilled water rinse bath. On those rare occasions that hydrofluoric acid is required, a Teflon TFE beaker on a sandbath on the hotplate must be substituted.

Billet slices, heavy sheet, or thin slabs are best sampled by shimming the piece on wood blocks in the drill press vise and drilling all the way through it. Wire, sheet, and thin rod material can be chucked into a milling machine. Sheet is typically folded over one or more times and milled on the sheered edges. Light sheet can also be nibbled with an electric or hand nibbler, and wire can be cut up with hand shears. If blacksmithing facilities are available, they can prove invaluable for flattening small odd-shaped samples—ball bearings, small parts, etc. When flattened, they can either be milled into chips or used directly for spectrometric work. Special jigs to hold rod, tubing, and other shapes in the drill press are sometimes used.

Pin samples for oxygen, nitrogen, and hydrogen determination and for certain mass spectrometric work can be produced with a trepanning tool that bores out a large hole, leaving a central pin that can be broken out of the recess. For gas determination, this operation should be conducted so as to generate as little heat as possible. And, in the case of hydrogen pins from low-alloy steel, the solid should be packed in dry ice before the machining. The hydrogen pins are then stored in liquid nitrogen. Sometimes bar slices are cut on a lathe or with a diamond saw, leaving a surface that may need little additional surfacing for spectrometric analysis.

There are situations, however, when no machining operation is adequate because the laboratory sample is too hard or work hardens readily. There are often two alternatives when this is the case. The sample can be annealed to soften it and can then be cut, drilled, or milled. Or the as-received sample can be crushed. Crushing is by far the more rapid approach when a particulate test portion is needed, but it is not the common choice. Only a limited range of hard alloys is brittle enough to be crushed. An alloy that is both hard and tough is not amenable to this approach. Among ferrous alloys, only high-carbon high-speed tool steels, a few high-carbon low-alloy steels, blast furnace cast irons, and white cast irons lend themselves to crushing.

Alnico magnet alloys are also routinely crushed. Many ferroalloys fall into this category as well, but they are more appropriately discussed in the next section on particulate lab samples. A brittle alloy is crushed by first putting it in a clean tempered alloy steel mortar, placing a tempered pestle on top of it, and striking several sharp blows with a heavy hammer. An alternate approach uses an air-operated pneumatic hammer with a tool steel pestle. The fragments are then transferred to a cup mill (or "shatterbox") and ground. At intervals the machine is stopped and the material screened on a 200-mesh (75-μm) sieve. Material that passes through is retained; material that does not is returned to the cup mill for additional grinding. The process is repeated until the entire sample has passed through the sieve.

If this process proves impractical, proportional weights of the screened fractions will have to be taken as the test portion. Sieving should employ both a bottom collection pan and a lid to prevent any dusting losses. Of course, the mortar and pestle and the cup mill must be carefully cleaned between samples. The alternative to crushing is annealing. In some facilities, expert metallurgical advice and heat treatment services are readily available; in others, the chemical analyst may be largely left to his own devices.

Fortunately the annealing requirements are not usually very critical. It is not necessary to achieve a "dead soft" condition, but merely a condition soft enough to allow the slow generation of some chips with a very hard tool bit. When a steel sample is reheated in a muffle or annealing furnace, the required cooling rate to soften it is roughly inversely proportional to its carbon content, although, of course, the alloy content plays a significant role. Air cooling or salt bath cooling will generally soften most reheated hard alloys. The cooled, annealed sample will have to be ground or pickled to remove oxidized scale before any drilling or milling work is done on it.

Sometimes the lab sample arrives in a form unsuitable for spectrometric work but in sufficient mass so that a "button" sample can be melted. There are a number of commercial machines for laboratory melting of spectrometric disk samples. They can accommodate material in a variety of forms—wire, chips, small parts, or small chunks of metal. The minimum charge varies somewhat, but generally at least 50 g are required. Some designs use an electric arc to melt the sample, but most employ a high-frequency induction coil. Usually nitrogen or argon is employed as a sheath gas, and the button is cast in either a copper or a ceramic mold. One commercial instrument produces centrifugally cast disks.

The frequent assumption that such remelting devices (or even the annealing operations, discussed above) never alter the gross composition of the laboratory sample is patently false. It is, however, undeniable that many alloys can be processed in these ways without effect. Every time a sample is heated, it is conceivable that something has been lost, gained, or redistributed (surface depletions and enrichments are sometimes a particular problem). Whenever the lab sample must be subjected to any sort of thermal processing, it is highly advisable to treat an analyzed sample of the same or similar grade in the same manner to check for changes in composition.

When the test sample has been prepared, whether it is in the form of chips, pins, spectrometric disks, or all three, it is labeled with its unique code that unambiguously identifies it. Most labs make effective use of small manila envelopes that can hold one disk, a small handful of pins, or 20 to 30 g of chips. The outside may be preprinted with relevant headings that are filled in with ink by the preparer, or a bar code label may be attached. If the chips are to be used for low-carbon determination, they should be placed in a clean glass bottle or large vial with a screw cap lid and a fiber-free plastic cap liner. Large amounts of chips, as for in-house standardization work, should, likewise, be placed in a wide-mouth glass bottle.

In some labs the test sample preparer is also charged with distributing the work to the appropriate analysts and archiving the excess material. Both unused portions of the laboratory sample and the excess test samples should be retained, but in separate bins. If the laboratory's administrative procedure involves eventual revert of the unused portions of the lab samples, it will probably pay to store this material by base metal composition or product category. The excess test samples—chips, pins, disks, etc.—should be stored sequentially by the assigned code they received when they were first logged into the laboratory.

PREPARING PARTICULATE LABORATORY SAMPLES

"Particulates" is being used here as a generic term to refer to any lab sample that arrives in two or more pieces. Thus, anything from a box of cabbage-sized lumps to a vial of −325 mesh powder is fair game provided that it is meant to represent one lot. Once the material has been logged in and a preliminary examination has revealed no insurmountable problem with the as-received laboratory sample, the preparer must decide on a course of action. Some samples arrive in a condition ready for analysis. They may be finely ground ores, or prescreened metal powders that have been sampled during loading for shipment or final processing. The only task of the test preparer may be to divide the lab sample for different analysts. Hopefully and usually, this is a trivial task, although, as we saw in the last chapter, the mere act of falling under gravity can segregate some particulate systems.

Much more often the particulate lab sample will arrive in a condition that requires some degree of processing. Comminution of some sort may be necessary to liberate all the required analytes, and mixing will be needed to distribute them uniformly. Also, it is likely that some degree of division or reduction of the lab sample will be required. The amount of work involved is directly related to the properties of the lab sample, especially its heterogeneity, and to the accuracy requirements of the analysis. Sample properties, like hardness and the presence of analyte-rich dense phases, sometimes greatly complicate the task. Among the more difficult-to-sample industrial materials are ferroalloys and slags because they are both hard and highly heterogeneous. Low-grade ores present more sampling difficulties than high-grade ores, especially if the analyte element is associated with a minor phase in the mineral. Very hard materials, like chromite ore, may require special equipment to adequately crush them to uniform size.

Comminution is usually the first step in the processing of the laboratory sample. Any pieces larger than 4 in. (100 mm) in any dimension are usually broken up manually using anything from a light tap with a hammer to the application of a compressed air jack hammer in a tempered steel mortar. Very brittle, easily crushed material can often be reduced to ¼-in. (6.4-mm) size manually by placing the pieces in a tempered steel mortar, placing a tempered steel pestle on top, and striking briskly with a heavy hammer. Harder materials, like ferroalloys, are best handled by a jaw crusher that is capable of reducing 4-in. (100-mm) pieces to ¼-in. (6.4-mm) size. These devices are generally powered by 220-V electric motors with a belt-driven flywheel. The "cheek" and "jaw" plates are constructed of heat-treated abrasion-resistant alloy steel. Jaw crushers must be operated with caution; belt guards must be in place, and the operator must beware of material that may pop out of the hopper. In general, the entire laboratory sample should be crushed to completely pass a ¼-in. (6.4-mm) sieve.

At this stage, mixing and division is often called for. Large samples may be placed in a V-blender and rotated for one or more hours. V-blenders must never be filled above a line level with the axis of rotation. Smaller samples should be thoroughly mixed mechanically or by hand. Gy does not recommend sheet mixing; he indicates that it is time consuming and not very effective. Division (or reduction) of the sample may be by the technique known as "coning and quartering" or by riffling. "Coning and quartering" (Fig. 5–1) consists of making a cone-shaped pile of the sample, then flattening it into a pancake shape. The pancake is then divided into four equal quadrants by forming a symmetrical "X" on the surface. Material from two of the opposing quadrants is retained, while the

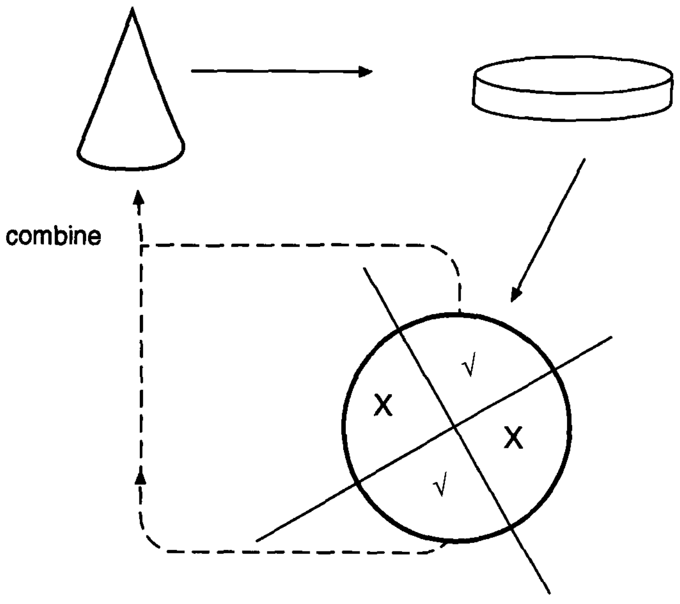

FIG. 5–1—Coning and quartering.

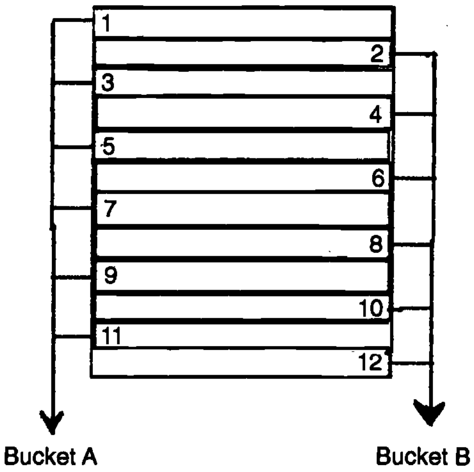

FIG. 5-2—Stationary riffles plan (½ split).

other two quadrants are rejected. The process can be repeated by mixing the two retained quadrants and forming them into another cone-shaped pile and reprising the operation. Each time a representative 50% of the lab sample is retained.

Riffling requires one of several types of sample splitters known as riffles or Jones dividers. These devices are designed to subdivide the sample without bias. Although other ratios are available (25%, 12.5%, etc.), typically a 50% splitter is employed. Stationary riffles (Fig. 5-2) consist of a linear array of slot-shaped openings connected to chutes that alternate connection to two collection containers. The device used must be selected so that its openings are appropriate for the sample top-size (the largest particles in the sample). In general the riffles openings should be two to four times the size of the top-size particles. Openings that are too small will tend to clog, and openings that are too large will tend to impede the use of the full array of openings, which is required for an accurate split. There should always be an even number of chutes in these devices (at least twelve total), and the sample feed pan should be exactly the same width as the array of chute openings.

Loss due to dust formation is frequently a problem with riffles, so some designs are completely enclosed. ASTM Practices for Sampling Ferroalloys and Steel Additives for Determination of Chemical Composition (E 32) (*Annual Book of ASTM Standards* , Vol. 03.05, ASTM, Philadelphia, 1992) recommends that stationary riffles with openings of ½, 1, 2, and 3 in. (12.7, 25.4, 50.8, and 76.2 mm) be kept on hand. Sectoral splitters or spinning rifflers are generally designed for moderate- to small-sized samples, but, if suitable, they are quite accurate. These devices come in two basic designs—those with a rotating feeder and stationary radial wedge-shaped collector pans and those with a stationary (usually vibratory) feeder and a rotating carousel with a radial splitting ring and collection vessels.

So far we have crushed our hypothetical sample to ¼ in. (6.4 mm), mixed it, and riffled it, say, twice. Now we must crush it to a finer mesh size. One of the best devices for intermediate size crushing is the roll crusher. This machine is capable of reducing the ¼-in. (6.4 mm) product of the jaw crusher to 1 or 2-mm particles. This is accomplished with two counter-rotating rolls of tempered steel. Something similar can be accomplished with a cone crusher, which utilizes a cone-shaped device to crush the fragments against a concave-shaped form.

After this step the sample is likely to be mixed and divided again. If we've started with a ton of ferroalloy and riffled it twice at ¼ in. (6.4 mm) and twice at 2 mm, we are now down to 125 lb (56.7 kg) of sand-like consistency. That's rather a lot of material, so we had better reduce it further by riffling three more times. This leaves us with 15.6 lb (7 kg) at 2 mm. This material is now pulverized to a 150-μm particle size (−100 mesh) using one of a number of possible devices.

The lab pulverizer may be a grinding plate design with one stationary and one revolving plate. It may be a vibrating disk or cup mill in which the sample is placed in a cup with rings and a puck of hardened steel or tungsten carbide. The sealed cup is clamped into the machine, which shakes it rapidly. Or it may be a planetary or centrifugal mill that utilizes the grinding and impact of hardened balls made from a variety of materials. Most of these mills are capable of reducing the sample particle size much lower than the requirements for the analytical work. This must be guarded against by interrupting the pulverizing process at the appropriate time. Samples finer than they need to be frequently present severe dusting problems.

The best course is to stop the grinding process at regular intervals and sieve the product. In our hypothetical case we will use a 100-mesh (150-μm) sieve (with the understanding that some analytical sampling protocols will have finer requirements). The sieving must always be conducted with a tight-fitting collection pan below and a cover above the sieve to prevent dusting losses. Sieves in a full range of mesh sizes should be kept on hand. Table 5-1 lists some common sizes and the dimension of their openings. They are available in brass or stainless steel in a selection of circular diameters and rim heights. If the lab does a lot of sieving, investment in a sieve shaker is justified. Designs vary in the sieve diameter and stack heights they can handle. Sound barrier enclosures are also available to control the noise these devices produce.

The material retained on the 100-mesh sieve is returned to the pulverizing mill, and additional 2-mm material is added to fill (but not overfill) the capacity of the mill. After a suitable grinding interval, the machine is stopped and the product sieved again. This process is repeated until all material has passed the 100-mesh sieve. In comminution operations of this kind, especially when labor-intensive hand-grinding opera-

TABLE 5-1—Some sieve conversions.

U.S. Standard	U.S. Alternate	Tyler Screen Scale	Openings in Inches
4.75 mm	No. 4	4 mesh	0.187
2.00 mm	No. 10	9 mesh	0.0787
1.00 mm	No. 18	16 mesh	0.0394
0.850 mm	No. 20	20 mesh	0.0331
0.600 mm	No. 30	28 mesh	0.0234
0.425 mm	No. 40	35 mesh	0.0165
0.300 mm	No. 50	48 mesh	0.0117
0.250 mm	No. 60	60 mesh	0.0098
0.180 mm	No. 80	80 mesh	0.0070
0.150 mm	No. 100	100 mesh	0.0059
0.075 mm	No. 200	200 mesh	0.0029
0.045 mm	No. 325	325 mesh	0.0017

tions are utilized, there is always the temptation to discard the small amount of material retained on the sieve. This temptation must be resisted since these abrasion-resistant particles are likely to be an important constituent of the sample—they may be rich in one or more analytes, for example, or they may be especially lean in analytes and thus their exclusion will lead to erroneously high results.

At the end of the pulverizing operation we are left with approximately 15½ lb (7 kg) of 100-mesh (150-μm) material. Some weight loss will have occurred, despite the best precautions, due to dusting and adherence to grinding surfaces and sieves, but it should not exceed 2.5%. Scraping and brushing of the pulverizer components and the sieves will be necessary to ensure that all avoidable sample loss has been eliminated. The pulverized sample is mixed thoroughly and riffled four times to produce a 1-lb (454-g) sample. This material may often be dried at 105°C (no higher) for an hour (or to constant weight) depending on the nature of the sample. Or some other drying scheme may be performed based on an empirically established or agreed-upon protocol.

The sample is mixed again and then poured onto a large sheet of clean glazed paper and coned and quartered. Each of the four 136-g quarters is placed in a wide-mouth glass jar with a plastic screw top, and each jar is marked in an identical manner with the appropriate sample code. Some industries will designate one jar for the producer, one jar for the consumer, one jar for any required umpire testing, and one jar as the archive sample. These are the test samples.

At each step in the conversion of the lab sample to the test sample, equipment has been contaminated and must all be thoroughly cleaned before it can be used again. A compressed air line and a shop vacuum cleaner are useful for gross contamination, but pulverizer components and sieves will have to be thoroughly rinsed with distilled water and dried at the very least. During cleanup with an air hose, as with all grinding, pulverizing, mixing, dividing, and sieving operations, the preparer and anyone else in the room must wear a suitable respirator.

The hypothetical scenario that we have outlined here probably bears only a slight resemblance to any given lab sample preparation scheme since protocols vary tremendously within and between industries. It has served, however, to illustrate a number of basic principles, as the one-ton laboratory sample was converted to the 136-g test sample. The sample sizes and processing variations actually employed are wide ranging. For example, many ore samples cannot be adequately crushed beyond the 1/4-in. (6.4 mm) stage unless a drying step is inserted at that size. Calcium carbide-bearing slags and other "disintegrating" slags should be bottled as soon as possible to prevent reaction with moisture in the air. Many mineral commodities are promptly analyzed for drying loss at 105°C "as received" or at an early stage in the comminution to reflect their true composition at the time they are received and weighed (which is often the basis for the cost of the shipment). This is because weather will affect moisture content in storage, while fine grinding will likely result in the loss of moisture and other volatiles.

In many labs it is standard practice to remove metallic iron with a magnet from slag samples after crushing. In those cases where the lab sample consists of a brittle matrix with embedded malleable particles (for example, precious metal ores with the presence of native gold, silver, or copper), crushing must be halted at the liberation size or the metallic particles are likely to coat the grinding surfaces. In some cases "metallics" are separated from the gangue matrix, and the two are further prepared as separate samples. Grinding a sample too fine can result in oxidation, which will ruin the partitioning of oxidation states (for example, the determination of ferrous and ferric iron in slags, rocks, and minerals). If water or occluded gases must be determined, a comminution plan must be carefully worked out because excessive grinding will probably result in the loss of both. Also, over-ground samples sometimes become hygroscopic and difficult to weigh accurately. Contamination by grinding media can be a problem. Samples known to contain no magnetic phases should be checked with a magnet to ensure that no introduced iron particles remain.

TABLE 5–2—Some particulate materials sampled in the steel industry.

Hard	Hard and Tough	Hard and Segregated
Chromite Ore	Low C Ferrochromium	Blast Furnace Slag
Fire Brick	Pig Iron	Ferrosilicon
Most Ferroalloys		
Moisture Sensitive	Moisture Assayed	Oxidation Sensitive
Electric Furn. Slag	Iron Ore	Ferrosilicon
Limestone	Manganese Ore	Slags
Dolomite		
Fluorine Bearing	Carbonaceous	As Rec'd Particulates
Fluorspar	Coal	Atomized Metal Powders
ESR Flux	Coke	
Slags	Coke Breeze	Bag House Dust

The variety of particulate materials prepared for testing in an industrial environment can be illustrated with a few selected materials encountered in the steel industry. These are shown in Table 5–2 and serve to illustrate the range of problems that must be addressed by the sampling plan. Many other metals industries will have a similar array. Scrap metal turnings are often sold severely contaminated with oil and water (which must be analytically determined), and even clean, processed scrap metal chips present serious division problems that may require melting a 12 to 30-lb (5.4 to 13.6 kg) ingot using a vacuum induction furnace under a partial argon atmosphere.

Some of the toughest sampling problems are encountered in the ore prospecting and processing industries, where the intricacies of rock and mineral sampling are compounded with large, often highly heterogeneous lots. But regardless of the magnitude and complexity of the task, all sample preparation has the same goal: to accurately represent that mountain of ore or that barge full of ferroalloy in the test portion.

SELECTING THE TEST PORTION

If the reader is inclined to skip over this section as representing a trivial part of the sampling process, he is strongly urged to persevere for a bit since some seldom-raised key points will be covered. Much more than the requirements of the analytical method are involved here. First, we have defined the test portion as that part of the test sample selected for an analyte determination. In many procedures this will refer to the portion weighed on an analytical balance and transferred to a beaker. It may vary between 100 mg and 5 g, but much more typically falls in the 0.5 to 1.0-g range. In spectrometric analyses with solid samples, the test portion is always much smaller. Here the test portion is that part of the test sample directly responsible for the measured analytical signal.

In destructive techniques like DC arc OES, the test portion may be several micrograms; in destructive techniques like glow discharge mass spectrometry, the test portion may amount to nanograms. In nondestructive techniques like X-ray fluorescence, the few atomic layers measured amount to even less (and the test portion never leaves the test sample!).

Testing such a minuscule part of the test sample almost always makes an undue assumption about its homogeneity. To compensate, spectrographers typically arc the sample at different regions or grind and repolish the surface before repeating the measurement. But averaging these replicates still amounts to selecting microgram- or nanogram-sized grab samples and combining the resultant data. What do these universally applied practices tell us about the homogeneity of the test sample? And what sort of trouble can they get us into?

One statistical test for sample homogeneity that is often applied to candidate material for development into a reference standard involves selecting a regular series of sample portions—say, slices along the length of a bar—and analyzing each portion a replicate number of times. The test then applies an analysis of variance (ANOVA) treatment to compare the analytical variance at one location to the sample variance between locations. If the sample variance is greater than the analytical variance by a statistically significant amount, the material is declared "inhomogeneous."

It is interesting that when major concentration elements (like nickel or chromium in austenitic stainless steel) are analyzed by X-ray fluorescence for such a study, the sample variance usually exceeds the analytical variance and the material often fails the homogeneity test. The X-ray variances are generally very low (even with a light repolish between exposures) and seem to reflect only electronic noise, but the differences between locations are noticeably greater. Is the sample material really that bad? Or is the X-ray fluorescence equipment looking at such a small test portion that it is placing an unrealistic criterion on the material? If one were to conduct a similar study using chemical techniques that employ 1-g samples milled at full cross section, the same material is much more likely to pass the homogeneity test.

Figure 5–3 illustrates how "stringer" inclusions (here, enriched in the component of interest and exaggerated in size in the illustration) could be responsible for this effect. This observation in no way reflects on the usefulness of X-ray fluorescence and other solids techniques for homogeneity testing, but rather suggests that a "go"/"no go" test may not be appropriate at certain concentration ranges. In fact, the high precision of X-ray fluorescence measurements make it an ideal technique to establish sampling frequency in the production of bar and strip.

A much more serious concern is the effect of small test portions on trace and ultratrace level determinations. Instrument manufacturers are continually extending the detection and quantitation limits of high-speed spectrometric equipment. For some solids-based instruments, the ppm and sub-ppm range is already accessible, and results in these regions are being routinely reported. In order to gain insight into what this implies, the concept of the analytical sampling constant will be briefly discussed. This was developed in its clearest form by Ingamells and Switzer (*Talanta*, Vol. 20, 1973, pp. 547–68), who use the term "laboratory sampling constant." It provides a measure of the subsampling size (the test portion size) necessary to achieve an accurate representation of the test sample (and, if we have done our job correctly up to this point, of the lot itself).

First, an analytical procedure must be chosen with a well-characterized variability. Alternately, it must be at least

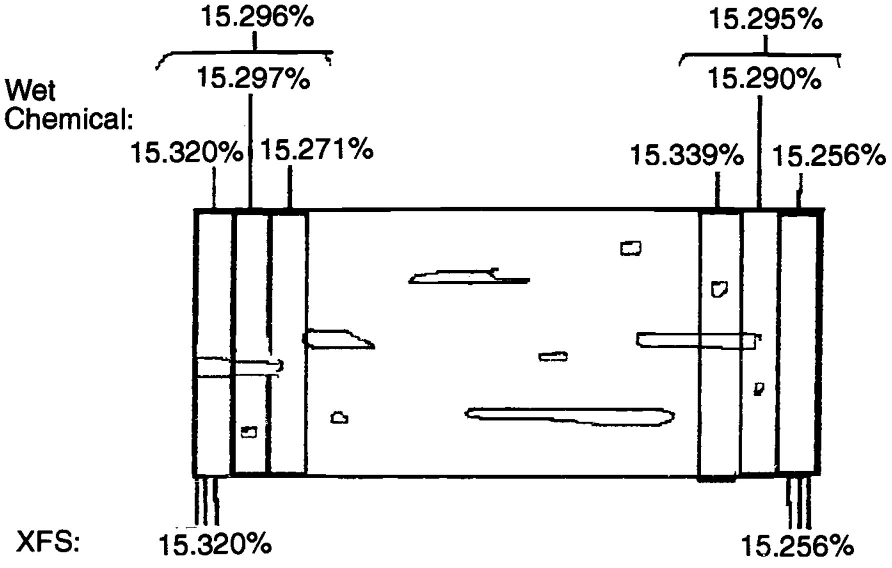

FIG. 5–3—A problem with homogeneity testing.

known with certainty that the procedure's analytical variability is low compared to the variability from the test sample. As a rule of thumb, analytical error should be less than one third of the variation due to sample heterogeneity.

Using this analytical method, the analytical sampling constant, K_s, can be estimated empirically using the relation, $K_s = R^2 w$, where R is the relative standard deviation of the results obtained from determining the analyte in a series of test portions of weight w (chosen to provide a reasonable level of accuracy). In other terms, $R = 100s/\bar{x}$, where s is the standard deviation of the results and $\bar{x}$ is the average result. K_s is in units of mass and represents the test portion size that will yield a 1% subsampling error with 68% confidence. The entire empirical process is then summarized by

$$K_s = (10^4 w \Sigma\ (x_i - \bar{x})^2)/((n - 1)\bar{x}^2)$$

where

$x_1, x_2, x_3, \ldots x_i$ = the analytical results,
n = the number of determinations,
w = the test portion weight for each determination, and
$\bar{x}$ = the average result.

The value of K_s is specific to the analyte and the test sample. If the test sample is further processed by grinding to a finer consistency and mixing and the tests repeated, the value of K_s sometimes (but not always) will drop. The values obtained for K_s are sometimes surprisingly large, especially for low-concentration samples. Table 5–3 lists some values for K_s from some hypothetical sample sets. Once the analyst has gone through the exercise of calculating K_s from a sample set at weight w, the relative standard deviation, R_a, to be expected at some other sample weight, w_a, can be calculated from $R_a = (K_s/w_a)^{1/2}$. For example, from the data in Table 5–3, if we insist on using a 1.5-g test portion for Trial No. 6, we end up with a relative standard deviation (RSD) of 7%, which is very respectable at the 7-ppm level. However, if we use an optical emission spectrometric technique, where the test portion is, say, 10 μg, the calculated RSD is 316%.

Ingamells and Switzer go on to examine the case of trace elements that are highly concentrated in a small sub-population of particles that are not uniformly distributed in the test sample. This is a situation that commonly occurs in many industrial materials. In this case, if the test portion contains less than about six analyte-rich particles, the analytical data will not follow a normal Gaussian distribution curve, but rather a skewed Poisson distribution with a large number of low values. They describe the value of a single result in this case in terms of its component contributions

$$x_i = H + cz_i$$

where

x_i = the value of a single result,
H = the concentration of the analyte in the matrix,
z_i = the number of analyte-rich particles in the test portion, and
c = the average concentration of analyte in the analyte-rich particles.

TABLE 5–3—Values of the analytical sampling constant for hypothetical sample sets (ten replicates).

Trial No.	Test Portion, g	Result Summary, %[a]	K_s, g
1	0.50	18.31 ± 0.12	0.21
2	1.0	7.66 ± 0.08	1.1
3	1.0	0.532 ± 0.009	2.9
4	1.0	0.0494 ± 0.0015	9.2
5	1.0	0.0055 ± 0.0003	30
6	1.5	0.00071 ± 0.00005	74

[a] Average ±1 sigma.

The strange properties of the data in this case derive from the fact that z_i is Poisson distributed. The mean value of the results is equal to their variance if a sufficient number of replicates are taken. In these situations such a small number of the replicates accurately represent the test sample that when they *do* occur they are likely to be rejected as outliers.

In actual analytical work, three distinct distributions are observed, as follows:

(A) Large Test Portion: $z > 6$; Gaussian; mean is accurate and precise.
(B) Intermediate Test Portion: $0 < z < 6$; Poisson; mean is accurate but imprecise.
(C) Small Test Portion: $z = 0$; Gaussian; mean is inaccurate but precise.

In the case of (B), it is often impossible to distinguish sampling error from analytical error unless the analytical error is extremely well defined. In the case of (C), one is only measuring the analyte in the matrix (H), the results look good, and it may seem impossible to resolve the conflict with the results in (A). Many seemingly irresolvable discrepancies between sets of trace results determined by different techniques may stem from such situations. This serves to illustrate the critical importance of test portion size in trace analysis. The quality of the results cannot be judged independently of such considerations.

Ingamells and Switzer illustrate their argument with a hypothetical case similar to the following. A wet chemical analyst uses a 1-g test portion and finds 11 ppm. A spectrographer uses a microgram and finds the same value. But they are both wrong because the spectrographer is at (C) and the wet chemical analyst has botched the determination. A third analyst at (B) may generate badly scattered data, but his average is closest to the truth. One of the key warnings that this treatment raises is that at trace levels with small test portions a low variance in the data may be symptomatic of serious error. The problem is generally confined to trace constituents, although at higher levels an effect may be observed when the highest accuracy is needed.

Gy treated the same problem, but he did not delineate it so clearly. Minkkinen (*Analytica Chimica Acta*, Vol. 196, 1987, pp. 237–45) points out that Gy defined a second sampling constant, Z, which is related through the top-size diameter to the sampling constant C (described in Chapter Four), which is identical to K_s.

$$R^2 = Z/w = Cd^3/w$$

where

R = the relative standard deviation of sampling,
w = the sampling weight,
C = the sampling constant, and
d = the dimension of the largest particles.

And

$$Z = Cd^3 = K_s$$

Ingamells and Switzer point out that the analytical sampling constant has implications for the development of calibration standards, and they outline the following protocol for cooperative testing:

1. All results should be derived from wet chemical analyses using noncomparative methods, and *all* results should be reported.
2. The most precise instrumental methods should be used to establish a value for K_s.
3. Subsampling procedures and subsampling weights should be reported with all results.
4. When certificate values are derived, they should be accompanied with recommended test portions.

FINAL THOUGHTS

Sampling is almost always the weak link in the analytical chain. Much has been written about it, but one feels that many of the substantive, practical issues remain elusive. Perhaps this is because the important aspects are so large and daunting. The analytical chemist will seldom have complete control over the process for which he or she is ultimately held responsible (a situation for which Gy urges change: *Analytica Chimica Acta*, Vol. 190, 1986, pp. 13–23). And yet there are clear paths to improvement.

First, the chemist must get his own house in order. We must not mistake precision for either accuracy or representativeness. We must never be guided by specifications or any other form of expectation in our analytical judgements, but only by the facts. We must treat the sampling process as part of our task and view it as critically as any other manipulative step.

Second, we must strive for a dialogue in those aspects of the sampling process that are beyond our control. If we know that something is wrong, we must make our case as strongly as we know how. It will not be easy, but it will be right.

REFERENCES

Annual Book of ASTM Standards, Vol. 03.05, ASTM, Philadelphia, 1992. Designations E 32, E 55, E 58, E 59, E 255.

Annual Book of ASTM Standards, Vol. 03.06, ASTM, Philadelphia, 1992. Designation E 877.

Cline, J. C., "Problems in Sampling Ferroalloys with Emphasis on Ferrosilicon," *Sampling, Standards, and Homogeneity, STP 540*, ASTM, Philadelphia, 1973, pp. 88–96.

Gy, P. M., *Analytica Chimica Acta*, Vol. 190, 1986, pp. 13–23.

Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley and Sons, New York, 1953, pp. 809–814.

Ingamells, C. O. and Switzer, P., *Talanta*, Vol. 20, 1973, pp. 547–68.

Ingamells, C. O., *Talanta*, Vol. 21, 1974, pp. 141–155.

Ingamells, C. O., *Talanta*, Vol. 23, 1976, pp. 263–264.

Ingamells, C. O., *Talanta*, Vol. 25, 1978, pp. 731–732.

Lundell, G. E. F., Hoffman, J. I., and Bright, H., *Chemical Analysis of Iron and Steel*, John Wiley, New York, 1931, pp. 50–60.

Minkkinen, P., *Analytica Chimica Acta*, Vol. 196, 1987, pp. 237–245.

Pitard, F. F., *Pierre Gy's Sampling Theory and Sampling Practice*, Vol. I: *Heterogeneity and Sampling*, Vol. II: *Sampling Correctness and Sampling Practice*, CRC Press, Boca Raton, FL, 1989.

Sampling and Analysis of Carbon and Alloy Steels (USX Corp.), Reinhold, New York, 1938, pp. 19–32.

Shephard, O. C. and Dietrich, W. F., *Fire Assaying*, McGraw-Hill, New York, 1940, pp. 14–38.

Sisco, F. T., *Technical Analysis of Steel and Steel Works Materials*, McGraw-Hill, New York, 1923, pp. 115–147.

Wilson, A. D., *Analyst*, Vol. 89, 1964, pp. 18–19.

Also, Technical information in the catalog of the Gilson Company.

6

Dissolution in Acids

GENERAL

ONCE THE TEST PORTION has been selected, we most often must perform a number of operations on it before the analyte content is ready for measurement. Usually the first of these is dissolution. What we mean generally by "dissolution" is the conversion of the total test portion into an aqueous solution of dissociated salts. However, even that definition fails to incorporate a number of important exceptions in metal and ore analysis. Sometimes the medium is nonaqueous, as in halogen-solvent treatment for inclusion isolation, and sometimes only the analyte is leached or distilled from the test portion. Some European workers prefer the term "decomposition" for the general process and subcategorize "dissolution" for low-temperature work like acid treatment and "opening out" for high-temperature techniques like molten salt fusions.

Rather than quibble about terminology, let us arbitrarily choose the term "dissolution" as an umbrella to encompass all processes that lead ultimately to a "solution"—complete or partial, aqueous or not. We *will*, however, pay some homage to the preceding distinction by dividing this rather broad subject into two chapters. In this chapter we will confine our discussion to acid-based dissolution processes, while in the next we will cover all the remaining techniques. There is quite a lot to cover, and while all of it is chemistry, much of it is grounded in lore.

In more than 90% of the situations, the analyst's task will be to completely dissolve the test portion. However, even this seemingly straightforward operation must be understood, like the sampling plan, in terms of the attributes (analyte concentrations) to be measured. Some test portion components will be lost as volatiles, some will precipitate, some may adsorb on the vessel walls. But none of these effects will usually matter if the *analyte* is retained quantitatively in solution.

If the analyte measurement depends upon subsequent chemical reactions, the analyst must proceed in a way in which no interfering species are introduced. For example, if one wishes to determine chromium in a high-carbon steel, one must first be aware that the chromium content of the test portion is likely to be divided between chromium dissolved in the iron matrix and chromium present as precipitated chromium carbide. The former is soluble in a mixture of hydrochloric acid and nitric acid, the latter is not. If one proceeds in this way, when the reaction ceases chromium carbide will remain as part of an undissolved residue on the bottom of the beaker.

Adding perchloric acid and heating the mixture to fumes of $HClO_4$ will likely dissolve the carbide residue, but it will also evolve volatile chromyl chloride, and the chromium results will be low. In this case, the correct approach is to dilute, filter, and ignite the insoluble residue, fuse it with an appropriate flux such as sodium bisulfate, and leach the cooled melt in the filtrate solution. Similarly, a niobium-bearing stainless steel will yield a clear solution if fumed in a mixture of phosphoric and sulfuric acids, but if phosphorus is the analyte, this approach is closed to the analyst.

Clearly, then, in a manner analogous to sampling, the analyst must prepare and follow a dissolution plan that will dissolve and completely retain the analyte and add no problems to the determination. The search for a universal approach that can be applied to all or most analytical situations is usually a vain effort unless the assortment of sample types is quite limited. Laboratories that have abandoned chemistry in favor of physical measurement soon learn that sample dissolution is not a trivial exercise, but a complex problem requiring the knowledge and experience of an analytical chemist.

Before beginning this two-chapter journey, we must acknowledge the invaluable aid of two excellent references: *A Handbook of Decomposition Methods in Analytical Chemistry* by R. Bock (John Wiley & Sons, New York, 1979) and *Decomposition Techniques in Inorganic Analysis* by J. Dolezal, P. Povondra, and Z. Sulcek (American Elsevier Publishing Co., New York, 1966). These texts have been the source for a significant amount of the detail in this chapter and the next.

ACID DISSOLUTION

All metals, alloys, and ores react with acid to some extent, and an acid attack is most often the method of choice due to simplicity and convenience. Like many solid/liquid reactions, the rate is diffusion limited and would eventually cease due to the buildup of product concentration at the solid/liquid interface without agitation of some kind. Fortunately, most metal-acid reactions generate hydrogen and other gases that provide the requisite agitation. While all acid attacks are exothermic, applying external heat to the solution produces extra convection currents that stir the solution as well as accelerate the reaction. As with all dissolutions, the rate of acid attack is inversely related to particle size and its attendant surface area relationship. A fine powder may dissolve in minutes, while one solid piece of the same weight may take hours or days.

Reaction rate may also be accelerated: (1) by pressure, which prevents the escape of reactive gaseous species; (2) by ultrasonic agitation, which both agitates the sample particles and produces localized heating due to the collapse of microscopic gas bubbles; and (3) by the action of catalysts. The loss of reactive species can also be prevented by the use of a reflux arrangement so that constant boiling azeotropes are continuously returned to the reaction vessel. This same stratagem can prevent the loss of volatile analyte compounds. In recent years, microwave heating has become an important laboratory tool. It can accelerate reaction rates both at atmospheric and elevated pressures. It must also be remembered that acids, like other dissolution media, react with vessels as well as samples. Thus the choice of vessel composition may be critical to a successful analysis.

Nonoxidizing Acids

As discussed in Chapter 3, it is often useful to distinguish oxidizing and nonoxidizing acids. Nowhere is this more apparent than in the selection of an acid attack for dissolution of the test portion. There are times when oxidizing conditions are best avoided, such as in situations where passivation of the alloy surface by oxidizing media (due to the formation of an acid-resistant oxide monolayer) is a problem. Most common nonoxidizing acids are strongly complexing, a characteristic that greatly facilitates dissolution and is often used to great advantage.

Hydrochloric Acid

The most commonly used nonoxidizing acid is hydrochloric acid. Some might suggest that it comes as close as anything to that mythical universal solvent since most metals and alloys and many ores will succumb to it, given enough patience. The dissolving strength of hydrochloric acid depends in part on the stability of chloride complexes that form with the reaction product cations. The ferromagnetic metals (iron, nickel, and cobalt) will all dissolve, as will the alkaline earths, zinc, cadmium, beryllium, gallium, aluminum, indium, and tin. Titanium is slow to dissolve, and aluminum will benefit from the introduction of a drop of mercury as a catalyst. Many ores and minerals will dissolve, including carbonates, sulfides, phosphates, borates, and some oxides and silicates. Iron ore, limestone, and dolomite dissolve relatively easily, while fluorspar requires the addition of borate to complex fluoride.

Attack on oxides depends to a large extent on thermal history, with certain ignited forms showing higher resistance. Thus, the ignited oxides of aluminum, beryllium, chromium, iron (Fe_3O_4), titanium, zirconium, hafnium, and thorium react slowly, if at all. Other impervious oxides include those of niobium, tantalum, tin, and antimony. On the other hand, the rare earth oxides, zinc oxide, gallium oxide, and cobalt oxide dissolve readily. Gypsum ($CaSO_4 \cdot 2H_2O$) dissolves easily, as do calcite and limestone (both $CaCO_3$), orpiment (As_2S_3), magnetite (iron (II, III) oxide), most manganese ores, and ferrotitanium. Somewhat slower reacting are dolomite ($CaMg(CO_3)_2$), magnesite ($MgCO_3$), siderite ($FeCO_3$), hematite (Fe_2O_3), galena (PbS), scheelite ($CaWO_4$), and apatite (a fluoride-bearing phosphate rock). Certain silicate minerals dissolve, leaving gelatinoid residues of silicic acid. Of course, carbonates dissolve with the evolution of CO_2, while sulfide ores evolve H_2S.

There are a number of ways to facilitate dissolution in hydrochloric acid aside from adding other acids. The addition of copper (II) chloride or mercury (II) chloride or metallic mercury to hydrochloric acid greatly speeds the dissolution of aluminum metal by the creation of a galvanic cell. Platinum (IV) ions will catalyze hydrochloric acid attack on nickel or titanium. Interestingly, platinum metal itself, as well as other members of the platinum group, appear to dissolve to some very minor extent in HCl containing dissolved oxygen in the presence of light. The suggestion has been made that the platinum metals under these conditions catalyze the breakdown of HCl into chlorine gas and some other corrosive, oxidizing chlorine compound. It *is* a fact that hydrochloric acid and a chlorate will dissolve the platinum group metals in a pressure bomb, although it is more than likely that an explosion hazard exists for this approach and it should be avoided.

Other nonacidic oxidizing agents are sometimes added to HCl for use in open vessels: bromine to dissolve lead alloys and antimony alloys; bromate to dissolve tellurium metal; stannous chloride to aid in the dissolution of certain zinc ores; ammonium chloride to aid in the attack on cements (silica, of course, remains undissolved). Carbon tetrachloride and hydrochloric acid under reflux has been recommended to aid the retention of germanium when dissolving soluble minerals. Boric acid or aluminum chloride greatly aid the dissolution of fluorine-bearing materials like fluorspar and phosphate rock. Probably the most useful nonacid additive is hydrogen peroxide, which produces oxidizing conditions in a transient, controlled manner. Excess reagent is easily removed by boiling. HCl and H_2O_2 make an effective medium for dissolving nickel, cobalt, iron, copper, manganese dioxide, bronze, and many other materials. It even attacks platinum and gold to a minor (but not analytically useful) degree. For many metals, the reaction is quite noticeably more vigorous than that from hydrochloric acid alone. The same mixture has been applied to dissolve tungsten, aluminum, Fe_2O_3, and uranium ores. HCl, H_2O_2 and Br_2 has been used to dissolve Sb_2S_5.

Probably the most universally effective stratagem for extending the dissolving power of hydrochloric acid is the use of pressure dissolution (to be discussed in detail later in this chapter). Many alloys and minerals that are resistant or slow at atmospheric pressure will quickly yield clear or nearly clear solutions by treatment in acid bombs or other sealed vessels, in microwave ovens, or in sealed glass tubes. Remarkably, high-carbon ferrochromium, normally resistant to HCl, will dissolve under pressure in a microwave oven. A small weight of chromium refractory can be dissolved in a small volume of HCl in a sealed glass tube held at about 400°C for almost a day. Rare earth phosphors, such as those used in color television picture tubes, are dissolved in a microwave with HCl. Among the many pressure dissolutions that employ hydrochloric acid alone, many prove unexpectedly successful. They also offer what is frequently a distinct analytical advantage in the avoidance of oxidizing substances and of a large excess of acid.

Pressure vessels offer yet another advantage in helping to retain volatiles, whose loss in open vessels can otherwise curtail the usefulness of hydrochloric acid. Ordinarily, some sample components will be lost when samples are dissolved in HCl in beakers or flasks. Arsenic (III), antimony (III), germanium (IV), and selenium (IV) are lost completely as chlorides, hydrides, or both. Phosphorus is lost as PH_3 and PCl_3 and sulfur as H_2S. Partial losses of mercury (II), tin (IV), boron (III), and rhenium (VII) also occur. Losses of indium, zinc, and tellurium may be observed if solutions or salt residues are heated vigorously for extended times.

Besides pressure vessel decomposition, another way to control volatiles loss (and limit acid volume) is to dissolve the sample under reflux. Allihn or straight tube condensers mounted vertically above the reaction flask are the most common approach. This technique will only be effective, however, for the high-boiling volatiles such as mercury, tin, indium, zinc, and tellurium. Another scheme could handle low-boiling volatiles by arranging to distill and collect the volatile species as they are being formed during sample dissolution. This approach is little used, however.

The loss of certain volatiles during open vessel HCl dissolution at low temperature is sometimes not as serious as depicted in the literature. With the exception of arsenic, antimony, germanium, selenium, sulfur, and phosphorus, losses are generally minor and may be tolerable, especially in trace analysis work, where they may represent an immeasurably small error. Of course, another answer to volatiles loss is to alter the oxidation state of the problem elements. Some judicious oxidation will thus convert arsenic, antimony, germanium, selenium, sulfur, and phosphorus to nonvolatile forms.

In addition to the loss of volatiles, a few compounds could precipitate in hydrochloric acid dissolutions—notably AgCl, Hg_2Cl_2, BiOCl, $AuCl_3$, CuCl, the partially soluble $PbCl_2$, and TlCl. In practice such precipitation seldom presents an analytical problem unless the metallic element is unexpectedly present in major amounts or if unusual reducing conditions prevail. In such a situation, a different dissolution medium would normally have been chosen. Traces and even minor amounts of elements that precipitate can be generally tolerated in hydrochloric acid dissolution for the determination of other analytes.

Far more serious concerns are inclusions and metallic phases that are not attacked by hydrochloric acid. Generally, concentrated or dilute HCl will leave considerable undissolved residue from most commercial plain carbon and low-alloy steels. This will usually consist of silica and some combination of aluminum oxide, aluminum nitride, graphite, and a mixture assorted metal carbides, oxides, nitrides, and carbonitrides. Often a major portion of the analyte is contained in one or more of these compounds. Certain higher alloy steels are likely to leave undissolved chromium carbides, vanadium carbides, chromium nitrides, and even chromium sulfides. Insoluble residues of titanium, niobium, tantalum, and other metal compounds are also possible. Nonferrous metals also exhibit HCl-resistant compounds and phases.

Several courses of action are open to the analyst: he may (sometimes at his peril) ignore the residue or he may filter it, ignite it, fuse it with molten salt, and leach the cooled melt in the filtrate. A third course is to try a pressure dissolution with HCl, which sometimes will dissolve otherwise resistant compounds. The utility of this approach is illustrated by the fact that mineral forms like spinel ($MgAl_2O_4$), beryl ($Be_3Al_2(SiO_3)_6$), topaz ($Al_2(SiF_6)_3$), bauxite ($Al_2O_3 \cdot 2H_2O$), cassiterite (SnO_2), corundum (Al_2O_3), and others will dissolve in HCl under pressure, leaving only some insoluble silica residue. A fourth alternative is to try a different acid or acid combination.

Hydrochloric acid is sometimes used as a leaching agent when the element of interest is known to be exclusively associated with the soluble portion of the sample. The sample must be finely divided to ensure that all the soluble portion is exposed to the acid. While this approach can prove useful, it can also be a scientifically hazardous practice and should not be widely applied. It has been used for determining the calcium content in finely ground bauxite and sometimes for certain determinations in slag and cement samples.

Perhaps the most chemically significant aspects of hydrochloric acid dissolution are the many anionic and neutral complexes that it forms with dissolved species. These include complexes with iron, nickel, cobalt, titanium, zirconium, and many others, even including the platinum group. The anionic complexes are particularly useful in ion exchange work, and all the complexes are useful in solvent extraction separations.

Hydrofluoric Acid

Hydrofluoric acid is another important complexing, nonoxidizing dissolution agent. It is unique in its aggressive attack on siliceous samples such as glasses, quartz minerals, and refractories, with all or part of the silicon being volatilized upon heating. The volatile species may be silicon tetrafluoride (SiF_4) or fluosilicic acid ($H_2SiF_6 \cdot xH_2O$), depending upon conditions. Because glass vessels cannot be used, it is necessary to find adequate substitutes that meet the other criteria of the analysis. Typically, polytetrafluoroethylene (Teflon TFE) or platinumware are the materials of choice because of both their resistance to HF and their heat tolerance (see Chapter 2).

With silicate rocks and similar materials, hydrofluoric acid is more effective alone than in mixtures with other acids. In contrast, for most other samples, including metals and alloys, it is a much more efficient solvent in acid mixtures. The acid alone has been used to dissolve quartz, borosilicate glass, bauxite, and titanium dioxide pigments in open vessels and zircon and certain resistant silicate rocks using elevated pressure. Nonoxidizing mixtures with HF include HF/HCl, which has been applied to cement, iron ores, magnesite, niobium and tantalum ores, and titanium and zirconium alloys. HF/H_2SO_4 finds wide application since the high boiling H_2SO_4 allows the complete removal of excess HF, which is a source of potential interference in many analytical procedures. Oxidizing mixtures with HF include HF/HNO_3 and HF/$HClO_4$. All acid mixtures will be discussed later under the appropriate headings.

Hydrofluoric acid, despite its incomplete dissociation at typical dilutions, still contributes a considerable degree of complexing power, forming both negatively charged and neutral soluble fluoride complexes with many elements. Like the chloride complexes formed by hydrochloric acid, these complexes generally show a range of coordination numbers with varying stabilities. Among the elements whose fluoride complexes tend toward great stability are zirconium, beryllium, and boron. Some other of the more stable anions that have been characterized are FeF_6^{3-}, AlF_6^{3-}, TiF_6^{2-}, $NbOF_5^{2-}$, and TaF_7^{2-}. Volatile compounds include SiF_4, BF_3, GeF_4, SeF_4, AsF_3, and AsF_5, but the losses of specific elements depend on conditions.

Arsenic, boron, germanium, and silicon are likely to be lost to some degree below the boiling point of a hydrofluoric acid solution. Evaporation of the solution to dry salts will result in major to complete losses of those four elements as well as significant losses of antimony. Some selenium, tellurium, and even titanium are likely to be lost as well, but other reported losses, such as zirconium, niobium, and tantalum, are doubtful at hotplate temperatures and are probably apocryphal. Evaporation of a mixture of hydrofluoric and sulfuric acids to strong fumes of SO_3 will volatilize arsenic, boron, germanium, silicon, selenium, antimony, mercury, rhenium, and osmium. If a mixture of hydrofluoric and perchloric acids is taken to fumes of perchloric acid, the same list will also include chromium (lost as $CrOF_4$) and ruthenium (lost as $RuOF_4$). The addition of mannitol or phosphoric acid to a hydrofluoric acid solution will prevent the loss of boron at moderate temperatures.

Another way elements are "lost" to the analyst is by precipitation. There are a fair number of insoluble fluorides: the alkaline earths—MgF_2, CaF_2, SrF_2, BaF_2; scandium, yttrium, and the lanthanides (almost all of the form, MF_3); also ThF_4, UF_4; and complex metal fluorides such as $MgAlF_5$ and Fe (II) (AlFe (III))F_5. Reported losses of alkali metal elements, especially potassium, may be traceable to the formation of compounds like $KSiF_6$, K_2AlF_6, and K_2FeF_6. A dry residue of the first of these can be decomposed by warming with calcium hydroxide, whereupon CaF_2 is precipitated and the K^+ is released into solution.

In addition, many common metal fluorides are sparingly soluble, even in dilute acid solution. Thus iron, nickel, and chromium fluorides may be difficult to redissolve once they "salt out" of solution. If the method can tolerate it, warming with boric acid solution will aid in the dissolution of fluoride salts; otherwise, dilution, stirring, warming, and patience are usually rewarded. The precipitation of insoluble fluorides during dissolution can be used to isolate them as analytes. Thorium, uranium, and the rare earths have been separated from mineral matrices in this way by simply diluting and filtering the dissolved sample. For trace quantities, the sample may be spiked with calcium to effect coprecipitation with calcium fluoride. Magnesium is a more useful coprecipitant for X-ray fluorescence micropore membrane work because that element's weaker X-ray response will provide lower background readings.

The use of hydrofluoric acid without its subsequent removal often presents problems later in the analysis. Excess fluoride may prevent an important precipitation from occurring, or it may bleach a color reaction for spectrophotometry or obscure an otherwise sharp visual endpoint in titrimetric work. There are generally three courses to follow when this is the case: (1) complex the excess HF (usually with boric acid, but occasionally with aluminum); (2) precipitate the excess HF (usually with calcium); or (3) drive out the excess HF by heating to fumes with a high boiling mineral acid (H_2SO_4, $HClO_4$, and sometimes one or both of these with H_3PO_4). Nitric acid is also often present, and if organic or other easily oxidizable matter is present, a large excess of nitric acid *must* accompany perchloric acid.

Sulfuric Acid

Sulfuric acid is a good solvent for many metal alloy systems, but is far from a universal one. Iron-base alloys, in general, show vigorous reaction with dilute sulfuric acid and significantly less with the concentrated reagent. The opposite is true for lead- and tin-based alloys. This odd behavior may be explained at least partly by the mild oxidizing effect of the hot concentrated acid and by sulfate complex formation in dilute aqueous solution. Many materials, including second phases and inclusions that may be present in low-alloy and stainless steels and temperature-resistant alloys, are not attacked by sulfuric acid in either concentrated or dilute form. Thus, the analyst must be cautious of residues left after sulfuric acid digestion since they may contain a significant portion of the analyte.

Some other metals that *do* yield to dilute sulfuric acid are beryllium, aluminum, chromium, and titanium metal, as well as ferrotitanium and low-carbon ferrochromium. Certain of these reactions tend to slow down after an energetic interlude, but sometimes a remedy can be found. For aluminum metal, a small amount of mercury (II) salt will produce a mercury amalgam that will accelerate the dissolution. The same device makes dissolution of copper metal in sulfuric acid feasible. Titanium metal requires a drop or two of nitric acid to reach completion (too much and TiO_2 is likely to hydrolyze).

Certain compounds like FeO and ZnO, many carbonates, and titanium and molybdenum borides will dissolve in dilute H_2SO_4 in open vessels. Other materials, like spinel ($MgAl_2O_4$), chromite, and alumina will yield to dilute H_2SO_4 in a pressure bomb. The hot concentrated acid will dissolve thallium metal as well as lead and tin. It is said to attack palladium, rhodium, and platinum to varying degrees and in that approximate order, but is not practical for analytical digestion. It dissolves cryolite (Na_3AlF_6) and fluorspar (CaF_2) by evolving HF.

It is an effective solvent for sulfide ores in general and the ores of tin, antimony, and arsenic in particular. Heating monazite sand (which is largely $CePO_4$) with hot concentrated H_2SO_4 for extended periods will convert it to a water-soluble product. This same technique is sometimes applied to TiO_2 and to certain thorium, niobium, and tantalum ores. Stable cyanide compounds like $KAg(CN)_2$ and $KAu(CN)_2$, which are encountered in precious metal refining, are destroyed by fuming with H_2SO_4 with the evolution of HCN gas. The concentrated acid can be used in a pressure bomb to dissolve orthoclase ($KAlSiO_4$), topaz ($Al_2(SiF_6)_3$), and boron nitride (BN), among other materials. In some cases a very slightly diluted acid is preferable.

The dissolving power of sulfuric acid can be enhanced in certain cases by the addition of solid compounds. The boiling point of the acid is raised and its solvent properties improved by the addition of anhydrous ammonium, potassium, or sodium sulfate. Such digestions are sometimes performed in a fused silica flask fitted with a reflux condenser to help retain volatiles. These mixtures have been used for TiO_2, ZrO_2, WO_3, niobium and tantalum ores, and tungsten carbide (WC), among other materials. In some cases a 0.5-g sample will dissolve in a mixture of 20 mL of concentrated H_2SO_4 and 5 g of anhydrous sulfate salt, although several hours may be required.

Ammonium sulfate is the lowest temperature compound of the three salts (it decomposes at 250°C), but is probably the most useful in this application. Mixtures of sulfuric acid and anhydrous ammonium hydrogen sulfate (NH_4HSO_4) have been used for niobium metal, tantalum oxide, and tungsten and tantalum carbides. Mixtures of sulfuric acid and potassium pyrosulfate are a standard approach for lead- and tin-based alloys and for niobium and tantalum metal. Typically for lead and tin alloys, a 1-g sample will dissolve in 20 mL of H_2SO_4 and 5 g of $K_2S_2O_7$. For niobium and tantalum, a 0.2-g sample will dissolve in 5 mL of H_2SO_4 and 10 g of $K_2S_2O_7$. The dissolution is often conducted in a small fused silica or Vycor Erlenmeyer flask, starting at low heat on a hotplate and finishing by heating to strong fumes over a Meker burner. In the case of the low melting lead and tin solders, it is important that the sample remain below its melting point before it dissolves. Clearly, this approach must be regarded as a hybrid of acid dissolution and molten salt fusion. The cooled salts are dissolved in water and generally yield a clear solution.

Another additive that has been used in the sulfuric acid dissolution of metallic mercury or its ore, cinnabar (HgS), is potassium permanganate. A 0.5-g drop of mercury will dissolve in 20 mL of H_2SO_4 and 0.75 g of finely powdered $KMnO_4$ with 10 min of fuming. The cooled sample is diluted and the permanganate is reduced with 3% H_2O_2. Bromine water and very dilute sulfuric acid has been used to dissolve magnesium alloys. And hydrogen peroxide is sometimes added to dilute sulfuric acid to aid in the dissolution of copper metal.

Volatiles losses from sulfuric acid heated to the fuming point include the mercury (II), the selenium (IV), and a significant portion of the rhenium (VII) (lost as Re_2O_7, which boils at 362°C), and the osmium (VIII) (as OsO_4, which boils at 130°C). Some phosphorus is also likely to be lost. Of course, sulfuric acid is most frequently used in the presence of other acids, and, when such solutions are brought to sulfuric acid fumes, quite different mechanisms of volatiles loss may be at work. The insoluble sulfates include barium, strontium, and lead.

Calcium sulfate is considered to be sparingly soluble, but the presence of major amounts of calcium in the sample frequently eliminates sulfuric acid as a dissolution agent. Sparingly, soluble double salts also form in the presence of potassium ion: $KCr(SO_4)_2$, $KAl(SO_4)_2$, and others. Iron (II) sulfate and iron (III) sulfate show limited solubilities that cause "salting out" of steel samples during sulfuric acid fuming. Similar effects occur with nickel sulfate during the fuming of nickel-base alloy samples. These salts cause bumping and spattering during fuming operations, which must be conducted with care to avoid sample loss. The slight oxidizing effect of fuming with sulfuric acid leaves the valence states of most common metals undisturbed; however, it *is* known that tin (II) is oxidized to tin (IV).

Other Nonoxidizing Acids

Other nonoxidizing acids are sometimes used alone or in nonoxidizing combinations, but these applications are comparatively rare. *Phosphoric acid* will put certain iron and chromium ores into solution and has also been used for a variety of finely ground refractory materials—chrome-magnesite, blast furnace slag, silica brick, and others. In one approach, 0.5 g of −200 mesh sample is reacted with 15 mL of 12.5M H_3PO_4 in a platinum crucible on a sandbath until the water is expelled. Then a lid is placed on the crucible, and it is heated at 300°C until the sample dissolves. Of course, silica must be filtered from the water-leached melt. Phosphoric acid has also been used to dissolve refractory ferrites in the presence of a weighed excess of solid oxidant (such as cerium (IV) or chromium (VI) salts). Total iron can then be determined by titrating the unreacted excess oxidant. Other materials that have been dissolved in phosphoric acid are alumina and high-alumina slags, uranium nitride, feldspar, mica, and kaolin.

Fluoboric acid (HBF_4) is used in specialized procedures to dissolve tin-based alloys, zeolites, and silicates. Since quartz particles are not attacked, it affords a convenient means of gravimetrically determining the quartz content of silicate minerals. *Hydrobromic acid* is much less stable than hydrochloric acid. It should be stored in dark bottles since it decomposes into bromine under the influence of light. HBr readily dissolves copper alloys, which are extremely slow to react with HCl. The reason for this great difference in reaction rates stems from the very stable bromide complexes that form with copper ion. The presence of traces of bromine in the reagent may also play a role. HBr also dissolves indium, antimony, and tin alloys. In the case of tin-base alloys, the base element matrix can be evolved away by fuming with perchloric acid. Interestingly, lead alloys dissolve to clear solutions in the concentrated acid, but $PbBr_2$ precipitates in 1:1 $HBr:H_2O$. Most commonly, lead and tin-base alloys are dissolved in a 1:9 $Br_2:HBr$ mixture (10 mL will dissolve a 1-g sample).

Hydrobromic acid or Br_2/HBr dissolution of lead alloys will result in the loss of tin, arsenic, antimony, and selenium. If the solution is fumed with a high boiling acid, these losses will be virtually complete and some indium is also likely to be lost. Once the volatiles have been expelled, any visible precipitate of $PbBr_2$ in the cooled solution can be dissolved with a few drops of nitric acid. *Hydroiodic acid* is less stable than HBr, breaking down into I_3^- ion. HI will dissolve SnO_2 and $BaSO_4$, although it is seldom used in inorganic analysis. *Acetic acid* has been used to selectively leach analytes from finely powdered samples, in particular, readily soluble calcium compounds from slag samples.

Nonoxidizing Acid Mixtures

Nonoxidizing acid mixtures are extremely useful for certain alloy and nonmetallic samples. Sometimes two volatile nonoxidizing acids are combined, as with HF/HCl mixtures, which are used for cement and silicon nitride (Si_3N_4) samples and also for certain zirconium and titanium alloys, glass, silicate rocks, magnesite, iron ores, and niobium and tantalum ores. Virtually the entire range of acid ratios have been used, from nearly all HCl (for cement) to equal parts of both acids (Si_3N_4) to 3:1 HF:HCl (for glass). The analyst must be prepared in these instances to potentially lose over a dozen elements as volatile compounds when an open vessel digestion is used. For this reason, pressure techniques are especially useful with this acid mixture. If one includes the rare earths, over two dozen other elements may precipitate, and here there is no facile remedy.

Much more common are mixtures of a volatile acid and a high boiling acid. These combinations, like HF/H_2SO_4 and HCl/H_2SO_4, may be premixed (but not stored) or, more commonly, added at the same time to the sample to take advantage of synergistic effects. Occasionally, it is more advantageous to add the volatile acid and allow it to react alone for a time before adding the high boiling acid. Mixtures of HCl, HF, and H_2SO_4, in particular, might utilize such a sequential addition approach to good effect for certain types of sample.

When the sample has dissolved, heating the solution to strong fumes of the high boiling acid will remove potentially interfering amounts of the volatile acids. Table 6–1 should help the analyst predict just which elements are likely to be lost at fuming temperatures, although it should be borne in mind that complex formation and the formation of uncharacterized intermediates often thwarts predictions.

As with much of inorganic analysis, experience is the best guide. Mixtures of HF and H_2SO_4 are commonly used to dissolve siliceous samples: quartz sand, soda lime glass, borosilicate glass, opal glass, and for zirconium alloys and ferrozirconium. Mixtures of HCl and H_2SO_4 have been used for lithium ores and antimony metal. Mixtures of H_3PO_4 and H_2SO_4 are commonly employed in certain steel dissolutions. This mixture is particularly useful for tool steels bearing tungsten, which is prevented from hydrolyzing to the hydrous oxide. Mixtures of HCl, H_3PO_4, and H_2SO_4 have been used to dissolve ferrotitanium. Such mixtures similarly hold the hydrolyzable titanium (despite an insoluble phosphate, which does not form under these conditions). Many of these procedures rely upon fuming with sulfuric acid (the highest boiling common mineral acid) to expel the other components of the acid mixture. However, hydrofluoric acid, or rather interfering fluoride, may be difficult to expel completely in the presence of large amounts of elements that form stable fluoride complexes, such as aluminum.

TABLE 6–1—Boiling points of selected compounds, degrees centigrade.

Acids
HCl (constant boiling:20%) 110
HNO_3 (constant boiling:69%) 121
HBr (constant boiling:48%) 126
$HClO_4$ (constant boiling:72%) 200
H_3PO_4 (ortho) 213
H_2SO_4 330

Fluorides	Chlorides	Bromides
PF_3 −101	BCl_3 12	BBr_3 91
BF_3 −99	PCl_3 76	$SeBr_4$ sublimes at 115
SiF_4 −96	$GeCl_4$ 89	$GeBr_4$ 186
PF_5 −84	$SnCl_4$ 114	$SnBr_4$ 203
AsF_5 −53	$AsCl_3$ 130	$AsBr_3$ 221
GeF_4 sublimes at −37	$SbCl_5$ 140	$SbBr_3$ 280
AsF_3 63	$SeCl_4$ sublimes at 196	
SeF_4 105	$SbCl_3$ 223	
SbF_5 150	$AuCl_3$ 265	

Hydrides	Others
PH_3 −88	CrO_2Cl_2 117
H_2S −61	OsO_4 130
AsH_3 −55	$RuOF_4$ 184
SnH_4 −52	SeO_2 sublimes at 315
H_2Se −42	Re_2O_7 362
SbH_3 −18	
H_2Te −2	
BiH_3 22	

Oxidizing Acids

Some of what has been discussed up to this point are admittedly oxidation reactions, and yet it is useful to distinguish them from reactions that drive the solutes to higher oxidation states. This category has two important members—nitric acid and perchloric acid. The former is a volatile, weakly complexing acid that is oxidizing at all temperatures; the latter is a high-boiling, completely noncomplexing acid that is essentially nonoxidizing at low temperatures but strongly oxidizing at high temperatures. Both find important uses in the dissolution of inorganic materials.

Nitric Acid

Nitric acid, although much more useful in combination with other acids, finds significant use alone. Metals that dissolve readily include nickel, cobalt, copper, mercury, silver, lead, selenium, bismuth, zinc, and cadmium. Many others form an impervious passivation layer, notably aluminum, chromium, titanium, zirconium, hafnium, gallium, indium, niobium, tantalum, thorium, and boron. The alkaline earths will dissolve in the dilute acid, but passivate in the concentrated acid. Iron-base alloys dissolve best in dilute nitric acid, as do thallium and lead oxide. Arsenic and antimony-bearing ores will dissolve, as will galena (PbS_2), MoS_2, certain uranium ores, and selenium and tellurium concentrates. Few elements form stable nitrate complexes—exceptions are $Au(NO_3)_4^-$ and $Th(NO_3)_6^{2-}$. Volatiles loss is limited to OsO_4 and, perhaps, RuO_4. Many elements precipitate as hydrous oxides, notably antimony, tin, niobium, tantalum, titanium, zirconium, hafnium, tungsten, and molybdenum.

Perchloric Acid

Perchloric acid in dilute solution is an excellent solvent for many metals, notably steels of all kinds. Hot, concentrated perchloric acid attacks all metals except gold and certain members of the platinum group. Except in the basic steel industry, where it is used to dissolve steel samples, it is infrequently used alone. For safety reasons, perchloric acid is nearly always used in the presence of a large excess of nitric acid, especially if the solution is heated to fumes of perchloric acid. Explosions have been reported in dissolving bismuth metal, antimony metal, and uranium turnings, and in dissolving steel in the concentrated acid.

After fuming, all metal species are generally in their highest stable oxidation states. Exceptions are lead, manganese, and cobalt, which are in the +II state. Perchloric acid alone or in the presence of nitric acid has been used to dissolve silver, arsenic, lead, manganese, copper, and nickel-copper alloys. Other materials include sulfide ores such as galena, chromite, apatite, and various fluoride-bearing minerals, and chromium carbide (Cr_3C_2) and various other carbides and nitrides extracted from steels.

To prevent the loss of silicon during the perchloric acid dissolution of fluoride-bearing samples, boric acid is added before the reaction is initiated. Even without the addition of any HCl or NaCl, some chromium will volatilize as chromyl chloride (CrO_2Cl_2) from a perchloric acid solution heated to strong fumes. Estimates are that from 1 to 3% of the amount of chromium present will be lost. About 30% of the rhenium will be lost as Re_2O_7, and up to 100% of the selenium will be lost as SeO_2. Likewise, all of the osmium and ruthenium will be lost as OsO_4 and RuO_4, respectively. Arsenic, antimony, and mercury will be lost to some degree as well. In addition, some sulfur will be lost as H_2S during low-temperature dissolution.

During fuming with perchloric acid, silicon precipitates as SiO_2, and antimony, tin, tungsten, titanium, niobium, and tantalum precipitate as hydrous oxides. Also, potassium, rubidium, and cesium precipitate as perchlorates. Fuming perchloric acid generates a fine aerosol spray that can result in mechanical loss of some sample solution if proper care is not applied. Typically, a watchglass and careful temperature control are all that are required.

Oxidizing Acid Mixtures

Oxidizing acid mixtures represent the category with the widest range of application. *Mixtures of hydrochloric and nitric acid* are among the most commonly used concoctions. *Aqua regia* (known as *Königswasser* in Germany) is 3:1 HCl:HNO_3. It is said to gain strength as a dissolution medium if allowed to stand for 3 or 4 min after mixing before it is applied to the sample. *Aqua regia* is an unstable mixture of free chlorine, nitrosyl chloride (NOCl), NO_x gases, and free HCl and HNO_3. Undoubtedly, the complexing power of chloride ion combined with the oxidizing power of free chlorine in aqueous solution are two of the keys to its efficacy as a solvent.

While *aqua regia* is a particularly effective mixture, there is nothing magic about the 3:1 HCl:HNO_3 ratio. Many labs routinely employ a 1:1 ratio of these two acids, and so-called LeForte (or inverted) *aqua regia* (1:3 HCl:HNO_3) is sometimes used to oxidize sulfur to sulfate. *Aqua regia* is particularly useful in the dissolution of stainless steels with moderate (about 2%) to low levels of molybdenum. Similarly, it will dissolve iron-, nickel-, and cobalt-based high-temperature alloys so long as the Group IVB, VB, and VIB elements do not exceed a critical level. In particular, as chromium and molybdenum levels climb in unison, *aqua regia* loses effectiveness. Frequently alloys that are slow or tend toward passivation with *aqua regia* will dissolve if they are started in concentrated hydrochloric acid with nitric acid added dropwise while heating over a period of time.

Some superalloys (especially cobalt-base high-temperature alloys like S816, MP35N, and L605) respond better to such treatment if they are *not* heated. *Aqua regia* will dissolve gold as well as platinum and palladium, but the other members of the platinum group are resistant. It is commonly used to dissolve steel of all kinds, silver, zinc alloys, nickel-copper alloys, nickel-chromium alloys, bronze alloys, copper-beryllium and aluminum-beryllium alloys. Ferroboron requires the dropwise addition of HNO_3 into HCl, as do ferromolybdenum and molybdenum metal. Germanium oxide requires large acid volumes and long digestion times.

Iron, manganese, mercury, lead, and zinc ores dissolve, as do molybdenite (MoS_2) and uraninite (UO_2). Tungsten ores dissolve with the hydrolysis of WO_3. *Aqua regia* oxidizes many elements, but not necessarily to their highest aqueous oxidation states. Both selenium and tellurium, however, are elevated to the +VI state, where their volatility is comparatively low. However, the analyst is cautioned to watch for losses of boron and germanium. If any rhenium or osmium has dissolved, it will be evolved from the boiling solution. There are also reported losses of gold if *aqua regia* solutions are rapidly evaporated to dryness. Antimony, tin, tungsten, niobium, tantalum, and major amounts of molybdenum, zirconium, hafnium, and titanium are likely to precipitate.

Mixtures of Hydrofluoric Acid and Nitric Acid—These are extremely effective solvents for a wide range of metals and alloys, including titanium, niobium, tantalum, and other metals that are impervious to *aqua regia*. Platinum does not dissolve, nor do the other five members of the platinum group, nor does gold. Alloys that are high in chromium react slowly. However, many other materials react with such rapidity that it is often best to add hydrofluoric acid to the sample (in a Teflon TFE or platinum vessel) first, then add nitric acid dropwise or in small increments to initiate and sustain the reaction at a controlled rate. Often copious amounts of NO_x gases are evolved. After the reaction subsides, the solution may be warmed if necessary to complete the dissolution.

All of the elements that hydrolyze in *aqua regia* (see above) are held in solution as soluble fluoride complexes in HF/HNO_3 mixtures. As with HCl/HNO_3 mixtures, the volume ratio of HF to HNO_3 varies widely and is not particularly critical. In general, the proportion of hydrofluoric acid should increase with the sample's estimated content of Group IVB, VB, and VIB elements. Sometimes it helps to add a little water to the mixture as well to help prevent the salting out of fluoride compounds.

A combination of 20 mL of HF, 10 mL of H_2O, and 5 mL of HNO_3 will dissolve a 1-g sample of a large number of different alloys, including some of the most acid resistant. HF/HNO_3 mixtures are used to dissolve titanium, tungsten, zirconium, hafnium, niobium, tantalum, and rhenium metals and their alloys, including their ferroalloys. These mixtures are also used for high-purity silicon, silicon-aluminum alloys, silicides, silicates, and ferrosilicon. Tungsten, silver, and lithium ores dissolve, as do apatite, bauxite, niobium and tantalum oxides and carbides, and tungsten carbide. Niobium-tin superconducting alloys dissolve and so do $CdSiAs_2$ semiconductors. More nitric acid than hydrofluoric acid is used in mixtures to dissolve copper-nickel, antimony-tin, lead-tin, and bronze alloys.

Volatiles losses include boron, silicon, and germanium. The alkaline earths and the rare earths are likely to precipitate, especially if present in major amounts. It should also be noted here that mixtures of fluoboric acid (HBF_4) and nitric acid have proved useful in dissolving solders and other alloys of lead, tin, antimony, and copper, and for dissolving uranium-zirconium alloys.

Mixtures of Hydrochloric, Hydrofluoric, and Nitric Acids—These are effective for high-chromium superalloys, which are often resistant to HF/HNO_3. A combination of 15 mL of HF, 5 mL of HNO_3, and 5 mL of HCl will dissolve 1 g of most superalloys. Titanium alloys, ferroniobium, silicate rock, pyrites, and a great many other samples will succumb to some ratio of these three acids. Volatiles and precipitate losses are about what would be surmised by inference from the previous sections.

Mixtures of HCl + HNO_3, HF + HNO_3, and HCl + HF + HNO_3 with High Boiling Acids—These provide an effective means of removing interfering anionic species (by heating to fumes of the high boiling acid). Sometimes two (or even three) high boiling acids are employed to aid in the dissolution and to prevent hydrolysis of sample component species. One extremely effective and versatile combination makes use of the complexing power of phosphoric acid to circumvent the need for HF. Sample size is limited to about 0.3 g, and the procedure must be followed in the sequence given.

1. Add to the sample in the following order:
   a. 25 mL of HCl.
   b. 5 mL of HNO_3.
   c. 25 mL of H_2O.
   d. 25 mL of a 10:3:12 mixture of H_3PO_4:H_2SO_4:H_2O.
2. Warm, then heat strongly until dissolved.
3. Heat to fumes of H_3PO_4 and fume for 1 min.
4. Remove from heat; cool for 1 min, then add 25 mL of a 7:13 mixture of H_2SO_4:H_2O and swirl to mix.
5. When cool, the sample solution may be diluted up to 100 mL with H_2O.

This procedure will dissolve difficult materials like tungsten metal and hold it in solution for weeks or months. This scheme is effective for: high-speed tool steels; iron-, nickel-, and cobalt-based superalloys; and many other alloys containing significant amounts of elements that ordinarily hydrolyze as hydrous oxides under oxidizing conditions. The dilution mixture is added while the sample is still hot to dissolve the gum-like polymeric metaphosphoric acid, which is otherwise a problem. The diluted sample solution may be conveniently used for inductively coupled plasma spectrometry or for certain spectrophotometric procedures like tungsten, titanium, or niobium determination as hydroquinone complexes. Even though titanium phosphate is insoluble, it does not form under the conditions described. In fact, mixtures of HCl, H_3PO_4, and H_2SO_4 will dissolve ferrotitanium. Similar dissolution procedures are used for nickel and iron ores, while H_3PO_4 and H_2SO_4 alone have been used for aluminum-vanadium alloys.

Sulfuric acid's role as a fuming acid after oxidizing dissolution has few challenges. Its high boiling point assures optimum removal of other acids. Mixtures of nitric acid and sulfuric acid are appropriate for most types of copper alloys and copper ores, for cobalt metal, nickel-iron alloys, molybdenum ores, iron pyrites, ferromolybdenum, lead ores and tin ores. Mixtures of nitric, hydrofluoric, and sulfuric acid apply to niobium and niobium alloys, to ferrophosphorus, uranium ores, titanium, zirconium, and tungsten metal, and have been used to dissolve niobium and tantalum carbide. Mixtures of nitric, hydrochloric, hydrofluoric, and sulfuric acid are effective for bauxite, vanadium ores, and a wide array of other industrial materials.

In certain industries, such as the ferrous metals industry, perchloric acid is the principal fuming acid. Its formidable oxidizing power is used to aid in the complete dissolution of carbides, to dehydrate silica, and to oxidize sample components. In addition, perchlorate salts, except for the alkali metal and ammonium compounds, are readily soluble, unlike sulfate salts, which can be a problem with sulfuric acid. Mixtures of nitric acid and perchloric acid work well for low- and medium-alloy steels, manganese metal and ferromanganese, as well as nickel-copper alloys. Mixtures of nitric, hydrofluoric, and perchloric acid have been used for silicomanganese and for mullite ($AlSiO_3$). A great many sample types are dissolved in HCl/HNO_3 or HCl/HNO_3/HF mixtures; perchloric acid is then added to the cooled sample, which is then heated to fumes of $HClO_4$. Stainless steels, iron-, nickel-, and cobalt-based high-temperature alloys, iron, manganese, and molybdenum ores, and molybdenum disulfide (MoS_2) are often treated in this way. Hydrous oxides of the "earth acids," of course, will precipitate.

Perchloric acid plus phosphoric acid is known in some quarters as "phosphodent." It is a powerful dissolution mixture by itself for many highly alloyed steels and high-temperature alloys. Resistant alloys will generally yield to the addition of small quantities of HCl, HCl + H_2O_2 or HCl + HNO_3. A disadvantage, however, is that titanium phosphate will precipitate. Mixtures of sulfuric and perchloric acid and sulfuric, phosphoric, and perchloric acid are sometimes used for special applications. Two serious concerns with their use are the precipitation of elemental sulfur and the evolution of explosive anhydrous perchloric acid, both of which occur upon strong fuming.

Additives in Oxidizing Acid Mixtures

Additives in oxidizing acid mixtures are often valuable, and some combinations are common. The oxidizing power of *hydrogen peroxide* appears to be directly proportional to the acid strength of the solution. With hydrochloric acid it has been used to dissolve copper, brass, and bronze, magnesium-copper alloys, steel, aluminum, tungsten, and MnO_2. Many highly alloyed iron-, nickel-, and cobalt-based alloys will eventually succumb. High-chromium/high-molybdenum combinations in many resistant stainless steels dissolve slowly, but, unlike attempts with nitric acid mixtures, do not passivate. Dissolution with dilute HCl and dropwise 30% H_2O_2 will keep up to 7 mg of silicon in solution for FAA or ICP determination.

The oxidizing power of hydrogen peroxide is exceptionally high in sulfuric acid (perhaps due to the formation of H_2SO_5). Such a combination (with added water) has been used for iron, nickel, and cobalt alloys. Hydrogen peroxide with concentrated H_2SO_4 has been used for zirconium. Very difficult materials like zirconium and hafnium carbides are also attacked with this approach. In combination with nitric acid, hydrogen peroxide will dissolve lead and lead oxides (including "red lead," Pb_3O_4), calcium tungstate (scheelite), and pyrite minerals, as well as cadmium, zinc, copper, and steels. Hydrofluoric acid and hydrogen peroxide has been used for titanium and titanium alloys, iron and steel, ferrotungsten, silicon metal, and many high-silicon alloys. This combination is especially useful for pickling solid pieces of titanium.

Mixtures of fluoboric acid and hydrogen peroxide have been used for lead alloys. After hydrogen peroxide, the next most useful additive is probably *bromine*. Combinations of hydrobromic acid and bromine are routinely used to dissolve lead- and tin-based solders, antimony and its alloys, and tellurium-bearing steel. High tin content requires a larger proportion of bromine, but the most common ratio is 9:1 $HBr:Br_2$. After dissolution is complete, perchloric acid can be added to the cooled solution; then heating to strong fumes of $HClO_4$ will expel the tin and antimony bromides (as well as the arsenic and selenium). It will also convert any insoluble lead bromide into soluble lead perchlorate. Combinations of hydrochloric acid and bromine have been used in similar applications.

Bromine is often added to a dissolution mixture to help prevent the loss of sulfur as H_2S or phosphorus as PH_3. Thus 0.2 g of an orpiment sample (As_2S_3) can be reacted with 2 mL of ethanol and 3 mL of Br_2, then warmed with 5 mL of HCl to convert the sulfur to stable sulfate. Similarly, 0.5 g of ferrophosphorus can be dissolved in 20 mL of HNO_3 that is saturated with Br_2, 1 mL of H_2SO_4, and 2 mL of HF in order to retain the phosphorus for its determination. Magnesium alloys have been dissolved in water-diluted mixtures of H_2SO_4 and bromine water.

Potassium chlorate ($KClO_3$) has been added to HCl/HNO_3 mixtures to dissolve pyrites. *Potassium bromate* ($KBrO_3$) and HCl will dissolve tellurium. One gram of *potassium dichromate*, 2 mL of H_3PO_4, and 10 mL of HF have been used to dissolve 0.5 g of tantalum metal. *Tartaric, citric, or lactic acid* added to HNO_3 will prevent hydrolysis in the dissolution of antimony and its alloys. There are many other rarely employed, but occasionally invaluable, "tricks" among the notes of experienced metals analysts. Tables 6–2, 6–3, and 6–4 summarize some common acid dissolution schemes for metals, alloys, and related materials.

TABLE 6–2—Suggested acid dissolutions—pure metals.[a]

Element	Dissolution Procedure	
Aluminum	50 mL	1:1 $HCl:H_2O$, plus 1 drop Hg°
Antimony	18 mL	HBr + 2 mL Br_2
Arsenic	20 mL	1:1 $HNO_3:H_2O$
Beryllium	50 mL	1:1 $HCl:H_2O$
Bismuth	20 mL	1:1 $HNO_3:H_2O$
Cadmium	25 mL	1:1 $HCl:H_2O$
Chromium	30 mL	HCl
Cobalt	20 mL	1:1 $HNO_3:H_2O$
Copper	20 mL	1:1 $HNO_3:H_2O$
Gallium	50 mL	1:1 $HCl:H_2O$
Gold	30 mL	3:1 $HCl:HNO_3$
Hafnium	15 mL	HF
Indium	25 mL	1:1 $HCl:H_2O$
Iron	20 mL	1:1 $HCl:H_2O$
Lead	15 mL	HNO_3
Manganese	20 mL	HCl, dropwise HNO_3
Magnesium	30 mL	1:10 $HCl:H_2O$
Mercury	20 mL	1:1 $HNO_3:H_2O$
Molybdenum	20 mL	HCl, dropwise HNO_3
Nickel	30 mL	1:1 $HNO_3:H_2O$
Niobium	20 mL	HF, then 5 mL HNO_3, dropwise
Palladium	30 mL	3:1 $HCl:HNO_3$
Platinum	50 mL	3:1 $HCl:HNO_3$
Rhenium	15 mL	1:1 $HNO_3:H_2O$ in ice bath; no heat
Selenium	10 mL	HNO_3
Silver	20 mL	HNO_3
Tantalum	20 mL	HF, then 5 mL HNO_3, dropwise
Tellurium	20 mL	HCl, dropwise HNO_3
Thallium	20 mL	1:1 $HNO_3:H_2O$
Tin	50 mL	1:1 $HCl:H_2O$
Titanium	20 mL	H_2SO_4, 3 to 5 drops of HNO_3
Tungsten	10 mL	HF, dropwise HNO_3
Zinc	20 mL	HCl
Zirconium	15 mL	HF

[a] One gram test portion is implied. Warm to complete reaction unless otherwise indicated. In most cases alternate dissolutions are possible.

TABLE 6–3—Suggested acid dissolutions—alloys.[a]

Alloy Type	Dissolution Procedure
Aluminum alloys	20 mL 1:1 $HCl:H_2O$, dropwise H_2O_2
Beryllium alloys	30 mL 1:1 $HCl:H_2O$, dropwise HNO_3
Bismuth alloys	20 mL 1:1 $HNO_3:H_2O$ + 5 g tartaric acid
Cobalt-base high temp.	50 mL HCl, dropwise HNO_3, low heat
Copper alloys	30 mL 1:1 $HNO_3:H_2O$
Die steel	50 mL 1:1 $HCl:H_2O$, dropwise H_2O_2
Ferroboron	50 mL 1:1 $HCl:H_2O$, dropwise HNO_3
Ferrochromium, low C	40 mL 1:1 $H_2SO_4:H_2O$
Ferromanganese	30 mL HNO_3
Ferromolybdenum	30 mL HNO_3 + 5 drops HF
Ferroniobium	40 mL 1:1 HCl:HF, dropwise HNO_3
Ferrosilicon	15 mL HF, dropwise HNO_3
Ferrotitanium	30 mL 1:1 $H_2SO_4:H_2O$, 5 mL HF, dropwise HNO_3
Ferrotungsten	15 mL HF, then 5 mL HNO_3 dropwise
Ferrovanadium	30 mL HNO_3 in small portions
Gray iron	25 mL 1:1 $HNO_3:H_2O$; filter
Iron-base high temp.	50 mL HCl, dropwise, HNO_3
Lead alloys	20 mL 9:1 $HBr:Br_2$
Low alloy steels	20 mL 3:1 $HCl:HNO_3$
Manganese alloys	20 mL 3:1 $HCl:HNO_3$
Nickel-base high temp.	50 mL HCl, dropwise HNO_3
Silicon steels	25 mL 3:1 $HCl:HNO_3$ + 5 drops HF
Stainless steels	30 mL 1:1 $HCl:HNO_3$
Tin alloys	30 mL 10:1 $HCl:Br_2$
Titanium alloys	100 mL 1:1 $HCl:H_2O$, 3–5 drops HNO_3
Zinc alloys	30 mL 1:1 $HCl:H_2O$, dropwise HNO_3
Zirconium alloys	40 mL $H_2SO_4:H_2O$; 2 mL HF, dropwise

[a] One gram test portion is implied. Warm to complete reaction. In most cases alternate acid dissolutions are possible and are sometimes necessary.

Special Situations

It sometimes occurs that even the weakest hydrogen donor, like neutral water, is too strong an "acid." This is the case with the alkali metals, which react with increasing violence as they go up in atomic weight (and electropositive potential). With lithium it is a matter of spattering and sample loss, but by the time we get to cesium we are in serious physical danger. Typically, these situations are handled by substituting alcohols for water and excluding atmospheric oxygen. Alcohols and similar polar compounds are more reluctant to release hydrogen ions than water, and in such media there is generally a lower heat of solvation. Cesium can be safely dissolved in butyl alcohol containing a small volume of ethanol. Lithium has been dissolved in a mixture of water and dioxane. Of the alkaline earths (the Group IIA elements, in this case excluding beryllium), calcium, strontium, and barium metal react with water, but magnesium forms a passive oxide. Magnesium metal does, however, react with methanol. Many very reactive metals, like the alkali and alkaline earth elements and the rare earths, are best treated by allowing them to react with atmospheric oxygen in the absence of moisture, weighing them in sealed glass vessels, and then reacting the oxides with dilute acids.

TABLE 6-4—Suggested acid dissolutions—miscellaneous materials.[a]

Material	Dissolution Procedure
Antimony ores	20 mL HNO_3
Bauxite	30 mL 3:1 $HCl:HNO_3$ + 15 mL 1:1 $H_2SO_4:H_2O$
Boron nitride (0.25 g)	15 mL HF in acid bomb, 150°C for 4 h
Borosilicate glass	10 mL HF + 2 mL 1:1 $H_2SO_4:H_2O$
Cobalt ores	30 mL HNO_3 + 20 mL 1:1 $H_2SO_4:H_2O$ (fume)
Copper ores	20 mL HNO_3 + 20 mL 1:1 $H_2SO_4:H_2O$ (fume)
Dolomite	40 mL 1:1 $HCl:H_2O$
Fluorspar	50 mL 1:1 $HClO_4:H_2O$ (fume)
Germanium oxide	50 mL HCl + 5 mL HNO_3 (boil)
Gypsum	50 mL 1:1 $HCl:H_2O$
Iron ores	40 mL 3:1 $HCl:HNO_3$
Lead ores	30 mL $HClO_4$ + 10 mL HNO_3
Lead oxide (Pb_3O_4)	20 mL 3:1 $HNO_3:H_2O$ + 3 mL H_2O_2
Limestone	40 mL 1:1 $HCl:H_2O$
Lithium ores	20 mL 1:1 $H_2SO_4:H_2O$ + 20 mL HF
Manganese ores	40 mL HCl
Mercury ores	30 mL 5:1 $HCl:HNO_3$
Molybdenum ores	20 mL HNO_3
Molybdenum disulfide	50 mL 1:1 $HCl:HNO_3$ + 10 mL $HClO_4$ (fume)
Nickel ores	30 mL 1:1 $HNO_3:H_2O$
Portland cement	20 mL HCl + 3 g NH_4Cl
Selenium ores	20 mL HNO_3 + 1 mL H_2O
Silicate minerals	10 mL HF + 20 mL HNO_3
Silicon nitride	15 mL HF
Steel-making slags	10 mL HCl + 10 mL HNO_3 + 10 mL HF
Tin ores	20 mL 1:1 $HNO_3:H_2O$ + 10 mL H_2SO_4 (fume)
Titanium dioxide	15 mL HF
Uranium ores	30 mL HF + 5 mL HNO_3 + 5 mL H_2SO_4 (fume)
Vanadium ores	40 mL 1:1 $HCl:HNO_3$ + 10 mL H_2SO_4 (fume)
Zinc oxide	15 mL 1:1 $HCl:H_2O$

[a] One gram test portion, except as noted. Warm to complete reaction. In most cases alternate acid dissolutions are possible and are sometimes necessary.

The practical inorganic analyst is well aware that the position of metal/ion half-cell potentials below hydrogen in the electromotive series is a poor predictor of how the metal will dissolve in acid. Passivation, complexation, and heat of solvation all play a role, and the nature of the solvent medium is critical. The importance of complex formation and oxidation is illustrated by the fact (incredible to some) that molybdenum, tungsten, and rhenium metal will dissolve in 30% hydrogen peroxide. The reaction is slow and favored by having the sample in a finely divided form, but it works and is even useful. For example, a gram of tungsten powder will dissolve in 50 mL of H_2O_2 overnight with gentle warming. Such an approach finds use where acidity must be restricted, as in the molybdenum blue spectrophotometric method for silicon determination.

Many metals and alloys will dissolve in acetylacetone (2,4-pentanedione), which forms stable complexes with many metal ions. There are also many other unusual low- or moderate-temperature metal dissolution reactions that rely on oxidation, complexation, or both. Some of these will be touched upon in the next chapter.

TREATMENT OF INSOLUBLES

When the analyst has done his best with an acid approach, either in open vessels or under pressure, sometimes insoluble matter still remains. This may be known to be innocuous to his purposes, in which case he can ignore it or filter it off and discard it. In another case, the insoluble residue may be known to contain a significant portion of the analyte, in which case the analyst has no choice but to take some action with it. But much more commonly the analyst has only a suspicion about that black smudge on the bottom of the beaker. The safest course is to treat every insoluble residue as if it was chock full of analyte. But the rigorous treatment of insolubles is very time consuming and may be a wasted effort. Sometimes it is possible to rapidly collect a sample of the insolubles from a trial dissolution and qualitatively or semi-quantitatively survey the composition using X-ray fluorescence (on a Mylar-covered membrane filter), optical emission (in a crater electrode), or even X-ray diffraction (for compound identification).

The treatment of acid insolubles involves first dilution of the solution to an acid concentration that will not destroy the filter. Hardened filter papers and certain membrane filter disks withstand more acid than common grades (see Chapter 2). Sometimes it is necessary to reduce matrix elements that are otherwise difficult to completely wash out of the filter. It is essential that the solution be filtered on a medium that completely retains the insolubles. In low-alloy and plain carbon steels, certain inclusion compounds can occur as extremely fine particles requiring 0.22-μm membrane filters. In other cases a fine porosity filter paper will suffice. The acid dissolution vessel is scrubbed with a rubber policeman and rinsed onto the filter.

The filter is then washed repeatedly, usually alternately with dilute acid and hot water. Rigorous washing of the residue is not a high priority, however, if the soluble and insoluble fractions will ultimately be recombined. The filtrate is retained, and the filter and residue are transferred to a crucible (usually platinum) and ignited in a muffle furnace, then cooled in a desiccator. If silicon is not to be determined, it can be volatilized at this point by heating on a sandbath with H_2SO_4 and HF.

When the residue has evaporated to dryness, the crucible is again cooled in a desiccator. A weighed amount of flux is added, and the residue is fused over a burner or in a muffle furnace and again cooled. The crucible's exterior is wiped clean and then it is immersed in the appropriate filtrate solution, which is then heated to leach the melt. The crucible is removed with Teflon-coated forceps and rinsed into the solution. Alternatively, the melt can be leached in a small amount of dilute acid that is then combined with the appropriate filtrate. Another choice is to analyze the acid soluble and acid insoluble portions separately. This approach is twice the work, but provides information that cannot be otherwise obtained. The two values can, of course, be combined mathematically to obtain the total analyte content. Details about molten salt fusions and high-temperature sinters will be presented in the following chapter.

PRESSURE DISSOLUTIONS

There is no doubt that dissolution in acid proceeds more rapidly and more completely if the reaction is conducted in a confined vessel above atmospheric pressure. This has been known for a long time, and much early work was performed in sealed glass tubes. More recently, armored acid dissolution bombs have been commercially available, increasing the safety and convenience of the approach. These devices consist of a Teflon TFE vessel and lid that contain the sample and the acid. This vessel and lid fit snugly in a heavy stainless steel or nickel alloy cannister that screws together to form a sealed reaction bomb that can be conveniently heated in a drying oven.

Typically, a small sample (0.5 g or less) and a small volume of acid (15 mL or less) are reacted for 1 to 4 h at a temperature of 150°C or less, then cooled to room temperature before the vessel is opened. It is possible with such devices to dissolve substances in a type and quantity of acid that would be impossible at atmospheric pressure. Moreover, volatiles that are normally lost in open vessels will be retained. The disadvantages are the danger and inconvenience. Although such bombs are used routinely, the analyst must always be aware that he is dealing with hundreds of atmospheres of pressure, and the manufacturer's instructions must be carefully followed. Also, the heating and cooling processes are time consuming, and it is a rare laboratory that can afford these devices in great quantity. Like microwave dissolution, the acid dissolution bomb offers its best advantage for well-characterized samples that are slow to dissolve in open vessels and for those cases where the dissolution medium is restricted by the requirements of the determination.

Certain sample/solvent combinations are too dangerous for any pressure dissolution approach. Perchloric acid with any sample is one example, and sulfuric and nitric acids with any organic material are another. Too much acid of any kind is another danger. Hydrofluoric and hydrochloric acids, however, are particularly effective under pressure, and sometimes amazing dissolutions occur with a minimum of acid. Method development, however, is often a lengthy process because of the time required for the vessels to heat and cool.

MICROWAVE DISSOLUTIONS

Even more recently, microwave techniques have entered the analytical laboratory, promising a revolution in dissolution procedures. Some facilities have benefitted greatly, while others have been left wondering what all the fuss was about. There are two approaches to microwave dissolution—open vessel and closed vessel techniques. Open vessel techniques offer only a little advantage over hotplate dissolution since the shorter heating times are offset by the time required to load and unload the microwave oven. Closed vessel techniques are essentially a more convenient way to perform pressure dissolutions. But that advantage is partly offset by the pressure limit of the plastic vessels, which is always significantly less than the pressure limit of metal acid dissolution bombs. Clearly, some surprising dissolutions can be routinely performed with a closed vessel microwave oven approach—for example, a high carbon ferrochromium sample will dissolve in a small volume of hydrochloric acid. And many day-long dissolutions can be reduced to an hour.

But it is always necessary to consider the loading and unloading times involved, as well as the development time required to establish a procedure. Labs that analyze only a few grades of alloy or ore may find that the microwave approach is a godsend, since they can usually develop one or two short compromise programs applicable to all or most of their workload. However, labs with more complicated requirements may become bogged down in a confusion of complex protocols or find themselves running every sample for 90 min or so, whether such a lengthy program is necessary or not.

Microwave usage usually involves considerable capital investment, whether the lab has opted for the expensive laboratory models that control power by pressure and/or temperature probes, or inexpensive home consumer ovens that corrode from fumes and must be regularly replaced. It is evident that the investment is justified in some cases. However, labs that expect a tremendous increase in sample throughput as a result of introducing microwave oven dissolution may be disappointed. Laboratory managers that view these devices as a supplement and expansion of their current capabilities are much more likely to ultimately feel satisfied.

REFLUX DISSOLUTIONS

One useful alternative to open vessel acid dissolutions is the use of a reflux condenser. In a sense, a beaker watchglass or the Tuttle covers designed for Erlenmeyer flasks are reflux condensers, albeit of limited efficiency. Water-cooled condensers, especially those with sizable internal cooling surface areas like the Allihn and Graham designs, can restrict or eliminate the loss of volatile acids. Many otherwise volatile sample components will also be retained. Thus, with such an apparatus it is frequently possible to dissolve a test portion in a very small amount of acid and to prevent the loss of analytes like boron, arsenic, and antimony, which are easily lost in open beakers.

In a typical arrangement, an Allihn condenser with a ground glass joint is fitted to the ground glass neck of an Erlenmeyer or round-bottomed flask. Sometimes a Teflon sleeve and plastic clip are used to seal and secure the connection. Erlenmeyer flasks are typically heated on small electric hotplates, while round-bottomed flasks are heated with electric heating mantles. The condenser is held in position above the flask with a three-fingered clamp attached to a ringstand or a "monkey-bar" arrangement. When the sample has dissolved, the condenser is rinsed down from the top into the cooled flask. A modified version of this basic arrangement is sometimes used for a different purpose. If the flask mouth is fitted with a side-arm joint, inert gas can be introduced to prevent the oxidation of analyte. Such setups are typically used for the dissolution of samples for ferrous iron and tin determinations.

OTHER STRATEGIES

There are certain other dissolution strategies that are used with acids. Ultrasonic agitation will accelerate reaction rates and sometimes help to expose undissolved sample particles to the acid if a compound has precipitated. Leaching techniques in which the analyte is dissolved but a major portion of the test portion remains untouched have been applied to calcium compounds in slags and cement (as discussed under HCl earlier in this chapter), among other analytes and sample types. Such approaches, in general, must be applied only to finely divided samples and always with cautious analytical judgement. The use of acids to "wet ash" organic materials for inorganic analysis will be discussed in the next chapter since the general topic of the decomposition of organics arguably constitutes a separate subject. Acids are also employed in some inclusion isolations, and, again, discussion is deferred to where that field is treated in the next chapter.

REFERENCES

Annual Book of ASTM Standards, Vol. 03.05, American Society for Testing and Materials, Philadelphia, 1992, Standards E 46 and E 50.

Beamish, F. E., *The Analytical Chemistry of the Noble Metals*, Pergamon Press, Oxford, 1966, pp. 1–4.

Bock, R., *A Handbook of Decomposition Methods in Analytical Chemistry*, John Wiley & Sons, New York, 1979.

Churchill, H. V. and Bridges, R. W., *Chemical Analysis of Aluminum*, Aluminum Company of America, New Kensington, PA, 1935, pp. 6–7.

Dolezal, J., Povondra, P., and Sulcek, Z., *Decomposition Techniques in Inorganic Analysis*, American Elsevier Publishing Co., New York, 1966.

Elwell, W. T. and Wood, D. F., *Analysis of the New Metals, Titanium, Zirconium, Hafnium, Niobium, Tantalum, Tungsten and their Alloys*, Pergamon Press, Oxford, 1966.

Hobart, E. W. and Kallmann, S., "Dissolution of Metals for Analysis," *Some Fundamentals of Analytical Chemistry, ASTM STP 564*, American Society for Testing and Materials, Philadelphia, 1974, pp. 68–72.

Hofton, M. E. and Baines, S., British Steel Corp. Open Report GS/EX/42/72/C, British Steel Corp., Sheffield, U.K., 1975.

Lange's Handbook of Chemistry, 11th ed., J. Dean, Ed., McGraw-Hill, New York, 1973.

Lundell, G. E. F. and Hoffman, J. I., *Outlines of Methods of Chemical Analysis*, John Wiley & Sons, New York, 1938.

Murau, P. C., *Analytical Chemistry*, Vol. 33, No. 8, 1961, pp. 1125–1126.

Povondra, P. and Sulcek, Z., *Methods of Decomposition in Inorganic Analysis*, CRC Press, Boca Raton, FL, 1989.

Van Nostrand's Scientific Encyclopedia, 4th ed., D. Van Nostrand, Princeton, NJ, 1968.

Zehr, B., *American Laboratory*, December 1992, pp. 24–29.

7

Miscellaneous Dissolutions

THIS CHAPTER IS DEVOTED TO those dissolution schemes that by reason of uniqueness deserve to be treated as separate categories from the straight acid methodology described in Chapter Six. Each of this diverse group of techniques occupies a special niche in the metals analyst's bag of tricks; however, it is unlikely that any laboratory will need to use them all routinely. Here, as with the straight acid dissolution of inorganic materials, the role of particle size is critical to the control of reaction rate. Thus, sinters and fusions will always require very finely divided materials to ensure an intimate mixture with the flux, while inclusion isolation techniques will always require a monolithic solid to moderate reaction rates and to prevent dissolution of the isolates. Before beginning, we must again acknowledge the invaluable aid of the referenced texts by R. Bock and by J. Dolezal, P. Povondra, and Z. Sulcek.

DESTRUCTION OF ORGANICS

While the dissolution of organic solids and liquids for *organic* compositional analysis is a complex and important area, it is outside the province of our subject. However, the decomposition of organic materials for *inorganic* assay is a quite separate field that deserves some mention here. Occasionally, the metals analyst may receive organic samples—coatings, lacquers, cutting and rolling oils, spent catalysts, process bath additives, and others—for elemental analysis. These will most often have to be processed by some technique which results in an aqueous solution that accurately represents the inorganic components of the original sample. Even more frequently, in the course of chemical separations a filtered metal/organic compound will have to be converted back into an aqueous solution. Several different general techniques for the destruction of organic matter will be described. Each of these has a place, but it must be realized that no one technique is suitable for all types of organic material.

Ignition in Air or Oxygen

This simple approach to organic destruction is sometimes the best and safest technique to use, but there are times when it can lead to serious analyte losses. Ignition in a platinum, Vycor, or fused silica vessel in a muffle furnace, with or without injected oxygen, is the usual approach. Bulky organics are sometimes first charred at the open muffle door before ignition at higher temperatures with the door closed. Temperature is often critical, such as when the analyte is molybdenum, tungsten, rhenium, ruthenium, or osmium, since the oxides of these elements volatilize at temperatures well within the range of an ordinary laboratory muffle furnace. There are, of course, other elements that are so extremely volatile that little can be done to prevent their loss by this approach. Thus arsenic, cadmium, mercury, sulfur, antimony, selenium, and zinc are likely to be lost in whole or in part, even at very low ignition temperatures. Ashing additives, like nitric acid or sulfuric acid, will help to retain silver and lead, and alkaline earth hydroxides will prevent the loss of boron. Alkaline conditions also favor the retention of phosphorus and fluorine.

Schöniger flask combustions are a means of organic material ignition with little or no associated volatiles loss. A small amount of absorbing solution is added to a 300-mL or larger Erlenmeyer flask with a ground glass neck flared for a waterlock. The absorbing solution may consist of dilute sodium hydroxide or sodium carbonate solution, perhaps with a little hydrogen peroxide added. If the sample is a liquid, it is weighed onto a small tared square of filter paper. If the sample is a solid, it may be weighed into an empty gelatin capsule, which is then wrapped in a small filter paper.

Sample weights are typically less than 10 mg and samples should be weighed on a microbalance. The folded filter paper with the sample is pinched in a platinum gauze clip attached below a ground glass stopper that fits the flask. A strip of the filter paper is allowed to extend from the packet as a "fuse." The flask is then purged with oxygen for several minutes; then the "fuse" is lit, the stopper is plunged into the flask and held firmly in place, and the flask is held in an inverted position until the combustion is complete. The flask is then agitated for 10 min or longer to facilitate absorption of the gaseous reaction products by the solution.

Additional absorbing solution or water may be added to the waterlock collar before the stopper is removed to aid in rinsing the flask neck. Schöniger flask combustions of difficult-to-burn organic material can be aided by adding a little fuel (like sucrose) or a little oxidant (like potassium nitrate) to the sample charge. The technique is most useful in obtaining aqueous solutions for the determination of sulfur, phosphorus, the halogens, mercury, arsenic, antimony, and selenium, although the platinum holder should be replaced with one of tantalum or silica for the last four mentioned elements. Some labs couple the approach with ion chromatography, employing a standard eluent as the absorbing solution.

Oxygen bomb combustions are conducted in an armored vessel at high pressure employing electrical ignition. These devices are essentially bomb calorimeters that are used to measure the fuel value of organic material by measuring the temperature rise in an insulated, stirred water bath that ordinarily holds the device. When oxygen bombs are used for dissolution, the water bath may be dispensed with. Typically less than 1 g of sample is weighed into the sample cup, which is placed in the vessel above a small amount of absorbing solution. An ignitor wire is laid across the sample. The lid is screwed on and the bomb is pressurized to about 25 atm with oxygen. The sample is ignited electrically and allowed to cool with occasional agitation for several hours. Then the pressure is slowly bled off and the bomb is opened. The possibility of sample loss during the outgassing of the bomb, of incomplete combustion, and of the reaction of analytes with the metallic vessel material are all criticisms that have been leveled at this technique.

Plasma dry ashing is a means of destroying organic material with a low-temperature oxygen plasma. Samples are placed in silica boats and inserted into a device that uses high-frequency RF coils to generate excited oxygen atoms from O_2 at low pressure. The sample remains below 200°C, and arsenic, cadmium, and antimony are retained. However, mercury and sulfur are lost.

Wet Ashing

The "liquid fire" technique is an old name for *perchloric acid/nitric acid* wet ashing of organic substances. In general, a large excess of nitric acid tends to remove some of the danger of an explosion, and these decompositions must always contain a large excess of that reagent. Even in the presence of a large amount of nitric acid, however, high-boiling or temperature-resistant organics present some danger since a significant amount of relatively intact sample may remain as the last of the nitric acid boils off and the fuming point of perchloric acid approaches. Fats such as in a tallow-based rolling oil emulsion or as might remain in a spent nickel hydrogenation catalyst are a particular danger and are best treated by a different technique such as muffle furnace ignition.

Sample size for the liquid fire method should be less than 1 g, with nitric acid volume as high as 100 mL and with perchloric acid volume at 10 to 15 mL. When working with an unfamiliar sample type, it is very wise to follow a published procedure specific for that material and to follow it exactly as written. In most cases, the nitric acid is added to the sample; then the perchloric acid is added and the sample is immediately heated to boiling on a hotplate. Copious NO_x fumes are evolved as the organic material begins to break down. The heating is continued, and, as the fuming point of $HClO_4$ nears, a noticeably exothermic reaction produces frothing. A clear solution results just as the white fumes of $HClO_4$ begin to evolve.

If an opaque black or brown syrupy solution forms, there is imminent danger of an explosion. In that case, the heat should be shut off and additional nitric acid should be added to the solution. Heating can then be resumed until a clear, fuming solution forms. Always wear and use proper safety equipment. The liquid fire method may be conducted in a beaker with a watchglass or in an Erlenmeyer flask with a Tuttle cover fitted in the neck. Fume the clear solution for about 2 to 3 min, then remove from the heat and cool to room temperature at the back of the hood. Volatiles losses are similar to those described for perchloric acid fuming in the last chapter: arsenic, antimony, mercury, selenium, rhenium, and ruthenium for certain, and possibly also boron, chromium, germanium, and tin, especially if the sample contains some chloride or if any HCl was added.

Less efficient, but perhaps at least marginally safer, is *sulfuric acid/nitric acid* wet ashing. The danger here is the formation of unstable nitrated organic compounds that can spontaneously explode. As with perchloric acid/nitric acid digestions, it is critical for safety considerations to begin heating of the solutions as soon as all the reagents are added and to continue with the process until all the organics have been destroyed. Under no circumstances should sample mixtures with these acids be allowed to sit at room temperature for more than a few minutes. Samples should be less than 1 g; nitric acid volume should be 50 to 100 mL; and sulfuric acid volume should be 10 to 15 mL. Once started, the heating should continue until the sample begins to form a black tar, at which point additional nitric acid must be cautiously added dropwise.

This process must be repeated as the sample begins to evolve white fumes of SO_3, until the fuming solution remains clear. This operation is best conducted in a beaker with the watchglass slightly pulled back from the pouring lip. The clear solution should be fumed for 2 to 3 min, then allowed to cool. Some labs refer to such decompositions as "kjeldahling" (after the classic procedure for organic nitrogen that initially uses sulfuric acid and a catalyst to decompose the sample). Volatiles that are lost include arsenic, mercury, selenium, and possibly germanium.

Perhaps the most efficient wet ashing procedure involves the use of *perchloric acid/sulfuric acid/nitric acid*. With less than a 1-g sample, 100 mL of nitric acid, 15 mL of sulfuric acid, and 10 mL of perchloric acid are added and the solution is boiled vigorously. As the first white fumes of $HClO_4$ eventually appear, a vigorous frothing should finally form a clear solution. The solution is then fumed for 2 to 3 min and then cooled. As with all the wet ashing procedures described in this section, a controlled heating rate is very important. In particular, the initial rate must not be extreme or the nitric acid will be driven off before it can complete its task. Once fuming begins, however, very high temperatures are called for.

MOLTEN SALT FUSIONS

When dissolution with acids runs into difficulties, the analyst's next recourse is usually a molten salt fusion. This category of techniques is quite broad, with diverse fluxes ranging from acidic to basic and from nonoxidizing to strongly oxidizing. Vessel materials and heating modes also vary widely, although they are often constrained by the nature of the flux.

When we speak of molten salt fusions, "oxidizing" and "nonoxidizing" carry their usual meanings, but the terms "acidic" and "basic" are used in the Lewis sense of electron-pair acceptor and electron-pair donor, respectively. Molten salt reactions are by their high-temperature nature water free,

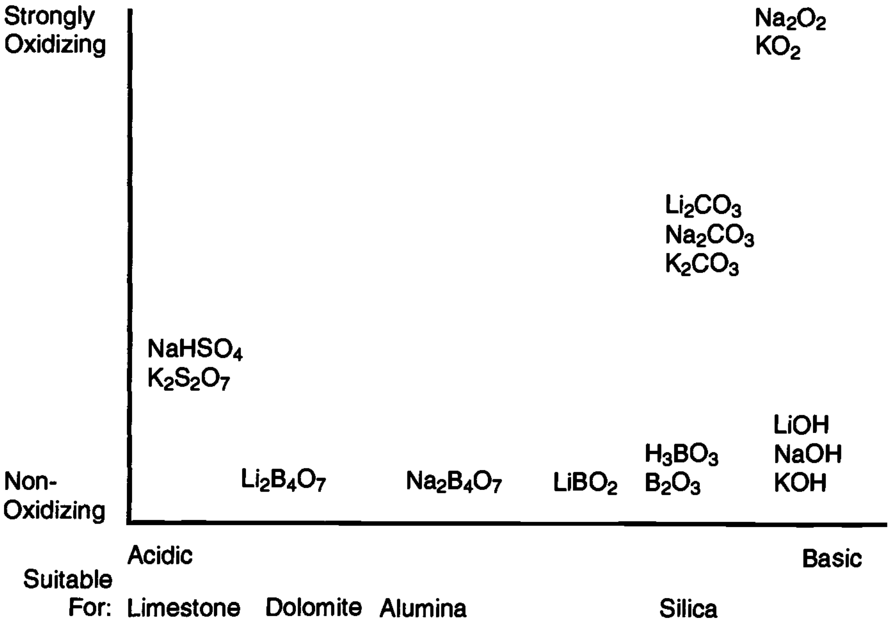

FIG. 7-1—A chart of molten salt flux properties.

but by intuitive analogy to aqueous systems we say that a sodium carbonate fusion is a "basic fusion" or that a sodium bisulfate fusion is an "acidic fusion." Figure 7-1 shows how some common fluxes relate to one another in terms of these properties.

All fusions start with a dry mixture of the sample and the flux compound (or compounds). It is usually very important that both the test portion and the flux are in a dry, finely divided form and that they be mixed as intimately as possible before heat is applied. The weight ratio of flux to sample is often critical; although, except where the flux contributes a very large blank to the analyte measurement, it is seldom weighed to the same degree of accuracy as the sample.

Fusions are either conducted over a gas burner or in a muffle furnace, most often using a lid to contain any spattering. The choice of vessel material is related to both the flux and sample characteristics, as well as the analytical requirements. Frequently it is necessary to swirl the molten contents with a pair of tongs to ensure a complete reaction. The cooled melt is either leached with water, which is then acidified, or it is leached directly with dilute acid.

Sodium Carbonate

The most generally useful flux for raw materials work is sodium carbonate. It melts at 851°C, but begins to lose CO_2 slightly below this temperature. There are sometimes trace impurities in ACS grade, but ultrapurity grades are available at a premium price. Sodium bicarbonate is much cleaner in reagent grade and *can* be substituted since it converts to sodium carbonate at 300°C, but this approach is seldom taken because of the excessive starting volume of sodium bicarbonate required. Fusions with sodium carbonate are almost always conducted in platinum crucibles since most other materials, including Vycor, fused silica, and porcelain, will dissolve.

If the fusion is conducted over a burner, a platinum lid is a necessity both to help achieve the melting point temperature and to limit the dissolution of platinum, which is minor but measurable. Apparently, air contributes to the attack on the platinum. Samples high in lead or iron (II) will result in these elements partially alloying with the platinum crucible. This effect can be discouraged by adding some sodium nitrate before fusing. All carbonate fusions are most commonly leached in dilute acid with the vigorous effervescence of CO_2 gas. This removal of the flux anion is a significant advantage for many methods and makes carbonate fusions a very popular dissolution choice. Carbonate fusions can also be leached in neutral water, with many sample components forming aqueous carbonato-complexes and others precipitating as hydroxides or insoluble carbonates.

Sodium carbonate fusions are classed as basic and nonoxidizing, but antimony, sulfur, chromium, and manganese will be partially oxidized by air unless a close-fitting lid is used. Mercury and thallium are completely lost by volatilization, while selenium and arsenic are partially volatilized. Weight ratios of flux to sample range from 1:1 to 10:1, and fusions generally require a half hour or more. As with all fusions, swirling the molten liquid at periodic intervals is usually required to ensure complete fusion. The crucible lid must be momentarily removed for this operation.

Sodium carbonate fusions are effective for a wide range of sample materials, especially siliceous samples and aluminosilicates up to about 40% Al_2O_3 equivalent. Quartz, asbestos, sillimanite (Al_2SiO_5), beryl ($Be_3Al_2(SiO_3)_6$), bauxite ($Al_2O_3 \cdot 2H_2O$), barytes ($BaSO_4$), mullite ($Al_6Si_2O_{13}$), feldspar, apatite, celestite ($SrSO_4$), and kaolin clays all fuse completely. Also titanium boride (TiB_2); tungsten, beryllium, and iron ores; silicate rocks, most refractories and ceramics; and all silica-based glasses will dissolve. In the steel industry, slag and coke are sometimes brought into solution by this means.

Sometimes sodium hydroxide is added to sodium carbonate to extend its dissolving power.

Potassium Carbonate

While this compound melts at 891°C, it does not begin to lose CO_2 until well above this temperature. It is not a particularly popular flux by itself because it is difficult to achieve a melt at gas burner temperatures. However, it does find use for Nb_2O_5 and Ta_2O_5 since their potassium salts are more readily leached in water than their sodium salts.

Sodium Carbonate/Potassium Carbonate

An equal weight mixture of these two compounds melts at a temperature below both of its components (710°C). It is a valuable flux for high-alumina silicates, molybdenum and tungsten ores, Nb_2O_5, Ta_2O_5, and tungsten metal after its oxidation to WO_3.

Lithium Carbonate

This is the lowest melting alkali metal carbonate. It melts and begins to lose CO_2 at 618°C. It is also the most corrosive carbonate in attacking platinum crucibles. Alone, it has found use for the determination of sodium in silicates and in alumina. It is more frequently used in combination with other fluxes.

Other Carbonate Fusions

Carbonates are commonly combined with borax (sodium tetraborate) to increase their dissolving power. Corundum (Al_2O_3), baddeleyite (ZrO_2), zircon, and titanium dioxide, among other sample materials, can be dissolved in this way. The so-called "Freiberger decomposition" is a fusion with a 1:1 mixture of an alkali carbonate and elemental sulfur used in a 7:1 mixed-flux:sample ratio. When the cooled melt is leached in water, arsenic, antimony, tin, germanium, molybdenum, tungsten, vanadium, palladium, and iridium are in aqueous solution, while lead, bismuth, iron, zinc, cadmium, and other metals are precipitated as sulfides; copper, selenium, and tellurium are present in both phases. Carbonates are combined with other fluxes as well. Sodium carbonate, for example, is often combined with sodium peroxide, where its principal function is to moderate the reaction rate.

Boric Acid and Boron Trioxide

These two compounds are essentially the same flux ($2H_3BO_3 \xrightarrow{\Delta} B_2O_3 + 3H_2O$). Both are useful for sample dissolutions, but since B_2O_3 is very hygroscopic, H_3BO_3 is more frequently employed. Pure boric acid melts at 169°C, while boron trioxide melts at 580°C. Platinum crucibles are the only vessels ordinarily used. When the alkali metals are to be determined, boric acid is a useful substitute for borax and other tetraborates. Boric acid is a useful addition to sodium and potassium carbonate fusion mixtures. Such combined fluxes are effective for a variety of materials, including aluminous and siliceous minerals, blast furnace slag, zircon, and barium titanate (see R. J. Julietti and D. R. Williams, *Analyst*, 1981, Vol. 106, pp. 794–796).

Other workers have recommended a 1:2 barium carbonate:boric acid flux in a 10:1 flux:sample ratio, especially for the determination of certain alkali and alkaline earth elements (see D. E. Campbell and W. O. Passmore, *Analytica Chimica Acta*, 1975, Vol. 76, pp. 355–360). And a 1:1 mixture of lithium carbonate and boric acid in a 5:1 flux:sample ratio has been advocated for use in the determination of major elements in silicate minerals (see F. B. Barredo and L. P. Diez, *Talanta*, 1976, Vol. 23, pp. 859–861). Boric acid and boron trioxide, as well as the borates described below, may form smooth, glass-like melts under some circumstances.

In certain cases dissolution of the cooled melt is slow, even in dilute acid. Sometimes the crucible is placed in a small beaker of dilute acid on a heated magnetic stirrer and a Teflon TFE-coated bar magnet is placed on top of the salt disk to facilitate leaching. This class of fusions is also widely used to cast disks for X-ray fluorescence work since the cooled melts are so chemically and mechanically stable. Another desirable feature of boron fusions is that the boron can be chemically volatilized away from the aqueous solution—either by boiling with methanol (to evolve the methyl borate ester) or by $HClO_4$ or H_2SO_4 fuming of an HF solution (to evolve boron trifluoride).

Borax (Sodium Tetraborate)

This flux is a good solvent for a wide range of materials, although the melts tend to be viscous. It is nonoxidizing and is not considered either acidic or basic. By itself, $Na_2B_4O_7$ melts at 878°C. Platinum is the vessel material of choice (with a lid), although there is a measurable attack. Fusing samples high in copper, iron, bismuth, or antimony may result in the reduction of these elements and the formation of alloys with the platinum. Mercury and thallium will be completely lost as volatiles, while selenium and arsenic will be partially lost. Flux:sample ratios range from 1:1 to 10:1, and heating times range from a few minutes to 2 h. Borax is used to fuse hematite, magnetite, and other iron ores; zirconium ores and minerals, including zircon; slags, coke, and coke ash; mica, tourmaline, and alumina; and rare earth, titanium, niobium, and tantalum minerals. Samples high in titanium produce a particularly viscous melt. Certain materials like rutile (TiO_2), perovskite ($CaTiO_3$), corundum (Al_2O_3), and niobium and tantalum minerals may leave insolubles, which must be filtered, ignited, and fused again.

More popular than borax alone is its use in combination with sodium carbonate. These two flux materials are typically combined in ratios of 1:1 or 2:3 borax:sodium carbonate, although many other proportions have been recommended. These mixtures have been used for corundum (Al_2O_3), baddeleyite (ZrO_2), spinel ($MgAl_2O_4$), sillimanite (Al_2SiO_5), bauxite ($Al_2O_3 \cdot 2H_2O$), granite, chromite, $ZrSiO_4$, SnO_2, basic refractory materials, and silicate minerals. Borax:sodium carbonate:potassium carbonate combinations in a variety of ratios have been applied to iron and manganese ores; to aluminosilicates, chromite, zircon, and TiO_2; and to phosphate ores (with the addition of KNO_3). Rarely, borax is combined with the acid flux, potassium pyrosulfate. This combination has been applied to rutile (TiO_2), ilmenite ($FeO \cdot TiO_2$), and cryolite (Na_3AlF_6).

Lithium Tetraborate

This flux is frequently used for casting "borax glass" disks for X-ray fluorescence spectrometry because its cooled melts are less hygroscopic than those of borax. $Li_2B_4O_7$ melts at 915°C. With sample materials the melts are highly viscous and require special platinum/gold alloy crucibles that are not wetted by the molten flux. With the nonwetting crucibles, any of several commercial automated "fluxers" may be used. These are special mechanical devices incorporating Meker burners or an induction coil, which allow samples to be fused and cast into disks (or in some burner designs, dissolved in beakers of dilute acid) automatically. Ideally, automated or not, X-ray disks should be cast onto preheated casting disks made of the same platinum/gold alloy. Alternatively, porous, pyrolytic, or vitreous graphite crucibles may be used for the fusion if heating is conducted in a muffle furnace.

Lithium tetraborate is an "acidic" flux, which means it is most effective in fusing "basic" sample materials like limestone or dolomite. Silica is the classic "acidic" sample, while alumina is "amphoteric" but with a "basic" proclivity. Thus lithium tetraborate is a good flux for very high Al_2O_3 samples, but is less effective for very high SiO_2 samples. It is recommended for zirconia (ZrO_2), titania (TiO_2), magnesite ($MgCO_3$), limestone ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), fluorite (CaF_2), cryolite (Na_3AlF_6), apatite (and bone ash), and witherite ($BaCO_3$), among other materials.

Lithium Metaborate

$LiBO_2$ melts at 845°C, a temperature that can be attained easily with a Meker burner. The melt is thin enough to be swirled readily. In casting X-ray fluorescence disks, those produced with lithium metaborate resist cracking better than those from other fluxes, but it is impossible to cast a clear disk in the absence of a sample. Since this is a basic flux, it is more suitable for high-silica samples and less suitable for high-alumina samples. In fact, X-ray disks cast from high Al_2O_3 samples often lack a "glassy" appearance. This devitrification is caused by undissolved sample particles. Cooled lithium metaborate melts dissolve easily in dilute acids for ICP, flame AA, or wet chemical determinations. This flux is recommended for quartz, sand, silicate minerals, basalt, biotite, orthoclase, spinel, chromite, ilmenite, and slags. In general, lithium metaborate is useful for samples up to about 80% Al_2O_3 equivalent, but is ineffective for basic refractories like magnesite.

Lithium Tetraborate/Lithium Metaborate

As one might imagine, a combination of these two fluxes proves to be more widely applicable than either is alone. A ratio of 1:4 lithium tetraborate:lithium metaborate shows a melting point eutectic of 832°C (lower than the melting point of either flux alone). This mixture will dissolve aluminosilicate materials across the entire range from 100% Al_2O_3/0% SiO_2 to 0% Al_2O_3/100% SiO_2. It has also been used for zircon, silicon carbide, boron carbide, bone china, and asbestos cement (up to 60% CaO). But it fails with highly basic materials like calcite ($CaCO_3$) and magnesite ($MgCO_3$). Other ratios have been used as well—1:1 for chromium ore (up to 50% Cr) and for chromium refractories, for example.

Potassium Pyrosulfate

Pure $K_2S_2O_7$ melts at 414°C, but the commercial reagent is likely to be the 97% $K_2S_2O_7$/3% K_2SO_4 eutectic, which melts a little lower (411°C). Potassium pyrosulfate is prepared from potassium bisulfate by heating to remove a molecule of water. Further heating produces potassium sulfate by the loss of SO_3:

$$2KHSO_4 \xrightarrow{\Delta} K_2S_2O_7 + H_2O\uparrow \xrightarrow{\Delta} K_2SO_4 + SO_3\uparrow$$

The pyrosulfate is more useful than the bisulfate as a starting flux material since it spatters much less. If the pyrosulfate is unavailable, however, the anhydrous bisulfate can be heated in a crucible to form the pyrosulfate. The crucible is then cooled in a desiccator and the test portion weighed into it. A second heating is then conducted to fuse the sample material. Potassium pyrosulfate fusions may be performed in platinum, Vycor, fused silica, or even (rarely) porcelain crucibles. Sometimes the fusion is performed in a fused silica, Vycor, or borosilicate Erlenmeyer flask held in tongs over a Meker burner. Less SiO_2 is lost from a fused silica crucible than platinum is lost from a platinum crucible.

Another disadvantage of platinum is that it tends to promote the rapid evolution of SO_3 and thus the formation of the comparatively inert product K_2SO_4, as indicated by a dry melt. Despite this drawback, platinum vessels are still widely used and prove to be reasonably effective. These fusions are slightly oxidizing, iron (II) being elevated to iron (III), but reduced chromium and manganese being mostly unaffected. Mercury, arsenic, and selenium are volatilized, and, if the sample contains halogens, antimony, tin, and germanium (and possibly others) will be lost.

Potassium pyrosulfate is one of comparatively few fluxes that can be used to fuse metals directly. Steels, both low- and high-alloy, can be fused, as can ferrovanadium, ferrotungsten, ferroniobium, and ferrotantalum. Brass, bronze, monel alloys, and alloys of niobium and tantalum all will yield to this treatment. Similarly, lead alloys, lead/tin solders, copper/lead/tin/antimony-bearing metal, and related alloys will dissolve. Sometimes concentrated sulfuric acid is combined with potassium pyrosulfate (especially for metal alloy dissolution) to reduce spattering and to reduce the amount of salt flux required.

Even though good acid dissolution procedures exist for these metals, there are often sound reasons for fusing with potassium pyrosulfate instead. Sometimes the best acid treatment (like the HF used with HNO_3 for niobium and tantalum alloys) is an interferent in the analytical method. A good alternative is to fuse in pyrosulfate and leach the cooled melt in a complexing medium (like 4% ammonium oxalate, which will keep niobium and tantalum in solution). In other cases, acid insolubles would have to be filtered, ignited, fused, and recombined with the filtrate. A direct fusion will save all these steps.

Since potassium pyrosulfate is an acid flux, it does not attack most high-silica materials. A few other types of sample, like cassiterite (SnO_2) and zircon, are left relatively unscathed. But most metal oxide mineral forms will dissolve. Flux:sample ratios range from 5:1 to 20:1. Cooled melts are typically leached in dilute hydrochloric acid or dilute sulfuric acid. But if the sample contains hydrolyzable elements, other media like concentrated sulfuric acid, hydrogen peroxide, hydrofluoric acid, or solutions of organic complexing agents can be used.

Potassium pyrosulfate is widely used for fusing acid insoluble residues from steels, especially after volatilization of the silica with HF. A broad range of ore and mineral samples will yield to this flux as well. Iron ores, pyrites (FeS_2), chromite, ilmenite, the three TiO_2 ores: rutile, anatase, and brookite, sphalerite (ZnS), thorianite (ThO_2), baddeleyite (ZrO_2), columbite and tantalite, perovskite ($CaTiO_3$), pyrophanite ($MnTiO_3$), molybdenite (MoS_2), and monazite ($CePO_4$) all can be fused. Niobium and tantalum carbides can be readily fused if they are first ignited to oxides.

Sodium Bisulfate

The pure substance $NaHSO_4$ melts at 185°C and begins to lose water with a good deal of spattering. At 390.5°C a eutectic is attained that consists of 85% $Na_2S_2O_7$/15% Na_2SO_4. This is approximately what is sold under the name "sodium bisulfate, fused." It can also be prepared and used from the bisulfate as described under potassium pyrosulfate. Since even the fused version shows some greater tendency to spatter, the sodium compound is almost always used with an addition of H_2SO_4 (which may amount to a few drops in a crucible of 5 g of flux or to 20 mL in a flask of 15 g of flux).

There are several reasons why an analyst might choose to use sodium bisulfate rather than potassium pyrosulfate despite the fact that their dissolution effects are similar. If a subsequent step in the method involves the use of perchloric acid, the potassium salt of the pyrosulfate would precipitate, whereas the sodium salt of the bisulfate would not. This situation is frequently encountered when acid insoluble particles are discovered in diluted samples that had been fumed in perchloric acid. In this case the clear choice for fusing the filtered, ignited residue is sodium bisulfate. Another reason is that certain elements (aluminum, zirconium, the rare earths, and others) tend to form sparingly soluble double salts with potassium. A final, obvious, reason for choosing sodium bisulfate is the need to determine potassium in the sample or to avoid its spectroscopic line interference.

Sodium Peroxide

As with perchloric acid, this reagent has an onus of fear about it for those individuals who are not experienced in its use. And, like perchloric acid, it deserves respect, but not to a point that precludes its routine application. For, in fact, sodium peroxide fusions are one of the most useful dissolution procedures in the analyst's tool kit. It is difficult to find a highly resistant substance that cannot be brought into solution by this means. Na_2O_2 melts at 495°C and soon begins to evolve oxygen in massive quantities. The cherry-red molten salt is highly corrosive to most substances, so the choice of crucible materials is limited to those with a controlled attack rate. The best material is zirconium (although there are advocates of *pyrolytic* graphite), with nickel as a poor second choice and iron as an even poorer third choice (see Chapter Two).

The commercial reagent is a yellow granular powder that must be protected from the air by keeping its can lid tightly sealed when not in use. At one time −40 mesh powder was available, but now the analyst must settle for the −20 mesh, which is still commonly sold. Since Na_2O_2 reacts with moisture in the air, NaOH is always a contaminant ($Na_2O_2 + H_2O \rightarrow 2NaOH + \frac{1}{2}O_2$), but does no harm in metals work. Other impurities include Na_2CO_3, potassium, calcium, and iron.

The hazard with sodium peroxide fusions is related to its use with easily oxidized sample materials, such as organics of any kind, and certain inorganic substances. While sodium peroxide bombs are used to effect dissolution of organic materials, this subject will not be discussed here. The reader is referred to the excellent treatment in R. Bock, *A Handbook of Decomposition Methods in Analytical Chemistry*, John Wiley & Sons, New York, 1979, pp. 252–254. For the metals analyst, however, peroxide fusions and organics are a combination to be avoided by every means. If a sample is suspected to be contaminated with organic material, it should be weighed, ignited in platinum, then reweighed (to determine a loss on ignition); then a portion of the ignited residue should be weighed into a zirconium crucible for peroxide fusion (zirconium crucibles should not be ignited in muffle furnaces—see Chapter Two). If an inorganic sample is known to be highly reactive with sodium peroxide, the reaction rate can be effectively moderated by adding sodium carbonate to the starting mixture (or an entirely different dissolution scheme can be used).

Sodium peroxide fusions should be conducted on a tripod over a Meker burner behind a suitable safety shield in a hood. The crucible should not be picked up or swirled for the first 5 min after burner heat is first applied. A runaway reaction is likely to burn through the crucible and spatter sparks and molten material. In this event, shut off the gas supply and keep well clear until the reaction subsides. Such events are infrequent, but always a possibility when working with incompletely characterized sample materials.

As with all fusions, the sample and flux should be intimately mixed (a platinum wire is useful for this purpose). Sometimes an additional layer of flux is placed on top of the charge. Most analysts prefer to use a lid to contain spattered melt material. After the crucible has been heated on the tripod for 5 min, the lid can be cautiously removed and the contents gently swirled. Then the lid is returned and the heating is continued. Every 2 min the melt should be observed and swirled until undissolved sample particles are no longer evident. Remove the crucible from the heat at this point since unnecessary heating will seriously erode the crucible. The effect of crucible material on subsequent chemical manipulations may be significant.

Thus, while zirconium is a preferred material, its presence in the leached solution will cause losses of phosphorus and arsenic due to the precipitation of insoluble compounds. When these elements (or zirconium, itself) are analytes, the less resistant nickel or iron crucibles are called for. Volatiles loss includes mercury, nitrogen, and possibly arsenic (but arsenic will be retained if sodium carbonate is included in the flux). These fusions are leached first in neutral water. Sometimes the cooled melt is knocked loose with a gentle rap on a hard surface; then it is dropped into a beaker of water along with the crucible and lid. The reaction is quite brisk, generating a caustic solution that can be useful for immediate separations. Generally, a precipitate will form that contains all the iron, nickel, cobalt, titanium, niobium, and tantalum, among others. The soluble fraction will contain all the chromium, vanadium, molybdenum, tungsten, lead, arsenic, sulfur, beryllium, tin, germanium, aluminum, and zinc, among others.

A simple filtration with a hardened filter paper will expedite many determinations. There is, however, evidence that some soluble species, such as lead and aluminum, may be partially adsorbed on the surface of $Fe(OH)_3$. Alternatively, the leach solution can be cautiously acidified with HCl or H_2SO_4. This reaction is also vigorous and exothermic since the leach solution is strongly basic. All of the sample elements will be in their highest stable oxidation states after a sodium peroxide fusion. However, zirconium peroxide, which will be present if a zirconium crucible was used, may partially *reduce* chromium (presumably by the intermediate formation of an unstable perchromate). The acidified leach is also highly concentrated in sodium ion, which results in problems for certain subsequent manipulations. In particular, fuming in perchloric or sulfuric acids will be difficult, requiring 100 mL or more of acid. An ammonia separation after a sodium peroxide fusion produces a great deal of salts along with the usual precipitate.

Despite these problems, the sodium peroxide fusion is an invaluable technique. It finds use for "easy" materials like sphalerite (ZnS); galena (PbS); arsenic, bismuth, and manganese; and iron ores. But its primary utility is for the "difficult" sample: platiniferrous minerals, chromium ores, cassiterite (SnO_2), ilmenite ($FeO \cdot TiO_2$), and other titanium minerals; zircon ($ZrO_2 \cdot SiO_2$), monazite ($CePO_4$), wolframite ($(Fe,Mn)WO_4$), and other tungsten ores and minerals; beryl ($Be_3Al_2(SiO_3)_6$), tourmaline, niobium, and tantalum minerals; all types of slags; and metal carbides like Cr_3C_2 and WC. It is also useful for metal dissolution, making otherwise difficult dissolutions relatively simple.

The metal sample should be finely divided, and often it is wise to protect the bottom of the crucible with a layer of sodium carbonate. Chromium metal dissolves easily, as do most high-temperature iron-, nickel-, and cobalt-base alloys. Otherwise intractable metals like ruthenium, rhodium, iridium, osmium, and palladium will dissolve. And all ferroalloys will yield to this technique, as will many other steel-making furnace additions. Caution is advised, however, with ferrosilicon, and especially with silicomanganese, which react exothermically. In these cases, the addition of sodium carbonate to the flux mixture is absolutely necessary to control the reaction. Sodium hydroxide is sometimes added to lower the melting temperature and thus reduce the erosion of the crucible. This approach is used for tin and lead ores, as well as for other materials.

Sample to flux ratios show a great deal of variation, and the entire subject, as with all fusions, is full of lore. Generally though, 0.5-g test portions are used with 10 g of Na_2O_2. If Na_2CO_3 is used, the $Na_2O_2:Na_2CO_3$ ratio ranges between 20:1 and 1:10, with 3:1 being more typical. On rare occasions, the sodium from a peroxide fusion is a real problem, and in these cases there is an alternative. Potassium superoxide (KO_2) is available commercially, although it is expensive. A 3:1 flux:sample ratio, using a 1:3 mixture of KO_2:KOH as the fluxing agent, has been used in a zirconium crucible and yielded results similar to sodium peroxide. Excess potassium can be removed from the acidified leachate by adding perchloric acid to the cold solution and filtering off the potassium perchlorate.

Sodium Hydroxide, Potassium Hydroxide, and Lithium Hydroxide

These fusions are not extensively used except in mineral analysis laboratories. The melting points of all three compounds are around 300°C, but variable due to the pickup of atmospheric moisture by these very hygroscopic materials. The best crucible materials are nickel and zirconium, the former being more frequently used. Iron, silver, gold, and graphite crucibles have also been employed. Platinum, however, is eliminated as a candidate material since it dissolves to some degree. Graphite has been cited as a poor choice since trace elements are irreversibly adsorbed. Because the flux spatters due to its moisture content, the standard procedure is to weigh the flux into a nickel crucible, fuse it, cool it in a desiccator, then weigh the sample into the crucible and refuse the flux.

Typical flux:sample ratios are 10–20:1. These fluxes have been used for quartz, silicates, silicides, slags, sand, tungsten, and titanium ores and minerals, for fluorite (CaF_2) and cryolite (Na_3AlF_6), for corundum (Al_2O_3) and bauxite ($Al_2O_3 \cdot 2H_2O$), diaspore ($Al_2O_3 \cdot H_2O$), mica, montmorillonite, kaolin, serpentine, scheelite ($CaWO_4$), cement, glass, fire clay, slate, feldspar, talc, lithium ores, and monazite ($CePO_4$). Nitrides, such as BN, dissolve with the evolution of ammonia.

Other Fluxes

Many other flux materials have been used for the molten salt dissolution of industrial materials, but only a few bear mentioning here. Sometimes it is advantageous to add sodium or potassium nitrate to sodium carbonate or sodium hydroxide fluxes to create stronger oxidizing conditions. Such a strategy will ensure oxidation of all the iron that is present in the sample. Fluoride salts are sometimes used in mineralogical analysis, though they seem to find their widest application in combination with pyrosulfate or borate fluxes.

Finally, the Lawrence Smith technique (technically more of a sinter) is sometimes employed for the determination of alkali metals. In this technique, the sample is mixed with ammonium chloride and calcium carbonate and heated in a special finger-shaped crucible with a lid.

Table 7–1 lists some molten salt fusion schemes for a selection of commercial materials.

SINTERS

It is possible to convert sample materials into a water-soluble state by heating them in an intimate mixture with a (typically 4 to 20-fold excess of) salt below the melting point. This

TABLE 7-1—Suggested molten salt fusions—miscellaneous materials.[a]

Material	Dissolution Procedure
Aluminosilicates	4 g 3:1 Na_2CO_3:$Na_2B_4O_7$; Pt c&l
Barytes	10 g Na_2CO_3, sinter: 300°C, then fuse; Pt c&l
Bauxite	2 g Na_2CO_3; Pt c&l
Chromite	10 g Na_2O_2; Zr c&l
Chromium metal	10 g Na_2O_2 + 1 g Na_2CO_3; Zr c&l (line bottom with 2 g Na_2CO_3)
Corundum	3 g Na_2CO_3 + 1 g H_3BO_3; Pt c&l
Cryolite	12 g H_3BO_3 + 5 g Na_2CO_3; Pt c&l
Ferroboron	10 g Na_2O_2; Zr c&l
Ferrochromium (high c)	10 g Na_2O_2 + 1 g Na_2CO_3; Zr c&l (line bottom with 2 g Na_2CO_3)
Ferromanganese	10 g Na_2O_2 + 5 g Na_2CO_3; Zr c&l (*Use Extreme Caution!*)
Ferromolybdenum	10 g Na_2O_2; Zr c&l
Ferroniobium	10 g Na_2O_2 + 2 g Na_2CO_3; Zr c&l
Ferrosilicon	7 g Na_2O_2 + 7 g Na_2CO_3; Zr c&l (*Use Extreme Caution!*)
Ferrotantalum	10 g Na_2O_2 + 2 g Na_2CO_3; Zr c&l
Ferrovanadium	10 g Na_2O_2; Zr c&l
High-temperature alloys	10 g Na_2O_2 + 5 g Na_2CO_3; Zr c&l (line bottom with 2 g Na_2CO_3)
Iron ores	5 g Na_2O_2 + 5 g Na_2CO_3; Zr c&l
Mullite	2 g Na_2CO_2 Pt c&l
Niobium alloys	10 g $K_2S_2O_7$; fused silica crucible
Silicate minerals	10 g 1:1 Na_2CO_3: $Na_2B_4O_7$; Pt c&l
Tantalum alloys	10 g $K_2S_2O_7$; fused silica crucible
Tantalum ores	10 g $K_2S_2O_7$; fused silica crucible
Tin ores	10 g Na_2O_2 + 5 g NaOH; Zr c&l
Titanium ores	7 g NaOH + 3 g Na_2O_2; Zr c&l
Tungsten ores	8 g 1:1 Na_2CO_3:K_2CO_3; Pt c&l
Vanadium ores	10 g Na_2O_2 + 2 g Na_2CO_3; Zr c&l

[a] One gram test portion is implied, except as noted. In many cases alternate fusions are possible and sometimes necessary. (*Note*: c&l = crucible and lid.)

technique is used much more frequently abroad than in the United States, but it deserves wider recognition generally. While platinum crucibles would be destroyed by a sodium peroxide *fusion*, they can be used routinely with little harm in sodium peroxide *sinters*. The temperature must be kept near 450°C in a muffle furnace to allow this solid state reaction to proceed. The cooled "clinker" is then leached in water, as with a fusion. Sinters with sodium carbonate, potassium carbonate, and sodium hydroxide are possible as well. But it is primarily sodium peroxide sinters that suggest a practical alternative to fusions, with their attendant contamination with crucible material. Chromite, ilmenite, cassiterite, quartz, zircon, and niobium and tantalum ores can be dissolved, among other materials. See J. Dolezal, P. Povondra, and Z. Sulcek, *Decomposition Techniques in Inorganic Analysis* (American Elsevier Publishing Co., New York, 1966, pp. 158–84) for a very detailed treatment of this subject.

INCLUSION ISOLATION

While inclusion work is somewhat of a specialized field, it relates directly to the general topic of sample dissolution. Unlike all that has been discussed up to this point, in this unique area the analyst is *not* trying to effect a complete dissolution of the sample, but rather the dissolution of a select portion of the sample, namely the metallic matrix. Here one tries to dissolve away everything except the compounds or phases in an alloy that are of metallurgical interest. Depending on the alloy and its metallurgical history, such isolates can be simple or complex, few or many. Interestingly, some of the lowest priced metal commodities, like plain carbon and low-alloy steels, contain the most bewildering arrays of carbides, sulfides, oxides, and nitrides.

High-strength low-alloy steel may contain extremely refractory compounds like vanadium carbide or titanium carbonitride. Nickel-base superalloys may contain unusual metallic phases that are essential to their properties. None of these things would ordinarily concern the chemist (except as they present special problems for the total dissolution of the alloy). There are, however, times and places where he is asked to separate and analyze these species. The means to comply with these requests are both unique and technically engaging.

Acid Treatment

The most simplistic approach to this problem, often tried for oxides, is to dissolve the metal matrix in dilute acid. It usually gives misleading information because even resistant compounds like SiO_2 and Al_2O_3 will dissolve to some extent in the form of ultrafine particles dispersed in the alloy. Often it *will* provide an empirical value that may be useful, but it seldom reflects the true nature of the inclusion content. When a refractory oxide is purposely added to an alloy, as Al_2O_3 sometimes is, to improve abrasion-resistance in iron-nickel systems, or with some of the so-called dispersion-strengthened high-temperature alloys, an acid treatment may prove the best solution. A hand-filed monolithic solid test portion is always necessary.

Ionic Displacement

Sometimes a solid steel sample is exposed to a copper (II) or mercury (II) salt solution to form a galvanic cell with the iron matrix metal, dissolving it. This approach is somewhat gentler than treatment with acid, but besides the stable oxides only a few additional compounds are preserved.

Bromine/Methanol, Bromine/Methyl Acetate

This is an interesting way to dissolve metal but leave even some very reactive compounds untouched. Water must be carefully excluded since it would tend to form some HBr that would attack the fragile carbides, nitrides, and oxides that are the main object of this treatment. Typically, the sample is a hand-filed 1-g (or larger) solid that is weighed and placed in a tall-form, lipless beaker. About 5 to 15 mL of solvent (methanol or methyl acetate in a good, water-free grade) is added, followed by 3 to 5 mL of Br_2. A watchglass is placed on the beaker, and it is immersed in an icebath to help control the exothermic reaction that ensues. The use of methanol is called for with slower-reacting samples, while the more moderate reaction with methyl acetate is applied to the isolation of delicate particles, like iron and manganese oxides and very minute AlN particles from certain aluminum-killed steels, and also to samples that react too rapidly with methanol.

Sulfides are destroyed by these processes and cannot be isolated. Filtration generally requires no special equipment, except a water aspirator for vacuum. Of course, all operations must be conducted in an efficient hood. In addition to steels, other metals are sometimes treated by these techniques. Thus Al_2O_3 can be isolated from aluminum, Cr_2O_3 from chromium metal, and BeO from beryllium. Many other alloys and metals are also amenable, but the analyst is cautioned to check reaction rates before proceeding since some reactions are quite violent. An older, but still important variation on this general scheme involves the use of alcoholic iodine solutions to dissolve steel. Methanol/iodine dissolutions are carried out under an inert gas to eliminate air and atmospheric moisture. Isolates are similar to those found with bromine, but reaction rates are much slower.

Chlorination

This is a very specialized technique found in only a few laboratories. The filed steel solid is weighed into a porcelain boat, which is placed in a tube furnace of Vycor or fused silica. It is heated to 400°C as a stream of chlorine gas passes through the tube. Ferric chloride is generated and carried to a cool collection vessel, where it crystallizes, while the oxides are left behind. Even "delicate" oxides like FeO and MnO_2 are supposedly left untouched. Other nonmetallic species, including graphite, are destroyed by this process. For Al_2O_3 in aluminum and BeO in beryllium, hydrogen chloride gas at 300°C is substituted.

Electrolysis

This subject is too large and complicated and the technique is too little used to devote much space to it here. Carbides, sulfides, phosphides, oxides, and nitrides are isolated by this technique. Electrolysis cells are "home-made" designs, often patterned after that of W. Koch and H. Sunderman (*Archiv für das Eisenhüttenwesen*, 1957, Vol. 28, p. 557—reproduced in Bock, p. 278). Electrolyte continuously flows through the cell, carrying particles of inclusions to be trapped in a vial below the cell. A circular copper cathode surrounds a porous barrier material in cylindrical form. The filed and weighed solid sample forms the anode inside the porous cylinder. The cell is purged with nitrogen gas to protect isolates from air oxidation. Cell potentials and electrolysis times vary based on the nature of the alloy and the surface area exposed to the electrolyte.

After the requisite time, the current is shut off and the etched sample surface carefully cleaned manually and by ultrasonic agitation, and the released particles are combined with those collected during the electrolysis. The dried sample is reweighed to obtain a weight basis for quantitative analytical work. The combined inclusion solution is filtered, and analytical techniques are applied to the residue. It is interesting to note that such residues may be pyrophoric, especially if dried in a flowing inert gas stream; so caution is advised.

Among a host of electrolyte "recipes," many contain citrate, iodide, bromide, and other complexing anions; they are also often buffered to a specific pH. For nickel and cobalt alloys and for stainless steels, ethylene glycol/hydrochloric acid electrolytes are recommended. Methanol and HCl at low temperatures have been used for niobium and molybdenum alloys. Electrolysis techniques are also applicable to the isolation of intermetallic phases from steels, nickel and cobalt alloys, aluminum alloys, and other metals.

Table 7-2 summarizes the most commonly employed techniques for inclusion isolation from steels.

TABLE 7-2—Summary of inclusion techniques for steels.

Technique	Isolate
Chlorination	Oxides
Bromine/methyl acetate	Oxides and nitrides (and numerous compounds of low stability such as (Fe,Mn)O and AlN as fine particles)
Iodine/methanol	Similar to the above entry but slower reacting
Bromine/methanol	Oxides and some additional compounds (suitable for fully killed steels)
Electrolysis	Oxides, nitrides, carbides, sulfides, phosphides; second phases
Ionic displacement	Stable oxides (and other very stable compounds)
Acid treatment	Added refractory oxides

OTHER TECHNIQUES

The ubiquitous "other" in this instance includes an extensive miscellany that finds limited application in certain industries. The technique known as "pyrolysis" or "pyrohydrolysis" and perhaps most correctly as "hydropyrolysis" consists of passing superheated steam over the sample in a high-temperature tube furnace in order to extract analytes directly from the test portion. It is used for fluorine determination with the use of accelerators such as U_3O_8 and WO_3 added to the sample boat for high-fluoride materials. It has also been used for glass, clays, ceramics, slags, tungsten, and tantalum metal, and other materials.

A similar approach is used for chlorine in glass and in metallic titanium and for boron in glass and in borides (using very high temperatures and a variety of accelerators). Often a preheating furnace is employed to superheat the steam. The various hot extraction techniques employed for carbon, sulfur, oxygen, nitrogen, hydrogen, and other analytes are obviously related to this general lineage of techniques. Also related are special treatments to convert the platinum metals to a soluble residue by heating them with sodium chloride in a tube furnace purged with chlorine gas. Temperatures used are in the 600 to 700°C range.

Minerals like pyrochlore can be heated in chlorine to produce soluble forms, and a mixture of silicon metal, silicon carbide, and silica will leave only the silica unreacted in chlorine. Hydrogen chloride gas is used to convert scheelite ($CaWO_4$) at 650°C or barytes ($BaSO_4$) at 1000°C to a soluble form. Hydrogen at high temperature will reduce the tin in cassiterite (SnO_2) to metallic tin and the iron in iron ore to metallic iron, both of which can then be easily dissolved in acids.

Electrolysis is sometimes resorted to for very resistant materials. Thus, niobium, tantalum, titanium, tungsten, zirconium, and hafnium have been totally dissolved in an electrolyte of 5% (w/v) NH_4Cl in methanol. Rhenium alloys and ruthenium alloys have been dissolved using a caustic electrolyte. Other noble metals have also been dissolved electrolytically. Electrolytic dissolution has the added advantage that when current efficiency is near 100% the weight of metal dissolved can be determined from current flow by a simple application of Faraday's law. This approach is sometimes used for metal dissolution in automatic flow injection determinators.

Aqueous caustic solutions sometimes are used to dissolve samples. Aluminum and aluminum alloys dissolve exothermically with the evolution of hydrogen: $Al^\circ + NaOH + H_2O \rightarrow NaAlO_2 + \frac{3}{2}H_2$. Beryllium also dissolves, as do compounds such as WO_3, MoO_3, V_2O_5, GeO_2, and AlN (but not other nitrides). Mixtures of sodium hydroxide and hydrogen peroxide have been used for rhenium, uranium, and silicon/aluminum alloys. Ammonium hydroxide dissolves MoO_3 and with some difficulty WO_3. Potassium hydroxide in aqueous solution with sodium peroxide has been used to leach tungsten from low-grade tungsten ores. Hydrogen peroxide alone will dissolve molybdenum, tungsten, and rhenium metal. Methanol will dissolve magnesium metal. Phenol will dissolve aluminum, leaving Al_2O_3 inclusions behind. Selenium dioxide (whose vapors are very toxic) will dissolve many refractory oxides when heated with them at 400°C in a sealed glass ampoule.

Finally, there are some "tricks" that can be used to aid in dissolving difficult materials. Platinum group metals can be fused with powdered zinc in a fused quartz crucible at 800°C (10 parts zinc to 1 part sample). The melt is stirred occasionally with a carbon rod. After about an hour of heating, the melt is cooled to room temperature and then dissolved in HCl. The zinc dissolves, leaving the platinum metals as a fine powder that can be filtered, ignited, (cautiously, since they may be pyrophoric), then fused with sodium bisulfate (platinum and rhodium) or sodium peroxide (osmiridium). Oxidizable metals like tungsten and molybdenum can be converted to oxides by heating at moderate temperatures in air or oxygen and then cooled and dissolved in caustic or acids.

FINAL THOUGHTS

The reader who has persevered through this and the previous chapter will realize that sample dissolution is full of lore. It should be well evident by this point that the idea of the mythical universal solvent remains as elusive as the Philosopher's Stone. But there is much more to be considered than how to convert a solid material into an aqueous solution. The dissolution plan begins at the point when a suitably sized test portion of properly prepared sample is weighed to an appropriate tolerance and transferred to a suitable vessel. It usually ends when an aqueous solution has been prepared that contains all the analyte in dissolved form and that contains no substances that will interfere in an irremediable way with subsequent analytical steps. This means that the analyst must select carefully among approaches to a dissolution problem.

The sample particles must be fine enough to react with reasonable speed, but special needs for monolithic solids must also be recognized. In Chapter Five it was shown how the degree of heterogeneity in the test sample must set a lower limit on the weight of the test portion. But there are also other factors to be considered in deciding upon the exact test portion weight such as the sensitivity of the method and the relative abundance of interfering elements. Similarly, the dissolution route chosen must take into account the speed and completeness of the reactions, as well as the safety of the operation. And a careful survey of potential interferences, from candidate reagents as well as from the sample, must be made.

One route may place an objectionable species in solution, derived from the reagents used (or from their attack on the vessel). A different route may volatilize or precipitate the analyte element. On the other hand, a third route may evolve or precipitate interferent elements from the sample as it dissolves, effectively removing a potential problem. As with most analytical processes, Occam's Razor should be applied—the simplest route that does the job is always to be preferred. The fewer the number of manipulative steps involved, the fewer the opportunities for manipulative error. On occasion great patience is rewarded and it is best to wait out slow reactions (for example, HCl and H_2O_2 will dissolve many materials, but sometimes the time required is excessive and the spent H_2O_2 must be patiently replenished from time to time). However, modern laboratories are nearly always under time pressure of some kind, so many slow-reacting samples get flushed down a hood sink and the analyst begins again, sometimes trying a radically different approach.

No matter how many or how few options for the dissolution plan present themselves, the analyst must be cautious and discerning in his final decision. He or she must be aware that the way an alloy or an ore sample is dissolved may be ideal for some analytes and really terrible for others. To illustrate this point, let us consider some options for a multi-element ICP/OES solution analysis of a stainless steel modified with minor additions of niobium, tantalum, and titanium.

Today, most analysts are likely to think first of a microwave oven approach, perhaps with HCl, HNO_3, and some HF. It is true that the sample will dissolve in a reasonable amount of time, and when the vessel is opened a clear solution will likely present itself. But when the sample is properly diluted for the major components, it is possible that some precipitation will occur. If the HF level is high enough to prevent that occurrence, it is also likely to require a plastic volumetric flask and an HF-resistant nebulizer and ICP torch, both of which will deteriorate accuracy. In such an approach, silicon, chromium, and nickel will present the greatest errors, but other components are likely to show some effect. A rather far-fetched alternative would be to fuse the sample with sodium peroxide and sodium carbonate in a zirconium crucible. Certainly silicon should hold in solution so long as the leach solution is not too strongly acidified, but the niobium and tantalum and titanium are likely to require a strong complexing agent to keep them in solution. The total salt content is now astronomical—a potential problem for even the best-designed high-solids nebulizer.

The best approach to this problem may be three approaches. With techniques like ICP/OES and the use of an internal standard, it is possible to prepare synthetic standards in one (or more) solution medium, establish calibrations, and then analyze samples prepared in different solution media using those calibrations. The internal standard will compensate for varying solution viscosity (and the accompanying mass transfer effects).

In the three-tiered approach to our hypothetical problem, one set of replicate test portions is dissolved in 1:1 HCl:H_2O with gentle warming and dropwise H_2O_2 additions, then immediately diluted with water and promptly analyzed for silicon. This sample is suitable for silicon provided that the solution does not boil and that the total silicon content of the test portion is less than about 7 mg. The ICP/OES measurement should be made within 4 h of the time the sample is dissolved and diluted. The second replicate set is dissolved in 1:1 HCl:HNO_3 with vigorous heating. This solution is suitable for chromium (carbides have generally been destroyed unless carbon is high), nickel, molybdenum, manganese, copper, and a few other elements. Silicon in this sample is partially precipitated, and niobium, tantalum, and titanium are completely precipitated. The third set of replicates is first reacted with dilute HCl, HNO_3, H_3PO_4, and H_2SO_4 until dissolved, then it is heated to white fumes, cooled for a minute, and diluted with dilute sulfuric acid. This solution is suitable for the ICP/OES determination of niobium, tantalum, and titanium. Silicon is precipitated, but other sample components can be determined. The dilution levels, however, will be optimized for the niobium, tantalum, and titanium.

Clearly, the analyst must not approach a dissolution problem with the preconception that only one dissolution plan must suffice for a complete analysis. Thus Occam's admonition to keep it simple must be intelligently applied.

REFERENCES

Barredo, F. B. and Diez, L. P., *Talanta*, Vol. 23, 1976, pp. 859–861.

Beamish, F. E., *The Analytical Chemistry of the Noble Metals*, Pergamon Press, Oxford, 1966, pp. 5–26.

Bennett, H. and Oliver, G. J., *Analyst*, Vol. 101, 1976, pp. 803–807.

Bock, R., *A Handbook of Decomposition Methods in Analytical Chemistry*, John Wiley & Sons, New York, 1979.

Bozic J., Maskery, D., Maggs, S., Susil, H., and Smith, F. E., *Analyst*, Vol. 114, 1989, pp. 1401–1403.

Bushina, I. S. and Headridge, J. B., *Analyst*, Vol. 106, 1981, pp. 221–226.

Campbell, D. E. and Passmore, W. O., *Analytica Chimica Acta*, Vol. 76, 1975, pp. 355–360.

Dolezal, J., Povondra, P., and Sulcek, Z., *Decomposition Techniques in Inorganic Analysis*, American Elsevier Publishing Co., New York, 1966.

Elwell, W. T. and Wood, D. F., *Analysis of the New Metals, Titanium, Zirconium, Hafnium, Niobium, Tantalum, Tungsten, and their Alloys*, Pergamon Press, Oxford, 1966.

Flinchbaugh, D. A., *Analytical Chemistry*, Vol. 41, 1969, pp. 2107–2123.

Flinchbaugh, D. A., *Analytical Chemistry*, Vol. 43, 1971, pp. 178–182.

Hobart, E. W. and Kallmann, S., "Dissolution of Metals for Analysis," *Some Fundamentals of Analytical Chemistry, ASTM STP 564*, American Society for Testing and Materials, Philadelphia, 1974, pp. 68–72.

Julietti, R. J. and Williams, D. R., *Analyst*, Vol. 106, 1981, pp. 794–796.

Lange's Handbook of Chemistry, 11th ed., J. Dean, Ed., McGraw-Hill, New York, 1973.

Matsumoto, K., Koizumi, S., and Kiba, T., *Analytica Chimica Acta*, Vol. 115, 1980, pp. 149–154.

Mulder, B. J., *Analytica Chimica Acta*, Vol. 72, 1974, pp. 220–222.

Povondra, P. and Sulcek, Z., *Methods of Decomposition in Inorganic Analysis*, CRC Press, Boca Raton, FL, 1989.

Rice, T. D., *Analytica Chimica Acta*, Vol. 91, 1977, pp. 221–228.

Smerko, R. G. and Flinchbaugh, D. A., *Journal of Metals*, 1968, pp. 43–51.

Westland, A. D. and Kantipuly, C. J., *Analytica Chimica Acta*, Vol. 154, 1983, pp. 355–358.

Zehr, B. D. and Zehr, T. J., *Spectroscopy*, Vol. 6, No. 4, pp. 44–47.

Also, The catalogs and brochures of Fernand Claisse, Inc., Johnson Matthey Chemicals, and Parr Instrument Co.

Part III: Separations

"What does it matter by what road each man seeks the truth?"

—Symmachus (383 A.D.)

"He had been eight years upon a project for extracting sunbeams out of cucumbers, which were to be put in vials hermetically sealed, and let out to warm the air in raw inclement summers."

—Jonathan Swift
Gulliver's Travels (1726)

8

Separation by Precipitation

INTRODUCTION

We concluded the last section of this book with a reference to the familiar principle popularly known as Occam's Razor. What William of Occam (Ockham) actually said was: "Entities should not be multiplied unnecessarily" (*Quodlibeta Septem*, c. 1320). It is sound advice for both life and science and for analytical chemistry in particular, where the practicing chemist must assemble a course of action from a large array of possible manipulative procedures. In today's laboratories, once the test portion has been dissolved it is frequently possible to proceed directly to the analyte measurement. Modern instrumentation has made this course of action much more common than ever before, and future developments will further extend this trend.

One could postulate then that Separation Science, the process whereby the analyte is isolated chemically from its sample matrix, is on a decline. Some would even argue that the "chemistry" in analytical chemistry is being replaced by physical measurement.[1] Certainly today no one would agree with what G.E.F. Lundell said in 1929 in the preface to the first edition of *Applied Inorganic Analysis*: "After all is said and done a good analyst is primarily a chemist who can quantitatively manufacture pure chemicals." There is, after all, nothing to be gained and much to be lost by attempting to isolate the analyte when it can be accurately measured in situ. Each chemical reaction has an associated yield which is never 100%. Reagents and labware contribute contamination. And every manipulative step raises the potential for losses and error.

There is, however, an alternate view that supports the preservation and cultivation of the rich chemistry associated with inorganic separation science. Even the most enthusiastic advocates of modern physical methods admit that these techniques have shortcomings. Interelement corrections are not a complete answer to spectrometric interference. Matrix background effects can be compensated for, but not always with complete assurance. And while one may calibrate with pure solutions or fundamental parameters, it is still necessary to validate the results. And how were the validation standards certified? Clearly, we are still a long way from an era when we can wave a wand at a solid or a solution and read out a complete and accurate analysis. We may no longer often need to manufacture pure chemicals in the analytical laboratory, but we *do* need to intelligently sample the abundant legacy of the past to support and enrich what modern instrumentation can do for us.

One chemical separation step that precedes an instrumental measurement may eliminate an interference or lower a background sufficiently to dramatically improve analytical performance. With comparatively little extra time and effort, sometimes the impossible becomes possible. There is also the matter of reference materials. Never in history have analytical laboratories been more dependent upon certified reference standards than they are today. Most physical measurement systems need them for calibration, and all instruments require them to validate their results. And the number and variety of the standards that are necessary increases proportionately with the size and complexity of the workload and the sample mix. These reference materials, whether generated "in-house" or purchased, must be certified by chemical methods founded on classical chemical separations. Any other course will inevitably erode confidence in all the marvels that technology has given us.

The modern dilemma ironically stems from the great advances in physical measurement, which promised so much that industries justified the large cost of instrumentation in part by eliminating wet chemical capabilities, both physical facilities and human expertise. It is now sadly true that multimillion-dollar facilities operate at only part of their potential. It is a potential that could be realized only by the judicious application of the old technology. Our purpose here is to record the most useful of the older techniques and to illustrate their application in the modern world in the hope that wisdom will prevail. Already some laboratories have recognized that chemical separation techniques have a significant role to play. Some even have an on-going program for the generation of in-house reference materials. While it is difficult to be sanguine, there is hope.

Our first aim in this section must be to set a realistic course. Much of the information in the older texts is unlikely to find any application in a modern context, and these topics will not be discussed. Areas of interest not specifically covered may be found described in detail in the referenced texts. We will also attempt to keep Occam's principle before us, opting where possible for the clean and quick in favor over the slow and elegant. We will separate by the best and fastest techniques, and only as much as we need to and not one iota more. Alternatives to separations, such as masking and blanking, will be taken up when we treat measurement in Part IV.

Inorganic separations fall into several categories: precipitation, distillation, solvent extraction, ion exchange, mercury

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[1] See the Guest Editorial in *Analytica Chimica Acta*, Vol. 278, Nos. 1–2, 1993, by P, K. Dasgupta for some interesting reflections on this subject.

cathode electrolysis, and even the specialized ancient art of fire assay. Of these, the first is by far the most generally useful and is complex enough to require a chapter to itself. The remaining techniques will be treated in Chapter Nine, and Chapter Ten will list the elemental analytes and the best separations that apply to them. Appendix II summarizes the chemical behavior of analytes both in regard to separation and measurement. It is not possible here to provide step-by-step "cookbook" details for each analyte and matrix, but the references in Chapter Ten should provide much of the necessary guidance. The reader is also referred to two important texts which, while somewhat dated, nearly always provide valuable information: *Applied Inorganic Analysis*, 2nd ed., by W. F. Hillebrand, G. E. F. Lundell, J. I. Hoffman, and H. A. Bright (John Wiley & Sons, New York, 1953) and *Outlines of Methods of Chemical Analysis* by G. E. F. Lundell and J. I. Hoffman (John Wiley & Sons, New York, 1938).

PRECIPITATION

One of the principal means by which an analyte is isolated is by reaction to form a product that has limited solubility in the solvent employed. The product may be an inorganic compound, an organic compound, or the element itself. We say *limited* solubility because K_{sp} is never 1. However, to be analytically useful, this is not a serious shortcoming so long as analyte yields remain within the statistical requirements of the determination. At one time solubility criteria were stretched to their limits in the absence of alternatives. Sodium, for example, was weighed as the sulfate. Today we have alternate ways to treat such analytical problems, and precipitation reactions are reserved for the lowest solubility products. Reaction rate and physical phenomena also come into play.

A precipitation may require a carrier element (often of similar ionic radius and properties to the analyte), or a lengthy reaction time to reach completion, or warming or boiling to coagulate the product to a filterable size ("Ostwald ripening"). Once down, the product must be filtered (or centrifuged) and washed free of its solution matrix. The first step in this process always involves a complete transfer of the precipitate from the reaction vessel to the filter (or centrifuge tube), which is somewhat of an art.

Some precipitates transfer easily, while others cling tenaciously to vessel walls. A rubber policeman at the end of a glass or plastic rod is an essential appliance for scrubbing vessels, and a fine needle-spray wash bottle is a necessity. The need for care is evident, especially when the analyte is a major component or extreme accuracy is required. The filter medium must be matched to the character of the precipitate. Thus, gelatinous precipitates like $Fe(OH)_3$ require a fast paper (like Whatman No. 41), intermediate forms like silica require a medium paper (like Whatman No. 40), and fine precipitates like $BaSO_4$ require a double slow paper (like a double layer of Whatman No. 42). If the solution is strong acid or base, a hardened version of these papers will be required.

Filter pulp is often added to the filter paper or to the solution as an aid in preventing clogging and in preventing the

TABLE 8-1—Selected inorganic precipitants.

Reagent	Pre-Conditions	Completely Precipitate	Completely Coprecipitate	Partially Precipitate or Coprecipitate
NH_4OH	Dilute HCl	Al, Be, Cr (III), Fe (III), Ga, Hf, In, Nb, Rare Earths, Sn, Ta, Th, Ti, Tl (III), U, Zr	As (V), Ge, P (V), Sb (III), Se, Te, V (V)	Au, B, Bi, Hg, Pb, Pt group, Si
NaOH	Dilute acid	Ag, Cd, Co, Cr (III), Fe, Hf, Mg, Mn, Ni, Rare Earths, Th, Ti, Tl (III), U, Zr		Cu, In, Nb, Ta
H_2S	0.25–13 M HCl ("Strong Acid Group")	"Copper Group": Ag, Bi, Cd, Cu, Hg, Os, Pb, Pd, Rh, Ru; "Arsenic Group": As, Au, Ge, Ir, Mo, Pt, Sb, Se, Sn, Te	Ga, In, Tl, V, W	Co, Ni, Zn
H_2S	pH 2–3	After above separation: Zn		
H_2S	pH 5–6 (acetic acid/acetate)	After Strong Acid Group separation: Co, Ni		Fe
H_2S	pH > 7	After Strong Acid Group separation: Co, Fe, Mn, Ni, Zn		
$HClO_4$	Fuming temperature	Hydrous oxides: Nb, Sb, Sn, Ta, Ti, W		
$HClO_4$	Cold neutralized	Perchlorates: K, Rb, Cs		
$(NH_4)_2HPO_4$	Ammoniacal	Au, Ba, Be, Bi, Ca, In, Mg, Mn, Pb, Rare Earths, Sr, Th		Al, Cr, Fe, Hf, Hg, Nb, Pt, Rh, Sb, Ta, Ti, Tl, U, Zr
$(NH_4)_2HPO_4$	Dilute H_2SO_4 + H_2O_2 after mercury cathode	Hf, Zr		
H_2SO_4	Neutral; iron reduced	Ba, Pb, Sr		
HCl	Neutral; (protect AgCl from light)	Ag, Bi, Hg (I), Tl (I)		Pb
HF	Neutral; ammonium fluoride; after mercury cathode	Rare Earths, Th		Ca, Mg
$K_2Cr_2O_7$	Neutral, ammonium acetate	Ba, Tl (I)		Pb

TABLE 8–2—Selected organic precipitants.

Reagent	Pre-Conditions	Completely Precipitate	Completely Coprecipitate	Partially Precipitate or Coprecipitate
Cupferron	10% HCl or H_2SO_4; cold	Fe (III), Ga, Hf, Zr, Nb, Pd, Sn, Ta, Ti, U (IV), V (V)	Ag, Cr, Co, Hg, Mn, Ni	Cu, Fe (II), Mo, Sb (III), Th, Tl (III), W
8-Hydroxyquinoline	Dilute acetic acid/ ammonium acetate	Al, Bi, Cd, Cu, V (V), Zn		Ag, Co, Fe, Hf, Hg (II), Mn, Mo, Ni, Nb, Pb, Sb, Ta, Ti, U, V (IV), Zr
8-Hydroxyquinoline	Dilute ammonium hydroxide	Mg		Ba, Be, Ca, Co, Fe, Hf, Hg (II), Mn, Mo, Ni, Nb, Pb, Sb, Sn, Ta, Ti, U, V (IV), Zr
Alphabenzoinoxime	10% H_2SO_4; reduced with H_2SO_3; cold	Mo	W	Nb, Pd, Si, Ta
Dimethylglyoxime	Dilute ammonium hydroxide	Ni		Au, Co, Cu, Mn, Pd
Dimethylglyoxime	1% HCl	Pd		Au, Se
p-bromomandelic acid	50% HCl (after mercury cathode electrolysis)	Hf, Zr		
Ammonium oxalate	Dilute ammonium hydroxide (pH 8)	Au, Bi, Ca, Fe, In, Nb, Rare Earths, Sn, Sr, Ta		Ba, Be, Co, Hf, Hg, Mg, Mn, Ni, Pb, Th, Ti, Tl, Zr
Ammonium oxalate	Dilute acid (pH 3.5)	Au, Ca, Rare Earths, Sr, Th		Ag, Ba, Bi, Cd, Co, Cu, Mn, Ni, Pb, Sn, Ta, Zn

loss of fine particles. Washing the filter paper is also an art requiring patience. Each washing must drain completely before the next is applied, and the wash solution used must be carefully selected to remove matrix elements without dissolving the analyte compound. Centrifugates are washed as well by adding wash solutions, agitating, and recentrifuging. The separated residues may be redissolved in acid (either by passing acid through the filter or by destroying filter and residue by "wet ashing"). Alternatively, the filter and residue may be ignited in a muffle furnace, then fused in molten salt, and then leached in acid. Many precipitation reactions are suitable for gravimetry, and a few of these will be encountered again when that subject is discussed. But our purpose here is to concentrate on the separation of analytes and interferents as a prelude to any sort of measurement.

Tables 8–1 and 8–2 summarize some relevant facts about selected inorganic and organic precipitants. Table 8–3 shows the names, formulas, and typical reagent preparation schemes for some organic precipitants.

AMMONIUM HYDROXIDE PRECIPITATION

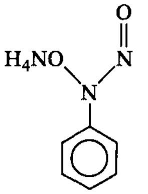
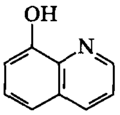
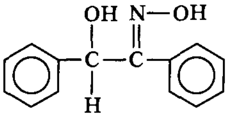
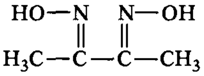
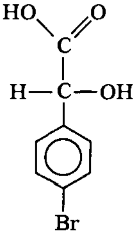
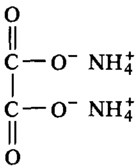
Precipitation with ammonium hydroxide is a relatively "painless" operation that can greatly benefit today's busy metals analysis laboratories. At one time this technique was popularly known as an "R_2O_3 separation," but that was an inaccurate name since a number of the elements that precipitate are not ignited into that oxide form (e.g., Ti : TiO_2; Nb : Nb_2O_5). Iron and aluminum, perhaps the two principal elements separated routinely by this approach, of course *do* ignite to Fe_2O_3 and Al_2O_3, as do a number of other group members. The other elements that precipitate are chromium (III), zirconium, hafnium, tin, indium, gallium, beryllium, thallium (III), thorium, scandium, yttrium, lanthanum and the lanthanides, tantalum, and uranium.

Certain other elements will be quantitatively carried down in massive iron or aluminum precipitates—notably phosphorus (V), arsenic (V), antimony (III), selenium, tellurium, germanium, and vanadium (V). Silicon will be carried down in large part, and the platinum metals and boron to some degree. This "carry-down" process is an adsorption phenomenon on the gel-like iron and aluminum hydroxide particles. With the exception of antimony (III) (which partially precipitates), none of the adsorbed elements precipitates alone with ammonium hydroxide. However, in addition to antimony (III), mercury, lead, bismuth, and gold *will* partially precipitate alone with the reagent, partitioning between the residue and the filtrate.

As with most basic medium precipitations, the adsorption effect can prove troublesome. Thus elements like cobalt, copper, and zinc are notoriously difficult to wash out of most ammonia precipitates, especially iron and aluminum precipitates. Reprecipitation helps to some degree and may lower the presence of these elements sufficiently to prevent their interference, but they themselves cannot be quantitatively recovered. High concentrations of the copper-ammonium soluble complex have been reported to dissolve the cellulose of filter paper, but this is unlikely to present a problem at ordinary analytical concentrations and contact times. Iron and aluminum can be separated from chromium only if the sample has been completely oxidized, such as by perchloric acid fuming. If perchloric acid is objectionable for subsequent analytical steps, an effective alternative is to oxidize the chromium in a sulfuric acid medium by adding ammonium persulfate and silver nitrate and boiling vigorously.

In contrast to chromium, which will only precipitate in reduced form, thallium will only precipitate in its oxidized (+III) form (i.e., Cr (VI) and Tl (I) do not precipitate). Nickel generally separates cleanly from the precipitate, but a sparingly soluble blue nickel precipitate of unknown composition forms when ammonium hydroxide is added to concentrated

TABLE 8-3—Organic precipitant names, formulas, and solution preparation.

Trivial Name	Common Name	Structural Formula	Suggested Solution Preparation
Cupferron	N-nitrosophenylhydroxylamine, ammonium salt		6% (w/v) aqueous solution; filter; keep cold and in the dark. Prepare fresh weekly.
Oxine	8-hydroxyquinoline (8-quinolinol)		5% (w/v) solution in 12% (v/v) acetic acid (prepare hot); store in the dark
alpha-benozinoxime (Cupron)	Benzoin monoxime		2% (w/v) solution in methanol
DMG	Dimethylglyoxime (2,3-Butanedione-dioxime)	 $H_3C-C(=N-OH)-C(=N-OH)-CH_3$	1% (w/v) solution in methanol
PBMA	para-bromomandelic acid		Add as solid crystals
. . .	Ammonium oxalate	 $(COO^-)_2 \cdot 2NH_4^+$	4% (w/v) solution (warm to dissolve)

nickel solutions that have been fumed with perchloric acid. If there is very much more nickel than iron, it is best to filter such solutions while still hot after boiling. The blue precipitate does not form in sulfuric acid solution and, therefore, may represent a rarely seen Ni (III) compound.

Manganese can be cleanly separated from the ammonium hydroxide precipitate if the solution is quickly filtered after boiling for only 1 or 2 min; otherwise, MnO_2 may begin to come down. Alternatively, small amounts of manganese can be purposely made to accompany the precipitate elements by treatment with bromine water prior to adding NH_4OH. The presence of fluoride ion generally prevents ammonium hydroxide precipitation, and it is best eliminated by fuming with a nonvolatile acid or by complexation with boric acid. Sometimes precipitates retain alkaline earth carbonates, which form from the pickup of CO_2 from the air by the alkaline solution. This is unlikely to be a serious problem unless solutions with a large excess of NH_4OH are allowed to stand for long periods of time.

The precipitates that form with ammonium hydroxide are mostly white or bluish-white. However, iron (III) and thallium (III) form brown or reddish-brown hydroxides; chromium (III) forms a pale green compound; erbium is pink; neodymium is blue; praeseodymium is green; and samarium is yellow. $Ce(OH)_3$ is white and $Ce(OH)_4$ is brown. The ammonium hydroxide group can be divided between those elements that require careful pH adjustment (often because the precipitate is soluble to some degree in excess reagent) and those that are tolerant of less exacting procedures. The latter subgroup includes iron (III), zirconium, hafnium, and titanium. The principal members of the former subgroup are aluminum, gallium, beryllium, and the rare earths.

Aluminum and gallium require a pH between 6.6 and 6.7; beryllium and the rare earths require the pH range of 8 to 9. Gallium, in particular, tends to form an adhesive precipitate that is difficult to scrub from vessel walls. Aluminum hydroxide cannot be completely dissolved by washing the filter paper with dilute acid. For these reasons the gallium and aluminum hydroxide filters are best returned to the original beakers and wet ashed. Chromium (III) hydroxide presents problems similar to aluminum, and, if it is present in the ammonia precipitate, the filter paper should likewise be wet ashed. Iron, on the other hand, can be readily dissolved off the filter paper and drained into the original beaker using alternate washings of 1:1 HCl:H_2O and hot water. An advantage here is that much of the silica that accompanies the iron precipitate will be left on the filter to be discarded.

Much has been made in some texts about the need for large amounts of ammonium chloride in the solution prior to the precipitation with ammonium hydroxide (5 g per 200 mL of solution is advocated). This common ion tends to reduce the adsorption effects previously mentioned. It should be noted, however, that beginning in dilute hydrochloric acid and adding ammonium hydroxide to the first appearance of a precipitate has already generated a significant amount of ammonium chloride for this purpose. The precipitation "endpoint" is often best determined by placing a strip of pH or litmus paper against the inside wall of the beaker so that half is above and half below the solution line. A pH meter may be used, but the electrodes must be carefully wiped with moist filter paper, which is then placed in the solution. The solution is then always briefly boiled to coagulate the precipitate. Such solutions are particularly prone to bumping and attendant sample loss, so they must be stirred as they are heated.

All operations, including the filtration, should be conducted in a hood. Filtration should be by gravity using a fast paper like Whatman No. 41 with filter pulp. The precipitate should be washed with dilute ammonia water or a solution of NH_4NO_3 or NH_4Cl. The latter is best avoided if the precipitate is to be ignited due to the volatility of $FeCl_3$. In any case, a final washing or two with plain water is appropriate.

Procedure

General Procedure

Weigh and dissolve a test portion that contains 50 to 500 mg of precipitable elements. The final sample should contain 25 mL of HCl and no HF. Dilute to 200 mL, add a strip of neutral litmus, and begin adding NH_4OH cautiously, with stirring, until the litmus just turns blue; then add 10 mL excess. Heat with stirring to boiling and boil for 1 min. Cool to room temperature and filter through a Whatman No. 41 (or equivalent) with filter pulp. Rinse the beaker with 2% (v/v) NH_4OH, but do not police it. Wash the precipitate eight times with 2% (v/v) NH_4OH and twice with water. Discard the filtrate. Place the original beaker under the funnel and wash the precipitate with 1:1 HCl:H_2O and hot water alternately until all traces of the precipitate dissolve and the addition of 1:1 HCl:H_2O produces no yellow iron color. Wash several additional times with hot water and discard the paper. Rinse the funnel into the beaker.

Special Procedure (for Al and Ga)

Weigh and dissolve (no HF) a test portion that contains 50 to 500 mg of precipitable elements. The final sample should contain 25 mL of HCl. Dilute to 150 mL, add five drops of methyl red solution (0.2% in ethanol), and heat to about 90°C. Add 1:1 NH_4OH:H_2O carefully in portions and then dropwise until the solution just turns yellow. Boil for 1 min. Filter immediately through Whatman No. 41 (or equivalent) with filter pulp. Rinse the beaker with hot 2% (w/v) NH_4NO_3 solution. Wash the filter eight times with hot 2% (w/v) NH_4NO_3, then twice with water. Place the paper in the original beaker, add 100 mL HNO_3, 30 mL 1:1 H_2SO_4, macerate the paper with a stirring rod, and immediately heat to boiling. Continue heating until the solution darkens; immediately and cautiously add HNO_3 dropwise while heating until the solution is clear and fumes of SO_3 are being evolved. Fume for 1 min more and cool to room temperature. [NOTE—To ensure that excess NH_4OH does not affect recovery, some books advocate taking the solution to a point just before precipitation with NH_4OH, then adding sodium thiosulfate:

$$2AlCl_3 + 3Na_2S_2O_3 + 3H_2O \rightarrow 2Al(OH)_3 + 6NaCl + 3S + 3SO_2$$

The SO_2 is removed by boiling, and the free sulfur acts as a filtration aid.]

Applications

The high concentration of ammonium ion in the filtrate limits its usefulness. In particular, it cannot be fumed in perchloric acid because an explosion is likely to result. Filtrates that already contain perchlorate salts should not be greatly reduced by boiling. It is also inconvenient to fume the filtrate in sulfuric acid since a great deal of acid is required to keep ammonium sulfate from salting out. It *is* possible to use the filtrate for ICP/OES measurements, but the total solids content is excessive and explosive perchlorate salts may accumulate if the sample had been fumed in $HClO_4$ prior to the ammonia separation. As a result, nearly all applications only make use of the precipitate (one exception is a procedure for lime and limestone, which retains the filtrate for the determination of calcium and magnesium).

The following are some typical examples of applications for this separation:

1. *Volumetric Iron Determination*. There is probably no better way to prepare most steels, stainless steels, and iron-, nickel-, and cobalt-base alloys for volumetric iron determination than by performing one or more ammonium hydroxide separations. Strongly colored ions like chromium, manganese, nickel, cobalt, and copper are removed completely or reduced significantly. These would otherwise obscure the redox visual endpoint (usually the titrant is $K_2Cr_2O_7$ and the indicator is sodium diphenylamine sulfonate). The only problem element is usually vanadium, which, as the metavanadate ion (VO_3^+) accompanies iron and, despite published reports to the contrary, definitely interferes with the titration. If not removed by other means (such as by a sodium hydroxide/sodium peroxide separation), vanadium produces a positive error, being titrated as iron.
2. *Molybdenum Interference on Al3961Å*. In ICP/OES work, the most popular aluminum line at 3961 Å has a direct line

overlap with molybdenum. One approach to this problem is to remove the interferent with an ammonium hydroxide separation. Great care must be exercised, as described above, to prevent an excess of reagent that may otherwise redissolve some of the $Al(OH)_3$. If aluminum is low (<50 mg), it is necessary to add iron as a coprecipitant. A less intense effect from calcium on the 3961 Å aluminum line is also removed by this treatment. For molybdenum interference, an ether extraction from hydrochloric acid solution is an alternative approach that is somewhat less technique-sensitive.

3. *Copper Interference on P2149 Å*. Both of the prominent phosphorus emission lines have serious interferences on them. Ammonium hydroxide separation can help to remove the effect of copper on the 2149 Å line by carrying down phosphorus in an iron precipitate. This approach will probably only moderate the influence of small to intermediate levels of copper. (It is no help with the 2536 Å line, where the inteferent is iron.)
4. *Spectrophotometric Methods for Phosphorus*. Major problems in the widely used and sensitive spectrophotometric methods for trace phosphorus involve the effects of chromium (III), silicon, and the solution turbidity due to the hydrolysis of elements like tungsten, niobium, tantalum, and titanium. Coprecipitation with iron and ammonium hydroxide plays a key role in solving both problems. Chromium, oxidized with silver-catalyzed persulfate, is washed out of the ammonia precipitate, as is most of the tungsten. The remaining hydrolyzable elements, if they remain a problem, can be held in solution by dissolving the precipitate in dilute HF (plastic labware is, of course, required). Silicon is likewise complexed. Excess fluoride is complexed by the addition of boric acid, and the phosphomolybdate complex is extracted away into an organic phase (see Zatka, V. J. and Zelding, N., *Analytical Chemistry*, Vol. 56, 1984, pp. 1734–1737).
5. *Gravimetric Molybdenum Determination*. When molybdenum is precipitated with alpha-benzoinoxime, filtered, ignited to the oxide, and weighed, it is always contaminated with sample matrix impurities such as iron and aluminum. After weighing, the crucible is treated with 10% (v/v) NH_4OH and warmed until the MoO_3 completely dissolves. The solution is then filtered, washed with 2% (v/v) NH_4OH, and the paper placed back in the original crucible. After ignition, the impurities are weighed and used to correct the original residue weight.
6. *Solvent Extraction-Atomic Absorption Method for Trace Lead, Bismuth, Tin, Silver, Thallium, and Antimony*. The trioctylphosphine oxide/iodide extraction of tramp elements into methylisobutyl ketone, which was developed by K. E. Burke (*Analyst*, Vol. 97, 1972, pp. 19–28; *Talanta*, Vol. 21, 1974, pp. 417–423; *Applied Spectroscopy*, Vol. 28, No. 3, 1974, pp. 234–237) was the first rapid, versatile, and reliable preconcentration technique for flame AA applicable to superalloys. Copper is a problem, however, since it is reduced by the ascorbic acid that is added to reduce iron. Copper (I) iodide then precipitates when KI is added, and the analyte recoveries deteriorate. An ammonium hydroxide separation to remove most of the copper while retaining the tramps in the iron precipitate restores the method to accuracy (see also Chapter Nine).

SODIUM HYDROXIDE PRECIPITATION

Unlike ammonium hydroxide separations, precipitation with strong base has not been regarded as a "user-friendly" lab operation. The precipitates are slimy and difficult to wash; the excess reagent attacks borosilicate glass and destroys unhardened filter paper; and solutions become loaded with alkali salts and can superheat and "bump" on the hotplate. And yet there are sound reasons for keeping this technique as an integral component of the metal analyst's repertoire. Sodium hydroxide precipitation is important not only for what precipitates but also for what dissolves, and both residue and filtrate are analytically important. An element is said to exhibit *amphoteric* behavior if its hydroxide precipitates with moderate hydroxyl ion concentration, then dissolves in the presence of strongly basic conditions. Since such a hydroxide compound can react with acid to form a cationic salt or with base to form an oxyanion salt, a better term for it is "amphiprotic." Classic examples of such behavior are illustrated by aluminum, beryllium, gallium, and zinc—all of which are found in the sodium hydroxide separation filtrate:

$$\begin{aligned}
Al(OH)_3 + NaOH &\rightarrow NaAlO_2 + 2H_2O \\
Be(OH)_2 + 2NaOH &\rightarrow Na_2Be(OH)_4 \\
Ga(OH)_3 + NaOH &\rightarrow NaGaO_2 + 2H_2O \\
Zn(OH)_2 + 2NaOH &\rightarrow Na_2ZnO_2 + 2H_2O
\end{aligned}$$

Other notable elements in the *filtrate* include tungsten and molybdenum (whose acid-insoluble oxides dissolve in strong base), vanadium, tin, lead, chromium (VI), rhenium, phosphorus, and arsenic. The *precipitate* will contain the iron, nickel, cobalt, chromium (III), titanium, magnesium, zirconium, hafnium, thorium, uranium, the rare earths, manganese, silver, cadmium, thallium (III), indium, niobium, tantalum, and copper. The precipitation, ordinarily carried out at about a 4% (w/v) excess of NaOH past the neutral point, is best limited to about 0.25% (w/v) excess for the last four named analytes.

A sodium hydroxide precipitation usually serves the interests of the analyst best when it is preceded by some preliminary separation—ion exchange, mercury cathode electrolysis, or even an ammonium hydroxide precipitation. Iron (III), which accompanies aluminum, beryllium, and gallium in an ammonium hydroxide precipitation, can be effectively separated from these three elements by a sodium hydroxide precipitation. Zirconium survives a mercury cathode separation along with aluminum and tungsten, but it alone of the three is precipitated by sodium hydroxide. Among other useful sodium hydroxide separations, vanadium, phosphorus, and molybdenum are passed into the filtrate, while iron or iron and titanium are held on the filter.

Manganese, nickel, and cobalt precipitate quantitatively and are readily separated from vanadium, tungsten, molybdenum, and other elements. Cobalt is best first oxidized with bromine since $Co(OH)_3$ can be filtered and washed more easily than $Co(OH)_2$. While the precipitation of chromium (III) is not quite complete, chromium can be effectively converted to a quantitative filtrate element by oxidizing it to chromium (VI) before precipitation. This may be accomplished with perchloric acid fuming or persulfate/silver treatment. Chromium, vanadium, and uranium separation can also be assured by adding sodium peroxide (and, in the case of uranium, sodium carbonate) to the caustic solution. This approach places these three elements in the filtrate quantitatively.

Dissolution of the test portion by means of a sodium peroxide fusion followed by filtration of the water leach is a closely related technique which results in a filtrate that contains all the chromium. If either Na_2O_2 or H_2O_2 are involved in a sodium hydroxide precipitation of titanium, it is important to boil the solution sufficiently long (10 min or more) to destroy the colored peroxytitanium complex, which will otherwise prevent the formation of titanium hydroxide. If sodium carbonate is added (as for uranium), the alkaline earth elements (except beryllium) will be precipitated.

Not all sodium hydroxide reactions result in clean separations, of course. Niobium, tantalum, copper, and indium are troublesome, partially redissolving if there is too great an excess of reagent. Silicon, gold, and the platinum group will partially coprecipitate, and bismuth and mercury will partially precipitate. The precipitation of titanium is not quite quantitative if iron is completely absent. In this case, an iron (III) spike as a carrier is called for. Zinc, which is normally expected in the filtrate, will be adsorbed on the surface of iron and especially chromium (III) precipitates. Aluminum will similarly be adsorbed on nickel or magnesium hydroxides. If there is at least a five-fold excess of iron (III) over nickel, however, the effect becomes negligible. Unlike ammonium hydroxide precipitations, the presence of fluoride ion has not been known to prevent the precipitation of most elements with sodium hydroxide. Specifically, iron, nickel, zirconium, cadmium, silver, and indium will precipitate from a fluoride medium. The two separation methods differ in another respect—with ammonium hydroxide, the boiling step is primarily to coagulate the precipitate into a more readily filterable form, but with sodium hydroxide the boiling step is essential to the actual precipitation of many elements. Also, with sodium hydroxide, acid redissolution of the residue on the filter paper is not an option; the filter paper and precipitate must either be wet ashed or ignited and fused.

The precipitates that sodium hydroxide produces are mostly white and resemble cake icing on the filter. Cobalt (II) first forms a blue species, then with excess NaOH the pink $Co(OH)_2$ forms. Oxidizing conditions prior to precipitation result in $Co(OH)_3$, which is black. $Ni(OH)_2$ is a creamy-green color, and $Cr(OH)_3$ is a bluish-green. Copper precipitates as $Cu(OH)_2$, which is greenish-blue but converts to black CuO upon boiling. Iron (III), thallium (III), and the other elements that also precipitate with ammonium hydroxide produce similar-colored precipitates with both reagents, although the sodium hydroxide products are slimy rather than gel-like.

Procedure

General Procedure

Prepare a solution that contains precipitable elements which in sum amount to 50 to 500 mg in acid solution. Dilute to 200 mL, add a strip of neutral litmus paper, and begin adding a solution of 25% (w/v) sodium hydroxide that has been prepared from carbonate-free ACS grade pellets. Stir vigorously as the reagent is added (you will note that amphoteric elements precipitate, then redissolve as the neutral point is approached). When the litmus just turns blue, add 15 mL excess reagent. If the analyte is niobium, tantalum, copper, or indium, add only 1 mL excess reagent. Place the beaker on a hotplate and heat gradually with stirring until boiling begins. Boil for 10 min and remove from the heat. When the solution has settled and cooled to near room temperature, filter through Whatman No. 541 (or equivalent) with filter pulp. Rinse the beaker with water but do not police it. Wash the residue with cold water ten times. Retain the filtrate for soluble elements. Place the filter and residue back into the original beaker and add 100 mL of HNO_3, 30 mL of 1:1 $H_2SO_4:H_2O$, and 10 mL of $HClO_4$. Macerate the paper with a stirring rod and immediately heat to boiling. Continue heating until $HClO_4$ fumes appear and the solution is clear. Fume for 1 min and cool to room temperature.

Special Procedure (for Placing Cr and V in the Filtrate Quantitatively)

Prepare a solution that contains 50 to 500 mg of precipitable elements in acid solution. Dilute to 200 mL, add a strip of neutral litmus, and begin adding 25% (w/v) carbonate-free sodium hydroxide with stirring until the litmus just turns blue. Add 2 g of sodium peroxide and stir. Then proceed as described in the general procedure above.

Applications

1. *Magnesium in Aluminum Alloys*. One of the simplest applications of a sodium hydroxide separation involves dissolving a test portion of aluminum alloy in dilute sodium hydroxide, then digesting the solution at low heat for 1 h. The solution is then filtered and the $Mg(OH)_2$ precipitate is washed with 1% (w/v) NaOH.
2. *Iron in High-Carbon Ferrochromium*. Place 1 g of Na_2CO_3 in a zirconium crucible, then add 5 g of Na_2O_2. Weigh a 0.5-g test portion of high-carbon ferrochromium into the crucible and place 5 g additional Na_2O_2 on top of it. Mix thoroughly with a platinum wire and fuse cautiously using a zirconium lid over a burner behind a suitable safety shield (see Chapter Seven). Cool to room temperature. Rap the crucible gently to release the salt cake and transfer to a 600-mL beaker containing 100 mL of water. Cover immediately and allow to react until complete. Remove the crucible and lid, policing and rinsing all surfaces. Dilute the solution to 200 mL and heat with stirring to boiling. Boil for 3 min, cool, and filter on Whatman No. 541 (or equivalent). Rinse the beaker and wash the residue with water. Place the filter paper in the original beaker and wet ash as described under the general procedure above. The fumed iron solution should then be precipitated with ammonium hydroxide, filtered, and dissolved off of the filter paper with 1:1 HCl and hot water prior to an iron titration.
3. *Titanium in Chloride/Fluoride Ion Exchange Eluent*. One of the most effective means of separating the major components of high-temperature alloys is the chloride/fluoride anion exchange scheme published by Machlin and Hague and elaborated by Kallmann and others (see Chapter Nine). The second eluent in this procedure yields titanium, zirconium, hafnium, tungsten, and vanadium. The first three elements will precipitate with sodium hydroxide, while the last two

will be placed in the filtrate. For most typically encountered alloys, the separation of titanium from tungsten is the most important aspect of this treatment. Iron must be added to insure complete recovery of the titanium.

4. *Aluminum after Mercury Cathode Electrolysis*. An important means of isolating aluminum is by mercury cathode electrolysis, which removes many major alloy components. Both gravimetric and volumetric methods usually begin with this approach as a first separation step. Elements that accompany aluminum after electrolysis include titanium, niobium, tantalum, zirconium, hafnium, and the rare earths. These can be precipitated with sodium hydroxide while aluminum is collected in the filtrate. For the determination of aluminum by the potassium fluoride/acid-base titration method, the sodium hydroxide sample solution is diluted to an exact volume, then "dry filtered" directly into a smaller volumetric flask that is overfilled, then taken to the mark by removing solution with a medicine dropper. The solution is then adjusted to a pH of 10.2, potassium fluoride is added to precipitate AlF_3, and the solution is titrated back to pH 10.2 with standard acid. The released hydroxyl ions titrated represent the aluminum content.
5. *Volumetric Iron Determination of Vanadium-Bearing Samples*. It is not widely known that vanadium is a serious positive interference in the redox titration of iron with potassium dichromate. It can be eliminated by means of a sodium hydroxide/sodium peroxide separation as described in the special procedure above. This must be followed by an ammonium hydroxide separation as well.

OTHER ALKALINE PRECIPITATIONS

There are numerous other precipitation schemes that depend on the presence of basic conditions. Many of these are too narrow in application to deserve any space here, but at least three are worthy of passing notice. Several elements will be quantitatively precipitated in the solution that results after the water leach of a sodium carbonate fusion, notably barium, beryllium, bismuth, calcium, iron, magnesium, silver, strontium, titanium, the rare earths, zinc, zirconium, and hafnium. And molybdenum will be left quantitatively in the filtrate.

After treatment of a sample solution with ammonium carbonate, uranium will be placed in the filtrate, while iron (III), chromium (III), and aluminum will end up in the residue. And zinc oxide has proved to be an effective way to separate small amounts of cobalt from iron. Here a slurry of the reagent is added to the sample solution until it looks like coffee with cream in it. The filtrate will contain the cobalt quantitatively. This approach finds use in the nitroso-R color method for cobalt.

CUPFERRON PRECIPITATION

Cupferron is one of those classical organic reagents that everyone wishes would go away, but it has proved too valuable in many applications to be ignored. Technically, it is the ammonium salt of N-nitrosophenylhydroxylamine—a pale yellow powder that must be protected from light and must be stabilized from air oxidation by storing it in the presence of ammonium carbonate. Its solutions are unstable but can be stored for a week under refrigeration. Worst of all, it is a known carcinogen and must be handled with protective equipment in an efficient fume hood. It is useful as both a precipitant and as a solvent extractant for many metals, although its use should be restricted to those applications where alternatives do not adequately serve. As a precipitant, cupferron will bring down niobium, tantalum, iron (III), vanadium (V), zirconium, hafnium, titanium, uranium (IV), gallium, tin, and palladium, all quantitatively. In addition, copper, iron (II), antimony (III), thallium (III), molybdenum, tungsten, and thorium will be partially precipitated. And chromium, nickel, cobalt, manganese, silver, and mercury will be coprecipitated in part.

At first sight, the nonspecific nature of this reagent and the health concern with its use would suggest its immediate replacement. But cupferron as a secondary precipitant, applied after at least one preliminary separation, remains valuable because it brings down the analyte rapidly and completely. Precipitation is conducted in reasonably strong acid solution (about 10% HCl or H_2SO_4) to limit the number of precipitated elements to those listed above. And precipitation is always performed with ice cold solutions. The solutions are then filtered with suction using pulp. The paper is washed with cold 5% HCl, then transferred to a large crucible or dish. A moistened filter paper is pressed on top, and the residue is dried for 2 h under an infrared lamp in a hood.

Afterwards, the residue is charred at the open door of a muffle furnace in a hood before it is ignited. These special heating precautions are required because the precipitate would otherwise liquefy and spatter, resulting in analyte loss. The filter paper and residue can also be wet ashed with 100 mL of HNO_3, 30 mL of 1:1 $H_2SO_4:H_2O$, and 10 mL of $HClO_4$, heating immediately to boiling, then reducing to a fuming clear solution.

Most cupferron precipitates are white or cream-colored, but iron (III) yields a brown precipitate, vanadium (V) a reddish-brown precipitate, copper (II) is gray, while titanium (IV) is yellow.

Procedure

General Procedure

(WARNING: Cupferron is a known carcinogen. Use protective equipment and work in an efficient hood.) Prepare a solution which contains 25 to 100 mg of precipitable elements in 10% (v/v) H_2SO_4 or 10% (v/v) HCl. If HF is present, add a hot 1:1 $HCl:H_2O$ solution of H_3BO_3 that is sufficiently concentrated to complex all free fluoride ion. Dilute the solution to 200 mL and chill it in an ice bath. Prepare the reagent by dissolving 30 g of cupferron in 400 mL of water with stirring. Dilute to 500 mL and filter through Whatman No. 4 filter paper (or equivalent). Store for no longer than one week in a refrigerator. Add 15 mL of this 6% (w/v) cupferron solution to the sample solution for each 5 mg of precipitable element expected to be present, with vigorous stirring. Filter with suction through Whatman No. 42 (or equivalent) with filter pulp. Rinse and police the beaker with cold 5% (v/v) HCl. Wash the residue five times with the same rinse solution. Transfer the paper and residue to the original beaker. Add 100 mL HNO_3, 30 mL 1:1 H_2SO_4:H_2O, and 10 mL $HClO_4$; macerate the paper with a stirring rod and immediately heat to boiling. Continue heating to $HClO_4$ fumes and a clear solution.

Special Procedure (for Ignition)

Proceed as described above until the residue has been washed. Transfer the paper and residue to a large platinum crucible. Press a moistened filter paper on top of the residue and heat under an infrared lamp in a hood for 2 h. Place the crucible at the open door of a muffle furnace set at 600°C in a hood until the paper is completely charred. Insert the crucible deep in the muffle, close the door, and ignite at 1000°C for 1 h.

Applications

1. *ICP/OES Determination of Nb and Ta in High-Temperature Alloys*. After chloride/fluoride anion exchange separation of the niobium and tantalum fractions, boric acid is added to the eluents to complex the excess fluoride and they are chilled in an ice bath. A cupferron separation is performed as described above under the special procedure. The ignited oxide is then fused with potassium pyrosulfate and leached in a 6% (w/v) solution of ammonium oxalate. The sample solutions are then suitable for ICP/OES measurement using a high-solids nebulizer and an internal standard.
2. *Hafnium Carrier for Minor Constituents*. Since hafnium is only rarely a component of commercial alloys, it can often be added to help carry down low-level analytes in a cupferron separation.
3. *Separation of Tin from Aluminum Alloys*. Since aluminum does not precipitate, cupferron appears to offer the best means of isolating low levels of tin from certain aluminum compositions.

It should also be noted here that the principal use of cupferron for many years has been as the final isolation step in classical gravimetry. Thus, many schemes yield pure cupferrates that can be ignited to stoichiometric oxides and weighed as such.

8-HYDROXYQUINOLINE PRECIPITATION

This reagent with a distinctive odor is also known as 8-quinolinol or as oxine. It can act as both a precipitant and an extractant (and, unlike cupferron, many of its metal ion solvent extracts have direct spectrophotometric applications). As a precipitant, the analytes it acts upon fall into two distinct categories—those that precipitate in acetic acid/acetate at around pH 4 to 6 and those that precipitate from ammoniacal solutions at pH 9 and higher. In the former category are copper, zinc, aluminum, bismuth, cadmium, and vanadium (V); in the latter category only magnesium is quantitative. Under both sets of conditions, a host of other elements will partially precipitate, and certain of them may be quantitative under selected conditions. Thus, for acetic acid/acetate, molybdenum, titanium, zirconium, hafnium, niobium, tantalum, manganese, cobalt, nickel, iron, antimony, lead, silver, uranium, vanadium (IV), and mercury (II) may be partially to completely separated.

In an ammoniacal medium, beryllium, calcium, strontium, barium, tin, and all the previously mentioned elements (except silver) may be partially to completely precipitated. Clearly then, this reagent must follow at least one preliminary separation. In practice the use of 8-hydroxyquinoline is usually restricted to the separation of a few elements, typically aluminum, zinc, and sometimes molybdenum from an acetic acid/acetate medium, and magnesium from an ammoniacal medium.

The most important applications of this reagent involve the separation of magnesium from the rest of the alkaline earth group and the separation of aluminum from beryllium. The separated analytes can be dried and weighed as quinolates or ignited to oxides and weighed as such. Or the metal quinolates can be dissolved in HCl; then the released quinolates are reacted with a measured excess of standard bromate/bromide. The solution is then titrated with standard sodium thiosulfate after the addition of potassium iodide. As a separation approach for alternate measurement techniques, the ignition to oxides can be followed by a molten salt fusion, or the quinolates can be wet ashed.

Procedure

General Procedure from Dilute Acid

Prepare a solution containing 50 to 100 mg of precipitable elements at pH 5. Prepare the reagent by dissolving 5 g of 8-hydroxyquinoline in 12 mL of glacial acetic acid and 75 mL of hot water. Filter if necessary; dilute to 100 mL and store in a dark glass bottle. Warm the sample solution to 60°C (thermometer) and add 10 mL of reagent for every 30 mg of precipitable elements plus a 50% excess. While stirring, add 2 *M* ammonium acetate until a permanent precipitate appears, then 25 mL excess. Stir well and let stand for 1 h. Filter through a medium porosity porous porcelain or glass frit crucible if the precipitate is to be weighed or through a Whatman No. 42 paper (or equivalent) with pulp and suction if it is to be ignited or wet ashed. Rinse and police the beaker and wash the precipitate four times with water. If the precipitate is to be weighed as such, dry it at 130°C for 1 h. If the precipitate is to be ignited, transfer it to a platinum crucible and ignite it at 1000°C for 1 h. If the precipitate is to be wet ashed, return the paper to the original beaker, add 100 mL HNO_3, 30 mL 1:1 H_2SO_4:H_2O, and 10 mL $HClO_4$, macerate the paper with a stirring rod and immediately heat to boiling. Continue heating until the solution is generating $HClO_4$ fumes and appears clear.

General Procedure from Ammoniacal Solution

Prepare a solution containing 50 to 75 mg magnesium containing sufficient NH_4^+ ion to prevent hydrolysis. Add ten drops of *o*-cresolphthalein (0.02% in ethanol) and then 6 *M* NH_4OH until a violet color develops, then 2 mL in excess. Heat to 70°C (thermometer), then add the 8-hydroxyquinoline solution (prepared as above) with stirring until the supernatant solution is deep yellow. Filter, wash, and proceed as described above.

Applications

1. *Separation of Aluminum from Beryllium.* Otherwise vexing, this separation out of acetic acid/acetate medium is clean and straightforward with 8-hydroxyquinoline. The filtrate can be reduced in volume and wet ashed for beryllium determination.
2. *Separation of Magnesium from Other Alkaline Earths.* Less important today with modern instrumental measurement, this technique still represents an interesting approach to a difficult chemical problem.

SULFIDE PRECIPITATION

Without exception, all the older texts characterize precipitation with hydrogen sulfide as the most useful separation technique for metals analysis. However, today it may be hard to find a laboratory that utilizes this approach routinely. The reason is that H_2S is a highly toxic, disagreeable reagent and that most schemes that employ it are lengthy and involved. While there are many routes around its use, there remains a place for this general approach in specialized niches.

Originally, the sulfide separation scheme was designed by early workers to progressively separate a wide array of elements. And even though there is little justification for pursuing the complete course in a modern laboratory, it will help to explain the chemistry if we step through this history one last time. The so-called "strong acid group" consists of those elements that are precipitated by hydrogen sulfide from 0.25 to 13 *M* HCl. These 20 or so elements, in turn, are divided into the "copper group," consisting of copper, silver, mercury, lead, bismuth, cadmium, ruthenium, rhodium, palladium, and osmium; and the "arsenic group," consisting of arsenic, gold, platinum, tin, antimony, iridium, germanium, selenium, tellurium, and molybdenum.

The copper group remains insoluble in basic sulfide solution, while the arsenic group dissolves. Thallium, indium, gallium, and (sometimes) zinc accompany the copper group, while vanadium, tungsten, and (sometimes) nickel and cobalt accompany the arsenic group. Mercury as Hg_2S is the only member of the copper group that survives boiling dilute nitric acid. Silver is then precipitated as AgCl, bismuth as BiOCl, and lead as $PbSO_4$. Then copper is electroplated as the metal.

The arsenic group is separated in part by distillation—germanium first by distillation with HCl and Cl_2, then arsenic at 112°C, antimony at 155°C, and tin with HCl/HBr at 140°C . Selenium and tellurium are reduced to the elemental form and filtered off. After the separation of the strong acid group, zinc, thallium, indium, and gallium can be precipitated with H_2S at pH 2 to 3, the cobalt and nickel at pH 5 to 6, and then manganese and iron at a pH above 7. In addition, some 20 elements were sometimes precipitated with H_2S in the presence of tartaric acid (Ag, As, Au, Bi, Cd, Cu, Ge, Hg, Ir, Mo, Os, Pb, Pd, Pt, Rh, Ru, Sb, Se, Te, Sn, Tl). If the acid group was first removed, ammonium sulfide and tartaric acid would precipitate only iron, cobalt, lead, and zinc.

Little of this has much relevance today. Which is not to say that a sulfide separation has no place in the modern laboratory. The use of thioacetamide to generate H_2S in situ has reduced much of the objection (although thioacetamide is a known carcinogen and must be handled appropriately). This "precipitation from homogeneous solution" minimizes coprecipitation effects and results in a precipitate that is readily filterable. There are, however, some claims that precipitation with thioacetamide is sometimes less complete than precipitation with H_2S gas.

The deleterious effect of iron on the electrogravimetric determination of copper can be eliminated by inserting a sulfide separation step wherein the copper is precipitated as the sulfide. Many methods for arsenic similarly benefit by first isolating the analyte with copper in the "strong acid group." Thioacetamide performs its function by hydrolyzing in dilute acidic or basic solution:

$$CH_3CSNH_2 + H_2O \rightarrow CH_3CONH_2 + H_2S$$

Samples are boiled in a hood to release the H_2S and complete the precipitation reaction. After cooling and settling, the solutions filter readily, but there is a marked tendency to "creep" (i.e., the residue particles climb the paper due to surface tension effects). The paper must, therefore, be washed cautiously to avoid particle loss, and the top edge of the funnel must be wiped with a piece of clean, moistened filter paper when the residue-containing paper is removed.

The sulfides are mostly black or brownish-black, but there are a few notable exceptions: CdS is yellowish-orange; As_2S_3 is yellow or red; SnS_2 is golden yellow; Sb_2S_3 is orange-red; ZnS is yellowish-white; MnS is green or pink while MnS_3 is black; VS is brown-black; V_2S_3 is green-black; and V_2S_5 is very dark green.

Procedure

General Procedure for the "Strong Acid Group" (H_2S Gas)

(WARNING: Conduct all operations in an efficient fume hood.) Prepare a solution that contains 50 to 500 mg of precipitable elements and that is 5% (v/v) HCl or H_2SO_4 (and free of HNO_3). Heat to boiling, remove from heat, and bubble a steady stream of H_2S gas through the solution as it cools. When it has reached room temperature, shut off the gas and let the solution stand in the hood overnight. Filter through Whatman No. 42 (or equivalent) with filter pulp. Rinse the beaker with 1% (v/v) HCl that has been saturated with H_2S and wash the paper five times with the same solution. Place the filter in the original beaker and add 100 mL HNO_3 and 30 mL 1:1 H_2SO_4:H_2O, macerate the paper with a stirring rod, and heat immediately to boiling. Continue heating until SO_3 fumes appear. If the solution turns black at this point, add HNO_3 cautiously dropwise while fuming until it is clear and fuming. Fume 1 min longer and then cool.

General Procedure for the "Strong Acid Group" (Thioacetamide)

(WARNING: Thioacetamide is a known carcinogen; use protective equipment and conduct all operations in an efficient fume hood.) Prepare a solution in a 500-mL Erlenmeyer flask that contains 50 to 200 mg of precipitable elements and that has been fumed in 10 mL of H_2SO_4 and cooled to room temperature. Rinse down the walls and add 125 mL of a 1.0F solution of thioacetamide (37.5 g of thioacetamide dissolved in 500 mL of water, filtered if necessary). Heat the flask in a boiling water bath (e.g., a 2-L beaker three fourths full of water with glass boiling beads to prevent bumping) for 45 min. Remove and allow to settle for 1 h. Filter on Whatman No. 42 (or equivalent) with filter pulp. Rinse the flask with 1% (v/v) HCl and wash the paper five times with the same solution. Place the paper in the original flask, add 100 mL HNO_3 and 30 mL 1 : 1 $H_2SO_4:H_2O$, macerate with a stirring rod, and heat immediately to boiling. Continue heating until SO_3 fumes appear. If the solution turns black at this point, add HNO_3 cautiously dropwise while fuming until it is clear and fuming. Fume 1 min longer, then cool.

Applications

1. *Copper by the Electrogravimetric Method.* The presence of iron interferes with the quantitative electrodeposition of copper. An ammonium hydroxide precipitate cannot be washed free of all copper and leaves objectionable ammonium ion in the filtrate. The best alternative is a double acid sulfide separation that places iron in the filtrate. The copper sulfide precipitate is then wet ashed and electrolyzed. In the case of high iron levels, it is necessary to precede the double sulfide separation with an ether extraction.
2. *Arsenic by an Arsine Generation/Spectrophotometric Procedure.* One common colorimetric procedure for trace arsenic is based on the evolution of AsH_3 and its collection in a pyridine solution of silver diethyldithiocarbamate, where it reacts to form a pink color due to the formation of colloidal silver. The color is measured spectrophotometrically at 550 nm. Iron is a major interferent that can be removed by acid sulfide separation. Arsenic-free copper is often added as a carrier for the arsenic if it is not a major component of the sample alloy.

ALPHA-BENZOINOXIME PRECIPITATION

Up to this point we have discussed group precipitants, but now we must briefly narrow our view to describe a few "specific" precipitants that have proven to be of lasting value. Alpha-benzoinoxime (also known as benzoin monoxime and as Cupron) under appropriate conditions is nearly a specific precipitant for molybdenum, which comes down as a white floc from acid solution. Tungsten will be carried down quantitatively in the presence of excess molybdenum but is only partially precipitated in the absence of molybdenum. Chromium and vanadium must be reduced with sulfurous acid to prevent their interference. After the initial addition of the reagent to the chilled sample solution, a small amount of bromine water is added to ensure that all the molybdenum is in the +VI oxidation state. This is followed by the addition of more alpha-benzoinoxime and 10 min or so of occasional stirring. Acicular crystals of excess reagent will precipitate in the vacuum-filtered filtrate. Besides tungsten, the molybdenum precipitate may be contaminated with silicon, niobium, tantalum, and palladium if they are present in the sample. The precipitate may be ignited (but at a temperature no higher than 525°C due to the volatility of MoO_3) or wet ashed. It is not stable enough to be dried and weighed, however. Alpha-benzoinoxime will also precipitate copper as a green floc from ammonium hydroxide/tartrate media.

Procedure

Weigh a sample containing 50 to 150 mg of molybdenum and transfer it to a 600-mL beaker. Dissolve it in appropriate acids and fume it in 15 mL of H_2SO_4. Cool, dilute to 150 mL, and boil the solution to dissolve the salts. Add 50 mL of H_2SO_3 and boil for 10 min. Adjust the volume to 250 mL and chill the solution in an ice bath. Prepare a 2% (w/v) solution of alpha-benzoinoxime by dissolving 20 g of the reagent in 1 L of methanol. Prepare a wash solution by adding 20 mL of 1 : 1 $H_2SO_4:H_2O$ and 10 mL of 2% (w/v) alpha-benzoinoxime solution to 470 mL of water; mix and chill in an ice bath. Add 5 mL of 2% (w/v) alpha-benzoinoxime solution to the sample solution for every 10 mg of molybdenum estimated to be present. Stir well; add 5 mL of saturated bromine water and stir for 1 min. Add 10 mL additional 2% (w/v) alpha-benzoinoxime solution and stir until all traces of the yellow bromine color are discharged. Let the solution stand for 10 min in an ice bath. Filter through Whatman No. 42 (or equivalent) with filter pulp and suction. Excess reagent will crystallize in the filtrate as the solution warms. This indicates that a sufficient excess was employed. Rinse and police the beaker with cold wash solution. Wash the paper five times with cold wash solution. Transfer the paper to a platinum crucible and place it in a closed muffle furnace set at 520°C. After the first hour with the door closed, begin opening the muffle door for a few seconds every 15 min to admit atmospheric oxygen as an aid to ignition. Ignition may require 4 h. Remove the crucible and cool in a desiccator.

Applications

1. *Gravimetric Determination of Molybdenum.* Either direct from acid dissolved samples or following ion exchange isolation, this is the classic gravimetric finish for molybdenum. The ignited oxide is always impure after the treatment described above. It is weighed, then dissolved in 10% ammonium hydroxide. The impurities are collected as the ammonia precipitate, ignited, and weighed as a correction as described under the applications for ammonium hydroxide precipitation.
2. *Tungsten Coprecipitation for Spectrophotometric Measurement.* Tungsten can be isolated by coprecipitation with added excess molybdenum using alpha-benzoinoxime. The approach finds use in the application of the hydroquinone spectrophotometric method for matrices that contain titanium and niobium. Using this separation, a scheme has been developed to determine tungsten, titanium, and niobium simultaneously using spectrophotometric measurements of the hydroquinone complexes.

DIMETHYLGLYOXIME PRECIPITATION

A structurally related compound to alpha-benzoinoxime is dimethylglyoxime (see Table 8–2). It is also a nearly ideal specific precipitant, in this case for nickel and palladium. Nickel yields a brilliant red precipitate from ammoniacal solution, while palladium produces a yellow precipitate from weak acid solution.

This is not to say that there are no problems with these two separations. In precipitating nickel from a faintly ammoniacal medium iron (II), cobalt (II) and copper will be caught in the precipitate; palladium will partially precipitate, and gold will be partially reduced to the metal. If present in great amounts, bismuth will form a yellow precipitate in strong ammonia solution. However, if iron and cobalt are oxidized to the +III state before precipitation (say with hydrogen peroxide or potassium ferricyanide), they become much less of a problem. And the addition of citrate or tartrate helps to keep them (as well as copper, aluminum, chromium, and bismuth) in the aqueous phase.

Precipitation from ammoniacal acetate solution also aids in freeing the nickel precipitate of cobalt, zinc, and manganese. Palladium and gold, if present in the sample, must be removed prior to the nickel precipitation. The same is true of the two principal concomitant elements in the precipitation of palladium from dilute HCl: gold and selenium. If these elements are not previously removed, they will be partially reduced to elemental form and accompany the palladium. Otherwise, dimethylglyoxime yields a clean separation of palladium from platinum, rhodium, iridium, and most other elements.

There are several ways to prepare dimethylglyoxime solutions even though the reagent is largely insoluble in water and hydrolyzes in acid. The most common preparation solvent is methanol or ethanol—generally a 1% (w/v) solution. A 1 to 3% (w/v) solution in 1 or 2% (w/v) caustic is also frequently employed. Least popular is a 1% (w/v) solution in 1:1 $NH_4OH:H_2O$ (or stronger), probably because this reagent solution will make it difficult to control the critical excess of NH_4OH required for nickel precipitation.

The alcoholic solutions of dimethylglyoxime exhibit a mild form of the same problem: alcohol must not constitute more than 50% of the total sample volume or nickel will not precipitate. The bulky nature of the nickel precipitate and the fact that it is often filtered into sintered glass crucibles usually limits the nickel which is reacted with the reagent to 20 to 80 mg. Thus, often very careful aliquotting is called for. Zinc, copper, cobalt, and manganese react with dimethylglyoxime to form stable, soluble compounds and in the process consume reagent that would otherwise be available for nickel precipitation. Thus, a measured excess is always required when these elements are present. And more time may be required for the competing reactions to reach equilibrium.

There are those who believe that nickel forms a more easily filtered precipitate if the dimethylglyoxime reagent is added to a hot, weakly acidic sample solution, followed by the addition of ammonium hydroxide to produce faintly ammoniacal conditions and bring down the nickel precipitate. The precipitate may be gravity filtered on paper or vacuum filtered onto sintered glass crucibles. In both cases, the residue is washed with plain cold water. The paper filters should be wet ashed, not ignited, since nickel dimethylglyoximate exhibits some volatility above 200°C. The sintered glass crucibles can be dried at 110°C and weighed since the residue is a stoichiometric compound (20.315% Ni). Palladium is precipitated from a 1% (v/v) HCl solution with the alcoholic reagent. The precipitate is washed with 1% (v/v) HCl and may be wet ashed or dried at 110°C and weighed as the dimethylglyoximate (31.612% Pd).

Procedure

General Procedure (Mn Co, Cu Each < 10% of the Ni Content)

Prepare a 200-mL solution that is either 10% (v/v) in $HClO_4$ or 10% (v/v) in H_2SO_4, which contains between 20 and 80 mg of nickel and is free of insoluble matter (silica may be volatilized with HF prior to fuming with either $HClO_4$ or H_2SO_4; other insolubles may be filtered off and discarded). Samples that contain more than 20% nickel should have been processed by a careful aliquot scheme from 1-g test portions. Add 10 mL of HCl and 20 mL of 20% (w/v) ammonium citrate solution. With a pH meter and dropwise additions of NH_4OH and HCl, adjust the pH to 6.3 ±0.1. Remove and rinse the electrodes. Add 10 mL of 1% (w/v) dimethylglyoxime in methanol, plus an additional 0.4 mL for each milligram of cobalt, copper, and manganese present. Add 1.0 mL of ammonium hydroxide by pipet and stir well.

Heat to about 60°C for 30 min. Remove from heat and let stand at room temperature overnight. Filter through Whatman No. 41 filter paper (or equivalent). Rinse the beaker and wash the precipitate five times with cold water. Transfer the paper to the original beaker. Use a moistened piece of filter paper to remove any precipitate clinging to the funnel and place it in the beaker. Add 100 mL of HNO_3 and 15 mL of $HClO_4$ (or 30 mL of 1:1 $H_2SO_4:H_2O$). Macerate the paper with a stirring rod and heat to boiling immediately. Evaporate to fumes of $HClO_4$ (or SO_3). If H_2SO_4 is used, it may be necessary to add additional HNO_3 dropwise as the solution turns dark; continue heating until the solution is clear and fuming. Fume for 1 min.

Special Procedure (Mn or Co >10% of the Ni Content)

Prepare a 100-mL solution that is otherwise the same as that described under the general procedure above. Add 100 mL of ammonium citrate buffer solution (500 g of citric acid monohydrate cautiously dissolved with stirring in 675 mL of NH_4OH; cool and dilute to 1 L) and 65 mL of NH_4OH. Then add 6 mL of freshly prepared 10% (w/v) potassium ferricyanide solution for every 100 mg of cobalt and manganese present, plus 10% excess. Stir well, and, using a pH meter and dropwise additions of acetic acid and ammonium hydroxide, adjust the pH to 8.0 ±0.2. Add 50 mL of ethanol and 100 mL of 3% (w/v) dimethylglyoxime solution in caustic (20 g KOH + 400 mL of water, add 30 g of dimethylglyoxime, stir to dissolve, and dilute to 1 L). Stir well and let stand at room temperature overnight. Filter and wet ash as described under the general procedure above.

Applications

Most applications of dimethylglyoxime precipitation are in the final separation stages of nickel and palladium determinations. These may be preceded by ion exchange or by group precipitations, especially if coprecipitating elements predominate. If nickel or palladium are to be determined gravimetrically as the dimethylglyoximate, at least two dimethylglyoxime precipitations are called for. The first is gravity filtered on paper and wet ashed, and the second is vacuum filtered into a tared, medium-porosity glass frit crucible. The crucibles can be cleaned by soaking in 1:1 $HNO_3:H_2O$ since the dimethylglyoximates dissolve in strong mineral acid. One dimethylglyoxime precipitation usually will suffice if the determination is to be finished by a titration or by ICP/OES measurement. Accuracy in the latter may be significantly improved over direct measurement of the unseparated solution since the effect of minor line interferences (e.g., Co on Ni2316 Å) will be greatly reduced or eliminated.

PARA-BROMOMANDELIC ACID PRECIPITATION

This reagent is not as widely known as those that have been discussed up to this point, but it fits our criteria of indispensability in the modern laboratory. At least *p*-bromomandelic acid is indispensable in those laboratories that determine zirconium and hafnium since it is a specific precipitant for those two elements. Actually, the *para*-bromo compound is merely the most effective member of a class of precipitants that includes mandelic acid and its derivatives.

Stoichiometric tetra-*p*-bromomandelates form with zirconium and hafnium as needle-like pale-straw-colored crystals. The reaction is conducted in fairly strong hydrochloric acid solution at boiling water temperatures. Even though most common elements do not interfere, the separation is best after some preliminary separation, such as electrolysis in a mercury cathode cell. Because of the strong acid conditions, the precipitate is filtered on fine-porosity, hardened filter paper. The residue may be wet ashed, ignited, or, if filtered on a resistant membrane filter, mounted for direct X-ray fluorescence analysis.

Procedure

Prepare a sample solution that contains 20 to 100 mg of zirconium, hafnium, or zirconium plus hafnium that has been fumed in 15 mL $HClO_4$, electrolyzed on a mercury cathode, filtered, and reduced to about 15 mL. Transfer the solution to a 250-mL Erlenmeyer flask and add 15 mL of HCl. Add 0.5 g of *p*-bromomandelic acid and place the flask in a 600-mL beaker one fourth full of water and containing glass boiling beads. Boil the water for 20 min. Cool and add 10 mL of water to the flask and let it stand overnight. Gravity filter on Whatman No. 542 (or equivalent) with filter pulp. Police and rinse the flask and wash the residue eight times with water. Transfer the paper to a platinum crucible and ignite at 1000°C for 1 h. Cool in a desiccator. Add 4 g of potassium pyrosulfate and fuse over a burner. Cool and leach in 10% (v/v) HCl.

Applications

Zirconium presents few spectrometric problems by ICP/OES when the 3391 Å line is employed, although hafnium at 2738 Å shows minor effects from iron, molybdenum, and tantalum. The hafnium problems from iron and molybdenum will be solved by the *p*-bromomandelic acid separation described above. If a potassium carbonate fusion replaces the potassium pyrosulfate fusion and is followed by a leach with KOH solution, most of the niobium and tantalum can be removed by filtration. The washed zirconium and hafnium residue can be reignited and fused with $K_2S_2O_7$ in the usual manner. *Para*-bromomandelic acid separation can also be used to isolate zirconium and hafnium for spectrophotometric procedures, such as those that employ chloranilic acid, pyrocatechol violet, xylenol orange, or other reagents. High concentrations can be conveniently weighed as the oxides.

OTHER PRECIPITATIONS

We have discussed nine useful precipitation techniques in some detail, but there are literally hundreds more that have been developed and used over the years. A fair percentage of these may find important uses in some of today's laboratories, and several should be in every metals analyst's bag of tricks. Now we will touch briefly upon some general approaches and some precipitants that undoubtedly remain important. But that is not meant to imply by any means that our list is exhaustive. The reader is referred to the excellent texts in the references for other important procedures.

Hydrolysis of Hydrous Oxides

This is the precipitation of metal oxide forms from solutions of strong acid. Hydrochloric, nitric, perchloric, sulfuric acid, or some combination of these act as the "precipitant." The "dehydration" of silica by fuming perchloric or sulfuric acid is an example of this class of reaction. Tungsten, titanium, niobium, tantalum, antimony, and tin are quantitatively precipitated as oxides when the solutions of these elements are digested with HNO_3, then fumed with $HClO_4$. The cooled solution is diluted and then the oxidized soluble elements like chromium are reduced with sulfurous acid; the excess SO_2 is expelled by boiling for about 5 min before the cooled solution is filtered. Since these precipitates are usually quite fine, a low-porosity paper and pulp as a filter aid are necessary. It is important to use only unetched beakers for these precipitations since otherwise the precipitate is impossible to police out completely.

Cinchonine

This reagent is best classed as a precipitation aid since its precise mode of action is not known. It acts to ensure the complete precipitation of tungsten in the hydrolysis procedure described above. After fuming with $HClO_4$, 10 mL of HCl is added to the cooled solution, which then is diluted to 200 mL with boiling water. This is followed immediately by 20 mL of a 12.5% (w/v) solution of cinchonine in 1:1 $HCl:H_2O$ and 1 g of cinchonine powder. The well-stirred solution is allowed to stand overnight, then filtered. Crystals of unreacted reagent will clog the filter unless the solution is first gently warmed.

Diammonium Phosphate

At one time this reagent provided the principal means for the gravimetric determination of magnesium after removal of most other elements by a series of separations. $(NH_4)_2HPO_4$ is added to an ammoniacal citrate or tartrate solution, and the precipitate is ignited at 1000°C to magnesium pyrophosphate ($Mg_2P_2O_7$; 21.842% Mg). Zirconium can be precipitated from 10% (v/v) H_2SO_4 and, if H_2O_2 is added, titanium will not precipitate. ZrP_2O_7 is 34.402% Zr. If this acid solution precipitation is applied after a mercury cathode separation, many of the other surviving elements such as aluminum, magnesium, vanadium, and tungsten are without any effect. Zinc and manganese can also be precipitated with this reagent.

Reduction to Elemental Forms

1. *Chemical Reduction*: A whole series of reducing agents have been applied to the precipitation of the elemental forms of analytes. Generally, the reducing reagent should be no stronger than what is required to do the job in order to prevent the precipitation of unwanted species. Thus, selenium requires only sulfurous acid or SO_2 gas or hydroxylamine hydrochloride to bring it down quantitatively. But tellurium with its higher reduction potential requires a mixture of sulfurous acid and hydrazine hydrochloride. The elemental forms of both these species can be collected on membrane filters for X-ray fluorescence analysis or they can be weighed or dissolved and measured by spectrophotometric, AA, or ICP/OES techniques.
2. *Applied Potential Reduction*: Electrogravimetric analysis can be an extremely accurate measurement technique, especially for copper, cobalt, lead (as PbO_2), and nickel. Today, only the first of these is much pursued and that only for high amounts that require the greatest accuracy. As a *separation* technique, electrolytic plating is best performed with the mercury cathode, a special approach that will be described in the next chapter.

Sulfates

Barium, strontium, and lead are precipitated as sulfates and can be ignited and weighed as such. The procedure is most often applied to barium determination. The solution must be very weakly acid (<1% HCl), and if iron is present it must be reduced with hydroxylamine hydrochloride. The best reagent is ammonium sulfate, although a small amount of sulfuric acid (no more than 5 mL for a 200-mL sample solution) is sometimes used. The stirred solution is digested at low heat for an hour to grow the $BaSO_4$ crystals to a more filterable size (Ostwald ripening), and then it is allowed to settle overnight. The very fine precipitate requires a *double* Whatman No. 42 filter (or equivalent) with filter pulp. The precipitation of lead and strontium are less ideal and generally require the addition of ethanol to lower the solubility of the precipitates. Barium and lead sulfates can be ignited at 1000°C and weighed. Strontium requires a lower temperature to prevent losses.

Chlorides

Silver, mercury (I), thallium, and bismuth (as BiOCl) are sometimes precipitated with HCl from dilute nitric acid solution. However, thallium is better separated as the iodide and the mercury (I) chloride is slightly soluble. Silver chloride must be protected from light to prevent photoreduction to silver metal. The bismuth oxychloride must be precipitated from a solution that has been neutralized with ammonium hydroxide.

Fluorides

Scandium, yttrium, lanthanum, and all the lanthanides, as well as thorium will be precipitated quantitatively using the following procedure. Weigh a sample that contains 20 to 150 mg of precipitable elements, dissolve it in suitable acids, and fume it in 15 mL of $HClO_4$. Cool, dilute to 150 mL, and electrolyze the solution on the mercury cathode for 4 h or until colorless. Filter on double Whatman No. 41 (or equivalent), collecting the filtrate in an 800-mL Teflon beaker. Reduce the filtrate and washings to about 25 mL and cool. Add 5 mL of HF and a small piece of litmus paper. *Very* cautiously, with stirring (using gloves and safety glasses), add NH_4OH dropwise until the litmus just turns blue. Beware of spattering! Then add 5 mL HCl, stir, and let the solution stand overnight. Add 100 mL of water and filter immediately on a resistant membrane filter (such as Duropore). The membrane is washed with 1% (w/v) NH_4F, then with water. It can then be air dried and mounted for X-ray fluorescence analysis. If the analytes are present in trace amounts, one of the precipitable elements can be added as a carrier at the outset of the determination. Calcium, or better, magnesium are also effective as carriers.

Oxalates

This separation falls into two distinct categories: a group of elements that precipitate around pH 8 and another that precipitates at pH 3.5. The former group includes iron, calcium, strontium, the rare earths, niobium, tantalum, gold, bismuth, indium, and tin. The latter consists of calcium, strontium, the rare earths, thallium, and gold. In practice oxalate is best used as a precipitant for calcium and (sometimes) the rare earths after mercury cathode electrolysis and other separations to remove interferences.

1-Nitroso-2-Naphthol

If cobalt has been isolated (by, say, ion exchange), this reagent will first oxidize then precipitate it from dilute hydrochloric acid solution as a brownish-red compound. The washed residue is ignited to Co_3O_4 and weighed. One gram of the reagent (a probable carcinogen!) is dissolved in 15 mL of glacial acetic acid for this purpose.

Tannin

Also known as tannic or gallotannic acid, this reagent is a precipitation aid. The precise mechanism of its effect remains unknown, but it acts in concert with other precipitants to ensure quantitative reactions. Little used today, it was formerly applied to the ammonium hydroxide precipitation of aluminum, to the cinchonine/hydrolysis precipitation of tungsten, to the separation of aluminum from beryllium, and to the separation of tantalum from niobium (see Hillebrand, W. F., Lundell, G. E. F., Hoffman, J. I., and Bright, H. A., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 126, 520, 552, and 603).

Chromates

Barium and thallium (I) can be precipitated as chromates. In this way barium can be separated from calcium and strontium in a neutralized solution with added ammonium acetate. Thallium (I) is precipitated from a slightly ammoniacal solution.

Molybdates

Phosphorus can be precipitated as ammonium phosphomolybdate. This was once an important reaction but is only occasionally employed today. The precipitate is usually dissolved in standard base and the excess titrated with standard acid. Another approach is to dissolve the precipitate in ammonium hydroxide and reprecipitate the phosphorus as magnesium ammonium phosphate using "magnesia mixture" (a solution of $MgCl_2$ and NH_4Cl containing excess NH_4OH). This compound can then be ignited to $Mg_2P_2O_7$ and weighed. Both lead and molybdenum can be weighed as $PbMoO_4$.

Perchlorates

Potassium, rubidium, and cesium can be precipitated as perchlorates. N-butanol is often added to the cold solution to lower the solubilities of the precipitates, which are dried at 110°C and weighed.

Nitron

This is a complex molecule that precipitates certain acids such as nitric and perchloric. An acetic acid solution of the reagent will precipitate rhenium (as a perrhenate complex) from dilute sulfuric acid solution. The precipitate can be dried at 110°C and weighed (33.040% Re).

8-Hydroxyquinaldine

This is the 2-methyl derivative of 8-hydroxyquinoline. It precipitates a more narrow array of elements from acetic acid/acetate solution. Notably, zinc precipitates but aluminum does not.

Sodium Tetraphenylborate

This reagent will precipitate potassium, rubidium, cesium, thallium (I), and silver from a sodium hydroxide solution containing formaldehyde (a carcinogen!). If only one of the precipitable species is present, it can be quantified by using a measured excess of standard reagent and back titrating with a quaternary amine to a Titan Yellow endpoint.

WHY BOTHER?

At some point the metals analyst must ask himself this question. Today's instrumentation allows the analyst to do a pretty good job without getting his hands wet. And even if he deems it necessary to put the sample into solution, there is admittedly a lot that can be done with blanking, masking, background, and interelement corrections. But can these clever tools solve every problem? And are the results always as good as they need to be? What has been described here and the techniques that follow in Chapter Nine represent more manipulative steps than many laboratory managers think they can justify. "This all sounds like a lot of work and we need the results yesterday. We have no choice but to use the most direct instrumental approach." There are two responses to this argument and neither is completely satisfying. The first is, yes, be as clever as you can be to do things fast and painlessly, but always weigh the quality of the work so that you really know what you have gained or lost by your economy. The second is also yes, but give a passing thought to the fact that standard calibration materials do not drop from heaven.

REFERENCES

Annual Book of ASTM Standards, Vols. 03.05 and 03.06, American Society for Testing and Materials, Philadelphia, 1992.

Black, J., Salesin, E. D., and Gordon, L. "Generation of Reagents in Homogenous Phase," *Standard Methods of Chemical Analysis*, Vol. 2, Part A, 6th ed., F. J. Welcher, Ed., D. Van Nostrand, Princeton, NJ, 1963, pp. 139–49.

Cheng, K. L., Ueno, K., and Imamura, T., *CRC Handbook of Organic Analytical Reagents*, CRC Press, Boca Raton, FL, 1982.

Cotton, F. A. and Wilkinson, G., *Advanced Inorganic Chemistry*, 3rd ed., Interscience Publishers, New York, 1972.

Erdey, L., *Gravimetric Analysis*, Part II, Pergamon Press, Oxford, 1965.

Gregory, E. and Stevenson, W. W., *Chemical Analysis of Metals and Alloys*, Blackie & Son, Ltd., London, 1942.

Handbook of Analytical Chemistry, L. Meites, E., McGraw-Hill, New York, 1963.

Heslop, R. B. and Robinson, P. L., *Inorganic Chemistry*, Elsevier, New York, 1960.

Hillebrand, W. F., Lundell, G.E.F., Hoffman, J. I., and Bright, H. A., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953.

Lange's Handbook of Chemistry, 11th ed., J. A. Dean, Ed., McGraw-Hill, New York, 1973.

Lundell, G.E.F. and Hoffman, J. I., *Outlines of Methods of Chemical Analysis*, John Wiley & Sons, New York, 1938.

Wagner, W., Hull, C. J., and Markle, G. E. *Advanced Analytical Chemistry*, Reinhold, New York, 1956.

Welcher, F. J., "Masking and Demasking," *Standard Methods of Chemical Analysis*, Vol. 2, Part A, 6th ed., F. J. Welcher, Ed., D. Van Nostrand, Princeton, NJ, 1963, pp. 150–65.

Welcher, F. J., "Precipitation by Change of Hydrogen Ion Concentration," *Standard Methods of Chemical Analysis*, Vol. 2, Part A, 6th ed., F. J. Welcher, Ed., D. Van Nostrand, Princeton, NJ, pp. 92–100.

Welcher, F. J., "Specific and Selective Precipitants," *Standard Methods of Chemical Analysis*, Vol. 2, Part A, 6th ed., F. J. Welcher, Ed., D. Van Nostrand, Princeton, NJ, 1963, pp. 101–38.

Van Nostrand's Scientific Encyclopedia, 4th ed., D. Van Nostrand, Princeton, NJ, 1968.

9

Separation by Miscellaneous Techniques

PRECIPITATION SCHEMES ASIDE, there remain several important categories of separation in inorganic analysis. In this chapter, we will discuss mercury cathode electrolysis, solvent extraction, ion exchange, and distillation/volatilization techniques, and at least touch upon fire assay. As in the previous chapter, for reasons of space and economy of effort on the part of both author and reader, the discussion will be confined to areas of the broadest utility in metals analysis. Since there is little that links this miscellany of isolation methodologies, perhaps it is best to just begin.

MERCURY CATHODE ELECTROLYSIS

The mercury cathode apparatus provides one of the most useful general approaches to group separation in inorganic analysis. As a concept, the technique is well over 100 years old, but the modern version of the instrument dates back to work at Battelle Memorial Institute (sponsored by Eberbach Corp.) published in 1951 (Center, E. J., Overbeck, R. C., and Chase, D. L., *Industrial and Engineering Chemistry, Analytical Edition*, Vol. 23, No. 8, 1951, pp. 1134–1138).

The basic principle is that of an electroplating cell using a 35 or 70-mL pool of mercury metal as the depositing electrode. Reduced metals form amalgams, which effectively permit 10 g or more of metallic elements to be removed from aqueous solution. In operation, a dilute sulfuric or perchloric acid solution of the sample is transferred to a 500-mL tall-form, lipless beaker with an integral stopcock and drain tube. The stopcock is located just above the mercury pool so that the aqueous solution can be drained out without disturbing the mercury.

Electrical connection to the mercury is achieved with a platinum wire fused into a borosilicate tube (this is either a blue uranium oxide or a yellow tungsten oxide graded seal to match the thermal expansion of the platinum to that of the glass). The tube is filled with mercury and connected to a d-c circuit at its other end. The anode is a flat spiral of platinum wire suspended parallel to and about 7 mm above the surface of the mercury. Its electrical connections are identical to those of the cathode. The anode and cathode assembly can be raised and lowered by means of an adjustable pedestal.

A large Alnico V "U"-shaped permanent magnet is located under the nonmagnetic stainless steel surface on which the beaker sits. The magnet is positioned so that one arm of the "U" is directly below the center of the beaker and the other arm is below the vertical wall of the beaker. When the electrolysis circuit is energized, the field of the magnet produces counter-rotating motion of the mercury and of the aqueous electrolyte solution. This expedites the removal of metals at the mercury/aqueous interface. In addition, the magnet attracts ferromagnetic amalgam to the bottom of the mercury pool, increasing the efficiency of removal for those metals. A glass cooling loop sits just above the anode for the circulation of cooling water to prevent boiling, which would disrupt the electrolysis. Current flow is generally set at 13 A—a setting that will remove 1 g of iron from a 5% (v/v) H_2SO_4 solution in about 1 h. Other metals may deposit at a much slower rate.

The full array of elements completely plated out by the mercury cathode includes the following: chromium, iron, cobalt, nickel, copper, zinc, gallium, germanium, rhodium, palladium, silver, cadmium, indium, tin, rhenium, iridium, platinum, gold, mercury, thallium, and bismuth. Elements effectively removed from solution, but not completely deposited in the mercury include: arsenic, selenium, tellurium, osmium, and lead. Elements that usually are incompletely removed from solution are manganese, molybdenum, ruthenium, and antimony. Note that the assembly of elements removed include nearly all those that form strongly colored species in aqueous solution. As a result, solutions on the mercury cathode frequently become water-clear, which can be a useful indication of the point when electrolysis is complete.

Little of use can be done with the mercury amalgam, but the electrolyzed supernatant solution contains many potential analytes, now free of major interferences. Among the elements thus freed of the "mercury cathode group" are the alkali and alkaline earth elements, scandium, yttrium, lanthanum, and the lanthanides, the actinides, titanium, zirconium, hafnium, vanadium, niobium, tantalum, tungsten, boron, and aluminum. And nearly all of these have been usefully separated and ultimately determined with the aid of mercury cathode electrolysis.

Problems with the technique often center around a small group of elements that can act as redox buffers. Titanium in amounts as low as 1% in the original test portion can form a deep blue color due to titanous ion (Ti^{3+}), which will interfere with the deposition of the more difficult members of the mercury cathode group, such as chromium, and may prevent all deposition of manganese and molybdenum. A few drops of 30% hydrogen peroxide to form the yellow peroxytitanium complex, added occasionally throughout the electrolysis, usually solves this problem. Similar problems related to large amounts of tungsten, vanadium, and molybdenum can sometimes be handled in the same way. Large amounts of manganese may coat the anode with MnO_2, or that compound may even precipitate in the electrolyte. A drop or two of sulfurous acid usually dissolves the precipitate.

Of the elements that are removed from solution quantitatively but not quantitatively deposited in the mercury, arsenic and osmium are at least partially volatilized (as is antimony), selenium and tellurium are reduced to elemental form as particles in the electrolyte, and lead may partially plate on the anode as an oxide. The amount of molybdenum and manganese removed is highly variable, ranging from nearly all to almost none. In particular, the mercury cathode is an unreliable means of removing the molybdenum interference on the 3961 Å aluminum line in ICP/OES work. Because chromium is removed slowly on the mercury cathode, particularly when it is in the +VI oxidation state, it is often prudent to remove the bulk of it by volatilization as chromyl chloride before electrolysis. The use of an ether extraction from hydrochloric acid solution (to remove molybdenum and most of the iron), digestion of the aqueous phase with HNO_3 and $HClO_4$, and the cautious addition of dropwise HCl to the fuming $HClO_4$ solution (to remove chromium) is a nearly ideal preliminary treatment for the mercury cathode when it is necessary to use the 3961 Å line for aluminum in high-molybdenum alloys.

It is possible to conduct mercury cathode electrolysis with sulfuric, perchloric, and phosphoric acids alone or in any ratio. However, volatile acids such as hydrochloric or nitric must be absent since they will form noxious gases and attack the mercury. In fact, the high hydrogen overvoltage of mercury (i.e., the difference between its observed potential for hydrogen evolution and the potential predicted by the reversible half-cell reaction) that accounts for the usefulness of the mercury cathode has been also used to good advantage in the commercial production of chlorine gas. Ammonium hydroxide solutions or high concentrations of ammonium salts at a pH of 2 or higher will form a gassy amalgam that is likely to short out the cell by touching the anode. Such solutions must be carefully acidified with sulfuric acid before proceeding with the electrolysis.

When the electrolysis has been deemed complete, the current is shut off and the electrodes are raised. The aqueous electrolyte is drained into a beaker (often the original beaker in which the test solution was prepared), and the electrodes and electrolysis cell are carefully rinsed with a fine spray of water. The collected solution is sometimes cloudy or may contain gray or black particulate matter. Some metallic mercury may also have escaped the cell and ended up in the sample beaker. Thus, it is always prudent to filter the solution before further treatment. A double Whatman No. 41 filter (or equivalent) without pulp is sufficient for this purpose. The residue should be washed about eight times with water. The mercury pool in the electrolysis cell may be used to collect and retain the amalgam from multiple samples (within practical limits).

The mercury should be kept covered with a layer of water at all times for safety in controlling mercury vapor and to prevent air oxidation of the mercury surface. The mercury will gradually thicken from the collection of reduced metals as amalgams until it will no longer rotate under the influence of the cell current and the magnet's field. In this state, it is likely to short the cell. Before this occurs, the mercury pool should be carefully poured (under a water layer) into a waste mercury vessel that is kept sealed and stored in a cool, well-ventilated area until it can be shipped to a refining company for redistillation. The electrolysis cell is scrubbed clean of any residues that have accumulated (HNO_3 will release any mercury mirrors that may have formed on the glass) and recharged with fresh mercury. For the shortest electrolysis times, for critical samples that require the most complete metal removal, and whenever there is concern about cross-contamination of sample solutions, the mercury pool should be changed with each sample.

Applications

The mercury cathode should be regarded as an important group separation tool in all modern metals analysis laboratories. With this device and a minimum of skill and effort, some very useful and otherwise difficult separations can be performed. In some spectrometric methods, it is used as a rough clean-up procedure to control the background from matrix components in preconcentration schemes for trace analytes. In many chemical and instrumental methods, it finds use as part of a larger separation scheme to isolate, or nearly isolate, just one element of interest. Trace mercury is nearly always present in the final solution (unless special pains are taken to eliminate it), but it rarely causes any problem.

Interference from Fe and Co on B at 2496 Å

The effect of iron and cobalt on the popular 2496 Å boron emission line is easily removed by mercury cathode electrolysis. The samples are dissolved in a perchloric acid/phosphoric acid mixture in boron-free or Vycor labware under reflux, then electrolyzed until clear. The electrolyte is then filtered into an 800-mL Teflon beaker and reduced to less than 25 mL on a sandbath. The cooled solution is spiked with an internal standard and diluted to volume. Pure boric acid standards prepared from acid blanks are used to calibrate the ICP/OES instrument.

The Effect of Certain Transition Metals on Other Lines

The following are some common problems with popular lines used in ICP/OES work, which can be corrected by the use of mercury cathode electrolysis: Fe on Hf2738, Mg2790, and Ta2400; Co on Ta2400; Cu on W2079; Cr on Ca3179, Mg2790, Hf2738, and W2079; Zn on W2079.

X-ray Fluorescence Analysis for Trace Levels of Rare Earths

The mercury cathode removal of matrix elements is essential to this determination, which was described under "Fluorides" in Chapter Eight.

Wet Chemical Methods for Aluminum

The volumetric potassium fluoride/acid-base titration method for major levels of aluminum was also described in Chapter Eight under applications for sodium hydroxide precipitations. The mercury cathode is the first separation step in that procedure, as it often is in gravimetric methods, such as those that employ 8-hydroxyquinoline or ammonium hydroxide as final precipitants. In spectrophotometric methods for trace aluminum, the mercury cathode almost always represents one of the preliminary separation steps, and often it is the first separation. Residual levels of iron and other interferents are then typically removed by solvent extraction (such as chloroform extraction of cupferrates).

Preconcentration Techniques for Flame Atomic Absorption

Flame AA is a versatile measurement approach with few interference problems, but by today's standards it is not particularly sensitive. In a heavy alloy matrix, quantitation limits for aluminum and titanium are typically no better than 0.005%. But if 1.5 or 2-g samples are cleaned up on the mercury cathode, filtered, and then fumed to near dryness, then digested with a small amount of HCl and a few drops of ultrapurity HNO_3, and finally diluted to the mark in 50-mL volumetric flasks, it becomes quite easy to see levels below 0.001%. This approach has some advantage over ICP/OES since it is free of the molybdenum interference that plagues the 3961 Å Al emission line.

Trace Methods for Zirconium, Hafnium, Vanadium, Tungsten, Niobium, Tantalum, Aluminum, Titanium, the Rare Earths, the Alkaline Earths, and the Alkali Metals

There is no better first approach than the mercury cathode to remove interferences, lower the background, and improve the sensitivity of most trace methods for these elements when they occur in transition metal alloys. This includes ICP/OES methods, spectrophotometric methods, and polarographic methods. Clearly it takes more time to clean up the matrix in this manner than simply diluting and measuring the sample by ICP/OES, but the improvement in performance is well worth the extra effort. With spectrophotometric and polarographic measurement, there is seldom any choice but to commit this time. In ICP/OES we can often make such a choice. And, too frequently, it is the wrong one.

SOLVENT EXTRACTION

When a solvated ion pair, a neutral organic complex, or a compound is agitated with two immiscible solvents, it distributes itself between them by some fixed ratio. If conditions are selected that favor a large value for this ratio (that is, conditions that favor the accumulation of the analyte species in one of the solvents), the process is called solvent extraction (or, sometimes, liquid-liquid extraction). In inorganic analysis, one of the solvents is always water. Nerst first mathematically defined this general process over 100 years ago (1891), but much of the molecular mechanics remains a mystery even today. Thus, no one can describe with certainty everything that is occurring at the molecular level when iron is extracted from hydrochloric acid solution into ethyl ether. As we have seen with previous subjects, here, as well, much of inorganic analysis is grounded in lore.

The most useful reference text in this area is *Solvent Extraction in Analytical Chemistry* by G. H. Morrison and H. Freiser (John Wiley & Sons, New York, 1957). Here we must limit our treatment of this broad field to those applications of the most current relevance for metals analysis. In this effort we are bound to overlook extraction processes routinely used in some specific industries, but, hopefully, enough examples will be included so that the reader can view trends and then search the literature for schemes that will solve a separation problem. The Morrison/Freiser text, which was used extensively as a reference in the preparation of this section, is an excellent place to begin such a search.

Solvent extraction separations, unlike precipitation separations, are very seldom troubled by concurrent phenomena, that is, while coprecipitation is common, coextraction is rare. In the ultimate case of precipitation from homogenous solution, the precipitation separation is unaffected by diffusion rates; however, solvent extraction is highly diffusion dependent. Agitation of two immiscible solvents in a separatory funnel produces a myriad of thin film interfaces toward which the analyte species must diffuse and then transfer across. Thus, the relative velocity of the two phases is all important, but excessive agitation that moves both phases in concert is without additional effect. In other words, very animated shaking of a separatory funnel is unlikely to increase the effectiveness of the separation, although contact time remains important.

In order for the analyte to transfer from the aqueous phase to the organic phase, it must be converted into an uncharged molecule or aggregate species. This process takes a number of different forms. The analyte element can react to form a compound (e.g., $GeCl_4$, which is extractable into CCl_4), but that is comparatively rare. It can react to form a neutral metal-organic complex. Or it can form an ion association complex that is effectively neutral. In addition, all coordinated water must be removed. Sometimes it is advantageous to add a large amount of a salt to the aqueous phase to decrease the solvating effect of the water molecules on the analyte (and to increase the activity of the analyte). The salt chosen must not be extractable and should have an ionic radius and charge that are both as large as is practical. For example, the addition of NH_4NO_3 to an HNO_3 solution of uranium facilitates that element's extraction into ethyl ether.

The formation of neutral complexes may involve many of the reagents familiar from precipitation reactions since these often form soluble extractable complexes under alternate conditions. The majority of these and other complex-forming agents are bidentate ligands exhibiting two coordinating groups. The formation of ion association complexes involves the displacement of coordinated water molecules by ions that have a greater affinity for the analyte. The aggregate, composed of clustered charged species, is, in sum, neutral and thus extractable. Often it is necessary to adjust the oxidation state of the analyte or of other sample components in solution in order to favor the extraction of the desired species and to diminish or eliminate the extraction of undesired elements.

Masking agents can be employed to eliminate the formation of undesired extractable species. For example, cyanide ion will prevent iron (III) from accompanying aluminum or cerium in an 8-hydroxyquinoline extraction into chloroform or cobalt from accompanying nickel in a dimethylgyloxime extraction into chloroform. Some masking agents, particularly chelating reagents like EDTA, will require longer extraction times in order to allow all reactions to reach equilibrium. When the extraction is deemed complete, undesirable components may have found their way into the organic phase despite these efforts. Sometimes washing the organic phase by extracting it with fresh aqueous solution is effective in eliminating them.

The formation of emulsions is another problem that often occurs in solvent extraction, usually when either the aqueous or the organic phase is relatively viscous. Longer, but less violent agitation, possibly with the aid of a mechanical shaker, will sometimes avoid this dilemma. But, if it occurs, there are several available options. Adding neutral salts to the aqueous phase is often effective, and adding an inert particulate solid that accumulates at the liquid interface sometimes works. Usually, the best choice is to apply the emulsion to phase-separating filter paper, which passes one phase and retains the other. However, this last approach is unsuitable for certain work, like trace silica determinations, since the paper will contaminate the analyte phase.

Once the analyte has been isolated in the organic phase to the analyst's satisfaction, it is often necessary to return it to an aqueous medium for further analytical processing. There are two basic approaches to this problem. If the solvent is relatively volatile (with a boiling point below 100°C), it can often be evaporated on a boiling water bath. A small amount of water must first be added to the organic phase to retain the analyte since it will likely be otherwise lost as a volatile compound. If the analyte is held in a coordination compound in the organic phase, some acid must be added as well to break the chelate complex as the solvent is removed. This operation is essentially hazardous since most light solvents are flammable. Often it is necessary also to destroy residual organic material by digestion and fuming with HNO_3 and H_2SO_4 and/or $HClO_4$. If the solvent is heavy (with a boiling point above 100°C), the best and safest course is to back-extract the analyte into an aqueous solution. Here, a fresh aqueous solution is added that contains components and conditions that favor the extraction of the analyte back into an aqueous medium.

In today's laboratory, the analyst must be provided with relevant safety information concerning the hazards associated with all chemicals used. Material Safety Data Sheets provide relevant information on the acute and chronic toxic hazards and fire and explosion hazards associated with reagents, including extractants and solvents. It is, of course, always prudent to select options that minimize risk. Within this framework and with the application of good and safe laboratory practices, solvent extraction provides an important analytical resource.

Ion Association Complex Extractions

By far the best-studied category under this heading are the *chloride complexes* of metal ions. Extraction with ethyl ether from dilute hydrochloric acid media is probably the oldest solvent extraction scheme that still finds practical use in metals analysis. First investigated by Rothe in 1892 for the extraction of iron (III) from 6 *M* HCl, this system is also suitable for the extraction of gold (III), gallium (III), molybdenum (IV), and thallium (III). Platinum (II) is best extracted from 3 *M* HCl in the presence of $SnCl_2$. And antimony (V) extracts best from 7.5 *M* HCl using isopropyl ether.

Some labs prohibit the use of ethers due to the fire hazard associated with their use, and so this valuable approach is closed to them. This is unfortunate because ether is one of the least toxic common solvents and can be handled safely with appropriate precautions. It should be purchased in small quantities and stored in approved solvent storage cabinets (see Chapters 3 and 18). "No Smoking" signs should be posted outside all entrances to rooms where it is used, and care must be taken to eliminate all flames and spark sources, including sparking motors and switches. The aqueous sample solution and the ether should be kept at ice bath temperatures before the extraction.

Other chloride extractions include: arsenic (III) from 11 *M* HCl into benzene (a carcinogen, now banned from many labs); germanium (IV) from 10.5 *M* HCl into carbon tetrachloride (also banned from many labs for the same reason); scandium (III) from 8 *M* HCl into tributyl phosphate; niobium (V) from 11 *M* HCl into diisopropyl ketone; and mercury (II) from 0.125 *M* HCl into ethyl acetate. *Fluoride* extractions require Teflon separatory funnels. Tin (IV) extracts from 4.6 *M* HF into ethyl ether; niobium (V) extracts from 9 *M* HF/6 *M* H_2SO_4 into methylisobutyl ketone (MIBK); and tantalum extracts from 10 *M* HF/6 *M* H_2SO_4/2.2 *M* NH_4F also into MIBK.

The best separations from nitrate medium are cerium (IV) and gold (III), both from 8 *M* HNO_3 into ethyl ether. *Bromide* systems have found little use except for the extraction of gold from iron by agitation of a 2.5 *M* HBr sample solution with either ethyl or isopropyl ether. None of the platinum group metals, except osmium, is extracted under these conditions. Indium (III) and thallium (III), however, *are* extracted. Also, gallium (III), antimony (V), and iron (III) will be extracted at 5 *M* HBr, and tin (II and IV) will be extracted at 4 *M* HBr.

Iodide systems, in contrast, are more widely employed, especially to isolate and concentrate tramp levels of tin, lead, antimony, mercury, cadmium, and thallium. Since hydroiodic acid decomposes to iodine quite readily, it is usually best to work from mixtures of potassium iodide and another mineral acid, such as H_2SO_4. Tin (II), mercury (II), cadmium (II), and indium (III) extract from 1.5 *M* KI/1.5 *M* H_2SO_4 into ethyl ether. Lead (II) extracts from an excess of KI in 5% (v/v) HCl into methylisopropyl ketone. Gold (III) and antimony (III) will extract from 6.9 *M* HI into ethyl ether, while both thallium (I) and thallium (III) extract from 0.5 *M* HI into the same solvent. Under these sets of conditions, many common matrix elements do not extract. Iron, however, must be reduced to the +II state to prevent its extraction.

The analytical legacy of early work in the nuclear energy field includes the development of *trioctylphosphine oxide (TOPO)*, a very stable white powder that forms ion association aggregates with a number of elements. Originally studied as a uranium (VI) extractant from nitrate solution, TOPO now finds many analytical uses. In the last chapter we briefly mentioned the important work by K. Burke (under the applications of ammonium hydroxide). Burke developed an extraction procedure that allows the MIBK extraction of trace levels of antimony, tin, lead, bismuth, silver, and thallium by combining the iodide and the TOPO ion association systems. Up to 3 g of sample can be employed with the use of sufficient ascorbic acid to maintain reducing conditions in the diluted solution. The MIBK extract may be directly aspirated into the flame of an atomic absorption spectrophotometer.

TOPO also provides an effective means of isolating zirconium and hafnium by extraction from 7 *M* HNO_3 into cyclohexane. This extraction is improved by the presence of sodium nitrite, but still requires about 15 min on a mechanical shaker. The organic layer is then washed for another 15 min with fresh 7 *M* HNO_3. It is possible to measure zirconium (in the absence of hafnium) by adding isopropanol, pyrocatechol violet, and pyridine and measuring the absorbance of the organic phase at 655 nm.

Species that TOPO will extract from 1 *M* HCl include chromium (VI), iron (III), molybdenum (VI), tin (IV), gold (I), uranium (VI), zirconium (IV), and hafnium (IV). At 7 *M* HCl, the list expands to include: antimony (III), gallium (III), vanadium (VI), and titanium (IV). A related compound, *tris-2-ethylhexylphosphine oxide (TEHPO)*, which is an oily liquid, associates with a much more limited array of ions. It has proved useful in the extraction of trace levels of tin (see applications).

Other ion association complex extractions include several familiar from widely used spectrophotometric procedures. The *thiocyanate complexes* with iron (III), molybdenum (V), and cobalt (II) are examples. Solvents employed include alcohols (amyl or butyl) and esters like butyl acetate, or butyl phosphate. Extraction imparts a degree of stability to the molybdenum complex, which otherwise must be measured spectrophotometrically under rigidly controlled conditions. The yellow *heteropolyacid complexes*, phosphomolybdic acid and the related compounds of arsenic, silicon, tungsten, and vanadium, can all be extracted into alcohols (1-butanol or isobutanol) and esters (butyl acetate). The complexes can be reduced to the blue form and then be back-extracted into an aqueous phase.

Tetraphenylarsonium chloride is a precipitating agent whose complexes with metal ions can sometimes be extracted as ion association complexes. Manganese and rhenium can be extracted in this way. And also elements that form thiocyanate complexes extract readily by ion association with this species. Several dye-type reagents, such as *rhodamine B*, form complexes that extract as ion associations. Methods for antimony and thallium are typical.

Applications/Procedures

More than most other separation procedures, solvent extraction schemes are often tailored for one specific determination. Very frequently a spectrophotometric procedure is involved, and often, as with thiocyanate and the heteropoly acids, the extracted complex is also the colored complex selected for measurement. It would be impossible to sample these here in a representative way. What follows are two examples of ion association extractions with broad utility and one that is more typically narrow.

Ether Extraction from 6 M *HCl (To Remove: Fe, Mo, Au, Ga, and Tl)*

[WARNING: Extreme flammability hazard; extinguish all flames, remove spark sources, and post room with appropriate warning signs.]

In a 250-mL beaker, prepare a solution containing between 200 and 300 mg of extractable elements (spike with an HCl solution of pure Fe (III), if necessary, to bring the total into this range) in 15 mL of 6 *M* HCl. Transfer the solution to a 500-mL separatory funnel with ice cold 6 *M* HCl that is saturated with ethyl ether (10 mL of ethyl ether shaken with 500 mL of 6 *M* HCl and chilled in an ice bath). Stopper the separatory funnel tightly and place it in an ice bath for several minutes. Remove, add 50 mL of ethyl ether, restopper, and return to the ice bath for at least 10 min.

Agitate the funnel for several seconds, vent the stopcock cautiously, then shake vigorously for 30 s and cautiously vent the stopcock. Set the funnel in a ringstand or separatory funnel rack, remove the stopper, and allow the layers to separate. Drain the (lower) aqueous layer into a 500-mL Erlenmeyer flask. Add 15 mL of chilled ether-saturated 6 *M* HCl to the funnel and repeat the extraction. Collect the aqueous layer in the same Erlenmeyer flask. Drain the ether layer into the original 250-mL beaker and cover with the watchglass. Evaporate the ether solution at a very low temperature on an electric hotplate or (better) a boiling water bath on an electric hotplate.

When the solution darkens, remove from the heat and cautiously add a few drops of HNO_3 (WARNING: spattering is likely). Return to the heat and then add additional dropwise HNO_3 until no further reaction occurs. Add 25 mL of water and 25 mL of HCl and boil down to 15 mL. Cool to room temperature, transfer to the same separatory funnel with chilled ether-saturated 6 *M* HCl. Chill the separatory funnel in an ice bath, add 50 mL of ethyl ether, then chill for 10 min more. Shake the funnel for several seconds, vent the stopcock cautiously, then shake vigorously for 30 s.

Vent the stopcock cautiously, remove the stopper, and allow the layers to separate. Drain the lower layer into the Erlenmeyer flask. Add 15 mL of chilled ether-saturated 6 *M* HCl and repeat the extraction. Collect the lower layer in the Erlenmeyer flask and discard the ether layer by flushing it down a sink with copious amounts of cold water or by an approved standard procedure. Heat the Erlenmeyer flask on an electric hotplate set at low heat to drive off residual ether, then gradually increase the heat until the solution is boiling quietly. Reduce the volume to less than 25 mL. Remove the flask from the heat, cool, add 25 mL of HNO_3 and 15 mL of $HClO_4$, and heat to strong fumes of $HClO_4$. If desired, the chromium may be distilled away by cautiously adding dropwise HCl to the fuming solution.

Note: If this treatment (including chromium distillation) is followed by a mercury cathode separation as previously described in this chapter, the resultant solution may be analyzed by ICP/OES for aluminum using the 3961 Å line with no fear of molybdenum interference.

TOPO-Iodide-MIBK Extraction (To Collect and Concentrate: Sb, Sn, Pb, Bi, Ag, and Tl)

Select and weigh a test portion that contains between 10 and 100 μg of total extractable elements, but no more than 3 g. Dissolve it in HCl with dropwise additions of HF. If HNO_3 is required to complete the dissolution (or to retain antimony), use it sparingly, and when the sample material has dissolved, reduce the solution to near dryness and add with caution to the hot solution dropwise portions of formic acid (HCOOH) until there is no further evidence of brown fume evolution. Reduce the solution to incipient dryness, add 15 mL of HCl and heat for several minutes, then cool to room temperature. Add 3 g of ascorbic acid for a 1-g sample, plus an additional 2 g of ascorbic acid for each additional g of the original sample. Transfer the solution to a 250-mL separatory funnel and add 15 mL of a freshly prepared reducing iodide solution (30 g of KI and 10 g of ascorbic acid dissolved in 60 mL of 1:5 HCl:H_2O, diluted with water to 100 mL). Adjust the volume in the separatory to approximately 50 mL with water. Add by pipet 10.0 mL of TOPO/MIBK solution (12.5 g of TOPO in 250 mL of MIBK) and extract for 1 min.

Note: If the extraction is conducted in a 100-mL volumetric flask instead of a separatory funnel, water can be added to bring the organic layer up into the neck of the flask where the aspirator capillary tube of a flame AA can be inserted. If copper is present above about 0.5% in the original sample, a preliminary ammonium hydroxide separation is necessary (see the applications of that technique in Chapter Eight).

Extraction and Spectrophotometric Measurement of Tin

[Reference: Ross, W. J. and White, J. C., *Analytical Chemistry*, Vol. 33, No. 3, 1961, pp. 424–427.]

Transfer to a separatory funnel a solution that is 1 *M* HCl/ 2.5 *M* H_2SO_4 and contains 10 to 100 μg of tin. Add by pipet 5.0 mL of a 0.01 *M* TEHPO/cyclohexane solution (dissolve 3.86 g of TEHPO in 100 mL of cyclohexane) and extract on a mechanical shaker for 10 min. Allow the layers to separate. Transfer a 1.0-mL aliquot of the organic phase to a 10-mL volumetric flask and add by pipet 2.0 mL of freshly prepared 0.05% (w/v) pyrocatechol violet solution in absolute ethanol. Mix, then add by pipet 1.0 mL of pyridine. Dilute to volume with absolute ethanol and mix. Place the volumetric flask in a warm water bath at 55 to 60°C for 20 min. Remove and allow to stand at room temperature for 10 min. Measure the absorbance versus absolute ethanol at 575 nm. In the same way, prepare and measure a reagent blank and calibration standards prepared from pure tin standard solution. Subtract the reagent blank reading from that of the test solution and convert the difference to tin concentration using a calibration curve.

Chelate Complex Extractions

Coordination compounds are metal compounds that do not obey simple valence rules; bonding in these molecules is termed "semi-covalent." Thus, hexammine cobalt (II) chloride, $(Co(NH_3)_6)Cl_2$, falls into this general class since the six ammonia groups each donate an electron pair to the central cobalt atom. In heteropoly acids, the central metal atom's place is taken by a complex ion. *Chelating agents* consist of molecules that each occupy two or more coordination positions on one metal atom. Two is, by far, the most common number of sites occupied by this class of compounds. Such chelating agents are termed "bidentate" ligands. (This becomes quite a mixed metaphor: *chelos* (Greek) means "claw," while *dentes* (Latin) means "teeth.") EDTA, however, occupies six sites and is termed "polydentate."

The result of a chelation reaction may be: (1) an anion, as when the bidentate ligand citrate reacts with iron (III) to form the negatively charged citrate complex; (2) a cation, as when *o*-phenanthroline reacts with iron (III); or (3) a neutral compound. Only the last of these is extractable as such. We have already encountered a number of chelating agents that form neutral compounds when we discussed precipitating agents in Chapter Eight. Many of these same reagents form solvent extractable complexes as well. Chelates that form anionic complexes can serve to mask undesired elements, however, preventing their extraction and increasing the selectivity of another chelating agent that forms a neutral complex with the analyte. Some charged chelate complexes *are* extractable, however, as ion association complexes (*o*-phenanthroline and bathophenanthroline complexes are examples).

While the practical analyst may feel that such details are extraneous to his task, it is important to know how these systems behave so that solvent extraction can become more of a selectable option rather than a method-specific recipe. The following are some typical neutral chelate formers that are useful in solvent extraction methods.

8-Hydroxyquinoline

We encountered this reagent in the last chapter as an important precipitant, where we described its bifurcated selectivity at two different pH ranges. This behavior continues when it is applied as an extractant. Thus, aluminum, bismuth, copper (II), iron (III), gallium, hafnium, indium, molybdenum (VI), thorium, thallium (III), tin (IV), titanium, tungsten (IV), vanadium (V), and zirconium can be extracted from acid solution. From basic solution it is possible to extract calcium, cerium (III), lanthanum, and the lanthanides, lead, magnesium, manganese (II), niobium, and uranium (VI). The preferred extractant is chloroform, although magnesium extracts best in a mixture of chloroform and 2-butoxyethanol (Butyl Cellosolve). The acid medium is typically dilute H_2SO_4, while the basic medium is typically NH_4OH.

Because so many elements form extractable complexes, 8-hydroxyquinoline extractions are applied after a series of preliminary separations and often in the presence of masking agents like cyanide. Practical methods commonly utilize the colored species that extract in a spectrophotometric finish. Examples are aluminum in steel (measured at 395 nm), magnesium in nickel (at 400 nm), and tin in cadmium metal (at 385 nm).

Cupferron

This reagent is also a familiar precipitant, but unlike the previous entry its solvent extracts have no spectrophotometric potential. Nevertheless, it is valuable as a "clean-up" reagent, removing elemental interferences. Its most common use in this regard is to remove residual iron after extensive preliminary separations in the spectrophotometric determination of aluminum in steel by the 8-hydroxyquinoline extraction method. A concentrated H_2SO_4 solution of the test portion is diluted and transferred to a separatory funnel. Cupferron and chloroform are added, and iron is extracted into the organic phase. Fresh chloroform is added, and the extraction is repeated several times until the organic phase shows no iron color. Other elements that extract from dilute H_2SO_4 or HCl are: titanium, zirconium, hafnium, vanadium (V), tin, uranium (IV), niobium, and bismuth. Chloroform is again the most commonly used solvent; however, methylethyl ketone (MEK) and methylisobutyl ketone (MIBK) are sometimes employed.

Dithizone

1,5-diphenylthiocarbazone or "dithizone" is a purple-black crystalline material, insoluble in water, but readily soluble in chloroform or carbon tetrachloride. The pure reagent in these solvents shows two absorption maxima corresponding to two isomeric forms: the thione and thiol tautomers. Dithizone forms extractable colored complexes with more than a dozen metals. Most of these can be measured spectrophotometrically. Selectivity is achieved by pH control and by the use of masking agents like cyanide, thiocyanate, EDTA, citrate, tartrate, thiosulfate, and others. From dilute acid solution, silver (yellow), mercury (II) (orange-yellow), copper (II) (violet-red), and palladium (brownish-red) complexes extract. From a solution above pH 2.0, bismuth (orange-yellow) extracts.

From weakly basic solution, it is possible to extract lead (red), zinc (purple-red), indium (red), and cobalt (II) (violet). And from 1 *M* NaOH in the presence of citrate, cadmium (red) can be extracted. Because the reagent itself is strongly colored, it is always necessary to carry one or more reagent blanks through the entire procedure. Also, since the commercial reagent may be impure, for the most accurate work it should be dissolved in 0.8 *M* NH_4OH and extracted several times with carbon tetrachloride, discarding the organic phases. Then the reagent can be reprecipitated with dilute H_2SO_4, filtered, and dried in a vacuum desiccator.

Dimethylglyoxime

Both the nickel and the palladium precipitates formed with dimethylglyoxime will dissolve in chloroform. In a typical application for nickel, the reagent (in methanol solution) is added to an ammoniacal citrate solution of the test portion (oxidized species having been previously reduced). The nickel complex is extracted into chloroform with several portions of that solvent. The combined chloroform extracts are washed with dilute NH_4OH. Then the nickel is stripped from the organic phase with several portions of dilute HCl. The colored complex is developed in the combined acid extracts by adding either bromine or iodine to create oxidizing conditions, then NH_4OH to create an ammoniacal medium, and finally dimethylglyoxime (in methanol). The spectrophotometric measurement is made at 530 nm.

A related compound, furildioxime, undergoes the same reactions as dimethylyglyoxime but is a more sensitive colorimetric reagent, and its nickel and palladium complexes are more soluble in chloroform and other solvents. With either reagent, the sample solution absorbance is a sensitive function of time and reaction conditions. Therefore, it is essential that all steps in a given procedure be followed identically for all samples and calibration standards.

1-Nitroso-2-Naphthol

We briefly discussed this reagent as a precipitant for cobalt in Chapter Eight. As an extractant, it is probably more important than as a precipitant, if only as a member of a class of compounds—the nitrosophenols—that includes 2-nitroso-1-naphthol and disodium Nitroso R salt (1-nitroso-2-naphthol-3,6-disulfonic acid, disodium salt) among others. They are all good spectrophotometric reagents for cobalt. The Nitroso R salt acts in aqueous solution, while the other two reagents and a third, 2-nitroso-4-dimethylaminophenol hydrochloride, are effective extractants for that element as well. The extraction solvent is often chloroform or dichloroethane. Citrate is a commonly used masking agent. These reagents can also be applied in a similar manner to the determination of palladium.

Dithiol

This is the trivial name for toluene-3,4-dithiol, a foul-smelling, but valuable reagent for low levels of tungsten. Machlan and Hague developed a procedure for steel and titanium alloys that eliminates the interference due to molybdenum (Machlan, L. A. and Hague, J. L., *Journal of Research of the National Bureau of Standards*, Vol. 59, No. 6, 1957, pp. 415–420). Molybdenum is complexed with the reagent in H_2SO_4/H_2SO_3 solution, extracted into chloroform, and discarded. Then HCl and $SnCl_2$ are added and the tungsten-dithiol complex is formed, extracted into butyl acetate, and measured spectrophotometrically at 635 nm. Rhenium will extract from near concentrated HCl.

Alpha-Benzoinoxime

This precipitant for molybdenum and tungsten can also be used as an extractant for these two elements. Molybdenum and small amounts of tungsten in the presence of molybdenum can be extracted from dilute HCl solution with a 0.2% (w/v) solution of alpha-benzoinoxime (bezoin monoxime) in chloroform. This suggests another solution for the molybdenum interference on the aluminum 3961 Å emission line. The extracted molybdenum can be stripped from the organic phase with NH_4OH.

Other Extractable Chelate Formers

There are literally dozens of reagents that could be mentioned here, but we must settle for only a few more. *Sodium diethyldithiocarbamate* has been used to extract bismuth into carbon tetrachloride from an EDTA and cyanide-bearing basic solution. It has also been used to extract away matrix interferences prior to the EDTA titration of aluminum in copper alloys. The test portion is dissolved in HCl, and water, sodium tartrate, and acetic acid/acetate buffer are added; then sodium diethyldithiocarbamate is added to the diluted solution, which is extracted with chloroform. The procedure removes antimony, cadmium, iron, nickel, manganese, zinc, tin, and lead, as well as copper (see *Annual Book of ASTM Standards*, Vol. 03.06, ASTM, Philadelphia, 1993, Designation E 478).

A related compound is *potassium ethyl xanthate*, which has been extensively exploited by E. M. Donaldson (*Some Instrumental Methods for the Determination of Minor and Trace Elements in Iron, Steel, and Non-ferrous Metals and Alloys*, Monograph 884, Canmet, Ottawa, Canada, 1982). Arsenic, antimony, bismuth, selenium, and tellurium have been extracted into chloroform from HCl and/or H_2SO_4 solution. Molybdenum can be extracted away from tungsten in 1.5 *M* HCl.

Acetylacetone (2,4-pentanedione) is both a solvent and an extractant. Ms. Donaldson employed this reagent to isolate aluminum (following mercury cathode electrolysis) for flame AA measurement. Many elements extract with acetylacetone: aluminum, beryllium, cerium, cobalt (III) (which can be separated in this way from nickel), copper, gallium, hafnium, indium, iron, manganese, uranium (VI), vanadium (IV), zinc, and zirconium. The colored complexes that form are not markedly sensitive for spectrophotometric work, however. McKaveney used the iron complex to good effect in a spectrophotometric method for free HF in stainless steel pickling baths. It is based on the bleaching effect of that species on the iron complex (McKaveney, J. P., *Analytical Chemistry*, Vol. 40, No. 8, 1968, pp. 1276–1279).

8-Hydroxyquinaldine (2-methyloxine) has been suggested as a "clean-up" extractant for trace aluminum determination since steric hindrance supposedly prevents its reaction with aluminum, unlike its analogue, 8-hydroxyquinoline (see Hynek, R. J. and Wrangell, L. J., *Analytical Chemistry*, Vol. 28, No. 10, 1956, pp. 1520–1527). More recent work suggests that aluminum is partially extracted as an ion pair in the presence of acetate (Cheng, K. L., Ueno, K., and Imamura, T., *Handbook of Organic Analytical Reagents*, CRC Press, Boca Raton, FL, 1982, p. 262). Aluminum does not precipitate with this reagent, however (see Chapter Eight).

N-benzoyl-N-phenylhydroxamine is related to cupferron but is more stable in the presence of acid. It is used to extract vanadium (V) or titanium (IV) from dilute HCl into chloroform or carbon tetrachloride. The colored complexes can be measured at 510 and 380 nm, respectively.

Applications/Procedures

The following are two, admittedly random, examples of chelation extractions. Hopefully, they will serve to illustrate the broad range of this area.

Extraction/Spectrophotometric Determination of Aluminum in Steel

[Reference: *Annual Book of ASTM Standards* , Vol. 03.05, ASTM, Philadelphia, 1993, Designation E 350.]

Weigh a sample containing 0.05 to 2.0 mg of aluminum (but not more than 2 g), dissolve it in 30 mL of HCl and 10 mL of HNO_3, then fume it in 30 mL of $HClO_4$, volatilizing any chromium with repeated dropwise additions of HCl. Fume to reduce the volume to 10 mL. Cool and dilute to 75 mL; filter through Whatman No. 40 (or equivalent) and wash with dilute HCl and hot water, reserving the filtrate. Ignite the paper in a platinum crucible, then volatilize the SiO_2 with H_2SO_4 and HF. Fuse the dry residue with 2 g of fused sodium bisulfate and leach in the reserved filtrate. Electrolyze the solution on a mercury cathode for 4 h, then filter through a double Whatman No. 41 (or equivalent); wash with water and discard the residue. Add 10 mL 1:1 H_2SO_4:H_2O and 10 mL of 10% (w/v) ammonium persulfate solution and boil down to approximately 75 mL.

Cool in an ice bath, then transfer the solution to a 250-mL separatory funnel. Add 15 mL of 6% (w/v) cupferron solution and shake for 30 s. Add 20 mL of $CHCl_3$ and extract for 1 min. Discard the lower organic layer. Repeat the extraction with fresh $CHCl_3$ until the discarded layer is colorless. Transfer the aqueous phase to the original beaker, reduce to about 35 mL, add 25 mL HNO_3, and evaporate to fumes of SO_3. Cool the solution, dilute to 75 mL, boil, and cool. Transfer the solution to a Teflon beaker and add 20% (w/v) NaOH to blue litmus plus 10 mL excess. Add 1 mL 30% H_2O_2 and digest near the boiling point for 5 min. Cool and filter through Whatman No. 540 (or equivalent) using a plastic funnel and collecting the filtrate in a plastic beaker. Wash the residue with hot water and discard it.

Add HCl to the filtrate to red litmus plus 1 mL excess, then transfer to a volumetric flask, cool, dilute to the mark, and mix. Transfer an aliquot containing 15 to 100 μg of aluminum to a 250-mL beaker. Add 1 mL of 18% (w/v) ammonium acetate solution. WARNING: Conduct the following operations in an efficient hood and observe proper procautions in the use and disposal of NaCN. Add 10 mL 10% (w/v) NaCN solution and adjust to pH 9.0 with NH_4OH or dilute HCl using a pH meter. Transfer to a 125-mL separatory funnel, add 1 mL of 5% (w/v) 8-hydroxyquinoline solution (25 g of reagent in 60 mL of glacial acetic acid, dilute to 300 mL with hot water; filter if necessary; dilute to 500 mL and store in a dark bottle). Add 10 mL $CHCl_3$, extract for 30 s, and drain the (lower) organic layer into a dry 25-mL volumetric flask containing 0.5 g of anhydrous Na_2SO_4. Repeat with a second 10 mL portion of $CHCl_3$, adding the extract to the volumetric flask. Dilute the flask to volume with $CHCl_3$, mix, and measure the absorbance at 395 nm versus $CHCl_3$. Prepare a reagent blank and calibration curve in the same manner.

Extraction/Spectrophotometric Determination of Trace Tungsten in Steel

[Reference: Machlan, L. A. and Hague, J. L., *Journal of Research of the National Bureau of Standards*, Vol. 59, No. 6, 1957, pp. 415–419.]

Dissolve a 0.2-g test portion in *aqua regia* and add four drops of HF to volatilize SiO_2. Cool the solution, add 20 mL of acid mixture (to 250 mL of water, add 100 mL of H_3PO_4 and 50 mL of $HClO_4$; mix and cool; add cautiously with cooling 100 mL of H_2SO_4; mix and cool to room temperature). Heat to fumes of SO_3 (as the last of the $HClO_4$ is removed, the fumes will sink back down into the vessel), plus 30 s of additional fuming. Excess fuming will precipitate sulfur and cause low results. Cool and transfer to a 100-mL volumetric flask with 1:3 H_2SO_4:H_2O. Dilute to the mark with 1:3 H_2SO_4:H_2O and mix. Remove an aliquot (no larger than 10.0 mL) that contains 5 to 50 μg of tungsten and place it in a 250-mL separatory funnel. Add 7.5 mL of 1:1 H_2SO_4:H_2O and 5.0 mL of sulfuric/sulfurous mixture (saturate 250 mL of 1:3 H_2SO_4:H_2O with SO_2 gas in a hood). Mix well, stopper, and place the separatory funnel in a beaker of hot water (40 to 45°C) for 10 min.

Add 5 mL of dithiol working solution. (In a hood with cooling dissolve 25 g of NaOH in 500 mL of water. Place a 5-g ampoule of toluene-3,4-dithiol in a beaker of hot water until it liquifies. Cautiously break the tip of the ampoule with clean pliers and transfer the contents to the NaOH solution. Dilute with water to 2.5 L and mix. Store in a refrigerator. Just before use, take 190 mL of this solution, add 3 mL of mercaptoacetic acid, and mix well to dissolve all the precipitate that forms.) Swirl the separatory funnel; mix and let stand in the hot water bath for an additional 5 min. Cool the solution to room temperature, add 10 mL $CHCl_3$, extract for 40 s, and discard the (lower) organic layer.

Repeat the extraction with 5 mL of fresh $CHCl_3$. Filter the aqueous layer through a glass fiber filter into a second 250-

mL separatory funnel, rinsing the first separatory funnel, and filter with 1:3 H_2SO_4:H_2O. Heat the second separatory funnel in a 40 to 45°C water bath for 10 min. Add 4 mL of dithiol working solution, swirl, and return to the hot water bath for 5 min. Cool to room temperature, add 10 mL of $CHCl_3$, and extract for 40 s. Discard the $CHCl_3$ (lower) layer. Repeat with 5-mL portions of $CHCl_3$ until the organic extract is colorless.

Heat the aqueous layer (in the separatory funnel) in a boiling water bath for 15 min. Add 50 mL of HCl and 5 mL of $SnCl_2$ solution. (Dissolve 5 mg of $CuCl_2 \cdot 2H_2O$ and 100 g of $SnCl_2 \cdot 2H_2O$ in 400 mL of 1:1 HCl:H_2O with heating. Cool and dilute to 500 mL with 1:1 HCl:H_2O.) Swirl to mix and continue heating in the boiling water bath for an additional 3 min. Add 15 mL of dithiol working solution, mix, and continue heating for an additional 10 min. Cool to room temperature, add 25.0 mL of butyl acetate by pipet, and extract for 30 s. Discard the (lower) aqueous layer. Drain the organic layer through a cotton plug placed in the stem of the separatory funnel into a 5-cm path length spectrophotometer cuvette and read the absorbance at 635 nm versus butyl acetate. Treat a reagent blank and calibration standards in a similar manner.

ION EXCHANGE

In its usual configuration, ion exchange is a form of column chromatography in which aqueous ions change places with ions in solid beads of an ion exchange resin. While many solids show some ion exchange properties, analytical chemistry requires precisely tailored synthetic polymer resins with a fixed degree of cross-linked bonding and a narrow cut of bead mesh sizes. Such polymers are available commercially as analytical grades in a variety of "backbone" and "cross-linkage" combinations.

Perhaps the most common backbone is polystyrene, and the most common cross-linkage is divinylbenzene; but there are many other combinations. Attached to this chemically resistant lattice structure are the functional groups that do the ion exchange. These have an associated charge that is balanced by an associated exchangeable counter ion of opposite charge. Some ion exchange resins are classed as strongly acidic or strongly basic, depending on the nature of their functional groups. Strong acid resins are cation exchangers, and strong base resins are anion exchangers. There are also weak acid and weak base resins, chelating resins, ion retardation resins, and others. For most work in inorganic analysis, however, a strongly acid cation exchange resin (like Dowex 50W with sulfonic acid functional groups), a strongly basic anion exchange resin (like Dowex 1 with quaternary ammonium functional groups), and, perhaps, a chelating resin (like Chelex 100 with its iminodiacetate ion pairs) will usually suffice.

Even within this restricted range, the number of options can be bewildering. First the counter ion must be selected—strong acid resins may be available in hydrogen, sodium, or ammonium forms, while strong base resins may be sold in chloride, hydroxide, acetate, or formate forms. (Chelating resins are sold in sodium form.) The choices merely provide a convenience for the analyst since it is not usually difficult to convert the ionic form of the resin. The extent of cross-linkage is another consideration. Useful resins range between 2 and 12% cross-linkage. Over this range, the physical properties of the resins change dramatically. Small amounts of cross-linkage allow the entry of very large sample ions into the interstices of the resin bead. These resins swell greatly in water and shrink in the presence of strong electrolyte eluents. This volume change can be great enough to crack the glass tube of the ion exchange column if sufficient expansion space is not provided.

Most of the low cross-linkage resins find use in organic and biochemical analysis where the large interstices are required to accommodate massive molecules. Most inorganic separations require 8% cross-linkage with its greater density of functional groups and consequent greater exchange capacity. Dowex resins are coded by a number following the type designation—thus Dowex 1-X8 indicates Dowex 1 with 8% cross-linkage. Mesh size is the next consideration. For most analytical work, 100 to 200 mesh is employed, although both 50 to 100 mesh and 200 to 400 mesh are sometimes called for. A finer mesh fraction will lead to greater resolution but will necessitate more time for a given column length since the flow rate will be reduced.

Packing and conditioning an ion exchange column requires a little art, but it can be readily mastered. Analytical-grade resins (such as those produced by Bio-Rad Laboratories) are prescreened to the designated mesh sizes so that column-clogging "fines" are not a great problem. Production-grade resins may have to be wet sieved before use. It is still a wise approach, however, even with analytical-grade resins to decant the supernatant several times from the prepared slurry before packing the column. Weigh the resin into a large beaker (weights are approximate and best determined by experience, although once established they should be noted for future reference), add water or the solution in which the sample will be applied, and stir for several minutes. Then allow the particles to settle, decant and discard the supernatant solution, and repeat the process several times. Then refill the beaker with the suspension liquid, adding only enough to produce a thick slurry by stirring.

Pour the slurry into a glass or plastic column fitted with a stopcock and some means to retain the particles. Columns fitted with a sintered glass disk are available, but often it is better to use an open column into which a Pyrex wool or plastic wool plug has been inserted. Allow the particles to settle in the column, then drain the headspace solution down to about 1 in. (2.54 cm) above the resin bed. Then insert a Pyrex or plastic wool plug at the top of the column. The specific analytical method used should specify any conditioning steps required for the proper functioning of the column.

Designing an ion exchange separation "from scratch" is *not* a trivial exercise, and unless the analyst has a great deal of experience to draw upon, it is usually smart to begin with an extensive literature search to try to find some scheme for the desired separation that has proven successful for other workers. Fortunately, there is a rich literature available that extends back to the 1930s and that includes extensive studies published by the nuclear field that drove developments in this area for several decades. A good text like *Ion Exchange in Analytical Chemistry* (Rieman III, W. and Walton, H. F., Pergamon, Oxford, 1970) is invaluable as well.

There are many physico-chemical processes that occur when a complex solution passes through an ion exchange column, and a host of different mechanisms can be brought to bear to achieve a separation of the solution components. Most of these need not concern the metals analyst. Our only focus here will be the elution by competing ions—in a sense, the exemplary ion exchange process. Counter-ions vary in their affinity for the functional groups of an ion exchange resin, some being tightly bound while others are very weakly bound. In a given ionic environment, the ion with the greater affinity will displace an ion with a lesser affinity, causing it to be washed off the column and collected in the eluent solution that passes out.

The relative concentrations of competing ions is critical to this process. In a typical ion exchange separation, the analyst creates a series of conditions on the column that cause the analyte to be expelled in pure form. For example, several sample analytes may be bound to a column by applying them in a dilute eluent. Then the ionic strength of the eluent is increased slightly, causing the most weakly bound analyte to elute. Further increases in the ionic strength of the eluent will then cause the more tightly bound analytes to elute. This is the principle behind most of the ion exchange work in the metals analyst's purview.

There is, of course, much more in this quite complicated field. Electroselectivity, for example, describes how higher charge ions are more strongly held in dilute solution while lower charge ions are more strongly held in concentrated solution. (This explains why water softeners can be regenerated by flushing the column with sodium chloride solution.) And Donnan Equilibrium describes the effects due to the electrostatic potential between fixed and diffusible charge and leads to a "Donnan Invasion" of the column by eluent electrolyte ions. The radius of the hydrated ions also plays a role in the exchange process. Finally, there is the application of chromatographic plate theory to ion exchange. For more information on these and other aspects of ion exchange, the reader is referred to the previously mentioned text by Rieman and Walton.

Anion Exchange Systems

It may surprise the uninitiated that, by far, the most useful ion exchange systems to the metals analyst are those based on strongly basic anion exchange resins. In these procedures, metallic elements are usually separated as their chloride or fluoride complexes (although work has been done with sulfate and nitrate systems as well). The first development in this area came during the analytical work on the Manhattan Project when it was discovered that the rare earths could be separated. This was vastly expanded in a seminal publication by K. A. Kraus and G. E. Moore (*Journal of the American Chemical Society*, Vol. 75, 1953, p. 1460) on chloride systems applied to many elements. The work was extended to fluoride and chloride/fluoride systems by F. Nelson, R. M. Rush, and K. A. Kraus (*Journal of the American Chemical Society*, Vol. 82, 1960, p. 339) and by J. P. Faris (*Analytical Chemistry*, Vol. 32, 1960, p. 520). Today, strategies based on these systems are in routine use in some laboratories, saving days of tedious sequential separations by other techniques and even in some cases allowing separations where none were practical before.

In the chloride system, typically the test portion is dissolved in either HCl or some mixture of HCl and HNO_3. In the latter case, the solution is taken to complete dryness and the residue is dissolved in HCl. If a nonvolatile "fuming" acid is required, it must be "baked out" of the sample before the final portion of HCl is added. When all salts have dissolved, the solution is diluted appropriately and is transferred to a column of Bio-Rad AG 1-X8, chloride form resin (usually 100 to 200 mesh). With such an approach, nickel, cobalt, and iron can be readily separated from each other. With some degree of greater care, it is possible to separate nickel, cobalt, copper, iron, and even zinc. A similar approach has been used for isolating gallium and zinc from aluminum and lead from steel. Uranium and thorium have also been separated from each other.

Using the first case as an example, a 0.2-g test portion of nickel-base high-temperature alloy in HCl is transferred to a 14-cm-long column of AG 1-X8 (100 to 200 mesh) resin in a 2-cm-diameter glass tube (pretreated by passing 50 mL of HCl through the column). Nickel is eluted by passing 250 mL of 9 *M* HCl through the column. Cobalt is then eluted by passing 250 mL of 4 *M* HCl. Finally, iron is eluted by passing 250 mL of 0.1 *M* HCl through the column (or more efficiently by 250 mL of 1M HNO_3; although this ruins the column for reuse). This separation scheme was made practical by L. L. Lewis and W. A. Straub (*Analytical Chemistry*, Vol. 32, No. 1, 1960, pp. 96–99).

The chloride/fluoride anion exchange system requires plastic columns manufactured from polystyrene or (better) polymethylmethacrylate pipe. The plug that retains the resin at the top and bottom of the column must be resistant to HF. Teflon wool is readily available from gas chromatography suppliers, but it is only suitable for the bottom of the column since it will float at the top. A better choice is SEF modacrylic fiber (available from Monsanto Chemical Co.).

In this approach, a 0.5 to 1.0-g test portion is usually dissolved in some combination of HF, HNO_3, and HCl in a Teflon beaker and then taken to dryness. The salts are dissolved in 4% (v/v) HF/1% (v/v) HCl and transferred to a 17.5-cm-long column of AG 1-X8 (200 to 400 mesh) in a 1-in. (2.54-cm)-diameter plastic tube (pretreated by passing 250 mL of 4% (v/v) HF/1% (v/v) HCl through the column). Then 350 mL of 4% (v/v) HF/1% (v/v) HCl are passed through the column, eluting iron, nickel, cobalt, chromium, manganese, and copper (there is some question as to the quantitative elution of aluminum). This is followed by 350 mL of 10% (v/v) HF/50% (v/v) HCl that elutes zirconium, hafnium, titanium, vanadium, and tungsten. Then 350 mL of 20% (v/v) HF/25% (v/v) HCl elutes molybdenum. Then 300 mL of 4% (v/v) HF/14% (w/v) NH_4Cl elutes niobium. And then 350 mL of 4% (w/v) NH_4F/14% (w/v) NH_4Cl elutes tantalum. Rhenium may then be stripped from the column with 400 mL of 10% (v/v) $HClO_4$.

It is interesting to note that in this scheme the tantalum fraction is stripped with the highest concentration of free fluoride (even though the eluent contains no HF) and that rhenium is removed with the only noncomplexing eluent. Such separations would be nearly impossible from a single sample by other routes. This ion exchange scheme thus greatly simplifies the separation of complex high-temperature alloys. The original work was published by J. L. Hague and L. A. Machlan (*Journal of Research of the National Bureau of Standards*, Vol. 62, No. 1, 1959, pp. 11–17) and J. L. Hague, E. D. Brown, and H. A. Bright (*Journal of Research of the National*

Bureau of Standards, Vol. 53, No. 4, 1954, pp. 261–262) and extended and elaborated by S. Kallmann, H. Oberthin, and R. Liu (*Analytical Chemistry*, Vol. 34, No. 6, 1962, pp. 609–613) and S. Kallmann and H. Oberthin (*Analytical Chemistry*, Vol. 37, No. 2, 1965, pp. 280–283).

Special care is, of course, necessary when working with such large volumes of high-concentration HF solutions, but with proper training and attention to detail the procedure can be used safely and routinely. Like many ion exchange procedures, the original work utilized classical (mostly gravimetric) finishes for the separated analytes. But today the options for instrumental measurement, especially at high concentrations, are much more reliable than any instrumental approaches available in the 1950s or 1960s. The HF-resistant torch and nebulizer for ICP/OES is one option, but in some configurations it suffers from poor precision.

A good alternative consists of removal of the fluoride by one of several schemes. The first (Fe, Ni, Co, Cr, Mn, Cu, Al) eluent can be simply fumed in $HClO_4$ or H_2SO_4. The second (Zr, Hf, Ti, W, V) and the third (Mo) eluents can be fumed in H_2SO_4/H_3PO_4 and diluted while hot with dilute H_2SO_4. The fourth (Nb) and fifth (Ta) can be precipitated as cupferrates from the boric acid-complexed solution, ignited to oxides, fused with potassium pyrosulfate, and leached in ammonium oxalate solution. If the niobium and tantalum analytes are low in concentration, hafnium can be added as a carrier for the cupferron precipitation. After such treatment, all the chloride/fluoride eluents are ready for conventional ICP/OES measurement.

Sometimes the first eluent from the chloride/fluoride anion exchange separation is fumed with $HClO_4$, then baked to dryness. The residue is then dissolved in HCl and separated a second time using the chloride system to isolate the nickel, cobalt, and iron.

Variations on this and other schemes are also possible. Once the analyst has successfully adapted a published procedure to his or her needs, it can become a "building block" in the overall separation plan. It is probably unwise to dabble too extensively in the mechanism of a given ion exchange procedure, however, since a sound scheme has usually been finely tuned, sometimes with tedious radio-tracer work to ensure clean separations.

Comparatively little work has been done with sulfuric acid systems and even less with nitric acid systems. The sulfate system has been applied to a delicate separation of hafnium and zirconium. It has also been characterized for many other elements by F. W. E. Strelow and C. J. C. Bothma (*Analytical Chemistry*, Vol. 39, No. 6, 1967, pp. 595–599). The nitrate system has been applied to some actinide elements.

Applications/Procedures

Anion Exchange of a Complex High-Temperature Alloy

1. Weigh a 1-g test portion into a Teflon beaker and dissolve it in 20 mL HF and 5 mL HNO_3 with dropwise HCl as required.
2. Heat to dryness and dissolve the residue in 4% (v/v) HF/1% (v/v) HCl.
3. Transfer to a prepared 17.5-cm-long column of AG 1-X8 (chloride form; 200 to 400 mesh) in a 1-in. (2.54-cm) ID plastic column (stored in 3 *M* HCl and preconditioned by passing 250 mL of 4% (v/v) HF/1% (v/v) HCl through it). Elute and collect the following:
   A. 350 mL 4% (v/v) HF/1% (v/v) HCl—Fe, Ni, Co, Cr, Mn, Cu, Al.
   B. 350 mL 10% (v/v) HF/50% (v/v) HCl—Zr, Hf, Ti, V, W.
   C. 350 mL 20% (v/v) HF/25% (v/v) HCl—Mo (gravimetric determination with alpha-benzoinoxime).
   D. 300 mL 4% (v/v) HF/14%(w/v) NH_4F—Nb (gravimetric determination with cupferron).
   E. 350 mL 4% (w/v) NH_4F/14% (w/v) NH_4Cl—Ta (spectrophotometric determination with pyrogallol).
   F. 400 mL 10% (v/v) $HClO_4$—Re (gravimetric as the metal).
4. Add HNO_3 and heat eluent 3A to fumes of $HClO_4$, bake to complete dryness; dissolve salts in HCl. Transfer the solution to a prepared 14-cm-long column of AG 1-X8 (chloride form; 100 to 200 mesh) in a 2-cm glass column (stored in water and pretreated by passing 50 mL of HCl through it). Collect the following eluents:
   A. 250 mL of 9 *M* HCl—Ni (gravimetric determination with dimethylglyoxime).
   B. 250 mL of 4 *M* HCl—Co (volumetric determination—ferricyanide/potentiometric).
   C. 250 mL of 1 *M* HNO_3—Fe (volumetric determination—$K_2Cr_2O_7$/visual endpoint).
5. Add HNO_3 and heat eluent 3B to fumes of H_2SO_4, dilute to volume and remove aliquots for the following:
   A. W—(gravimetric determination with cinchonine).
   B. Ti—(spectrophotometric determination as the peroxy-complex).
   C. Zr—(spectrophotometric determination as the pyrocatechol violet complex).

Cation and Chelating Ion Exchange Systems

Strongly acid cation exchange systems have found their greatest use in concentrating metal ions from very dilute samples such as water, air impinger samples, and biological extracts. In very simple systems, such as pure brine, a hydrogen form column can be used to take up the sodium ions quantitatively. The released hydrogen ion can then be titrated with standard base to yield a value for the original sodium concentration. Trace metals can be placed on a similar column and then be selectively eluted with various combinations of acetone and dilute HCl. F. W. E. Strelow, R. Ruthemeyer, and C. J. C. Bothma have published an extensive treatment of cation selectivity in nitric and sulfuric acids (*Analytical Chemistry*, Vol. 37, No. 1, 1965, pp. 106–110). But little work of practical value to alloy analysis has been published. A similar situation prevails with chelating resins, which have proved to be of great value for the preconcentration of trace metals from water and other environmental samples, but find little use in the main work of the metals analyst.

DISTILLATION/EVOLUTION

The dual title of this section suggests the two distinct ends to which this separation process applies: (1) to remove an analyte from its matrix for ultimate measurement or (2) to remove an interference from the solution bearing the analyte.

In both cases, the chemistry involves the formation of a volatile species driven out of a solution by heat. Quite clearly, the means by which this process occurs must differ radically. When an analyte is isolated by distillation a closed system is mandatory, but when an interference is evolved an open beaker will suffice. For our purposes here, it is probably simpler and more logical to reverse the order and begin with a discussion of the elimination of interfering species since these techniques are often incorporated in the dissolution scheme for the test portion. A few mechanisms will find application in both strategies, and these will be treated under both headings.

Evolution of Interferences

Chromium

This element can create a number of problems in various analytical schemes. It is strongly colored in all oxidation states and thus obscures visual endpoints in titrimetry and is a major contributor to background in spectrophotometry. It is difficult to remove by mercury cathode electrolysis, often acting as a redox buffer to retard the removal of other species. It is one of the more difficult elements to completely wash out of filter paper. And its redox chemistry often interferes with desired reactions. One important solution to these kinds of problems consists of the evolution of chromyl chloride (CrO_2Cl_2) from fuming perchloric acid.

The simplest approach is probably the cautious dropwise addition of HCl into the fuming sample. If the $HClO_4$ is hot enough, this immediately generates dark brown fumes in copious quantity if the chromium is present in high concentration. Since water in the HCl cools the sample, it is necessary to wait until the temperature is regained before more HCl is added. About four treatments usually suffice.

More efficient means to evolve chromium are available, however. Sodium chloride can be added—it cools the fuming solution much less but adds sodium to the sample. An HCl azeotrope generator containing boiling HCl can be fashioned from an Erlenmeyer flask, some glass boiling beads, a stopper, and a bent glass tube. This can be used to direct the azeotrope directly onto the surface of the fuming sample solution. Perhaps the best (and most elaborate) approach is to use a bent glass tubing probe connected to a tank of anhydrous HCl gas. Most (but not the last traces) of chromium can be removed by using one of these approaches.

Silicon

This element may be undesirable because the insoluble oxide slows subsequent filtration. High silicon levels may also leave silica-encapsulated analyte undissolved. For these reasons, silicon is often volatilized during the dissolution of the test portion. Another frequently used option is to volatilize the silicon from the filtered and ignited acid insoluble residue. This removal process simply involves the addition of HF, but it requires subsequent fuming with a nonvolatile acid to be most effective. Such fuming also serves to remove excess HF that itself interferes in many procedures. In a borosilicate glass vessel, more than five drops of HF will create an equilibrium condition so that about as much silicon as is evolved from the sample will be added by attack on the vessel. Thus only in Teflon or platinum vessels can large amounts (>20 mg) of silicon be removed by evolution.

Boron

This element can be removed as the methyl borate ester by adding methanol to the acidic sample solution and boiling it. Another alternative is to add HF to form the volatile BF_3, then evolve it out of the solution with fuming H_2SO_4. Such procedures are rarely necessary, however. An exception are cases when the sample has been fused in a borate salt and boron is a chemical (or spectrometric) interference.

Tin

Lead and tin-base solders, pewter, bronze, and other tin-bearing alloys are sometimes dissolved in HBr or HBr/Br_2, followed by fuming in $HClO_4$ to remove the tin as volatile $SnBr_4$. Tin removal is desirable since it otherwise tends to hydrolyze as hydrous SnO_2, clogging filters, and coating glassware. Tin also has a lively redox chemistry that may interfere with desired reactions.

Others

Volatile mineral acids can be removed by fuming with nonvolatile mineral acids, but removal of all traces of the associated anion is sometimes difficult. For example, the presence of aluminum in the sample solution retards the evolution of fluoride with $HClO_4$. It is possible to remove HNO_3 without resorting to fuming with $HClO_4$ or H_2SO_4 by cautiously adding formic acid or urea crystals to a boiling syrup of low volume. Many sample components are incidentally lost during sample dissolution (see the discussions on volatiles losses in Chapters Six and Seven), but only rarely are these processes considered beneficial. Exceptions include the evolution of H_2S from the acid dissolution of sulfide ore, the evolution of CO_2 from the acid dissolution of limestone, and similar situations where the sample matrix is somewhat of an analytical nuisance.

Distillation of Analytes

Antimony

An all-glass distillation arrangement with a dropping funnel, an inlet for the flow of inert gas (N_2, CO_2, or Ar), and a thermometer well is necessary for the collection of germanium, arsenic, antimony, and tin halide distillates. A vertical water-cooled condenser should be arranged with its discharge tube below the surface of about 75 mL of water in a beaker in an ice bath. Antimony is always distilled *after* germanium and arsenic have been removed. Antimony must be in the +III oxidation state. It is distilled out of a H_2SO_4/H_3PO_4 mixture, which is heated to 155°C before HCl is added slowly dropwise. The temperature is maintained between 155 and 165°C (with inert gas flowing through the system) until about 75 mL of HCl has been added to the sample solution.

Arsenic

Using the apparatus described above, arsenic (III) may be distilled out of 10 mL of a 1:1 $H_2SO_4{:}H_2O$ solution to which 100 mL of HCl is added. The temperature should be maintained at about 112°C until the flask volume has boiled down to about 50 mL. Inert gas should flow during the distillation. Once arsenic has been distilled over, then antimony may be distilled from the sample solution. Alternatively, sometimes the solution remaining in the distillation flask after arsenic has been distilled is analyzed directly for antimony.

Boron

Boron is distilled from strong acid solution with methanol as the methyl borate ester ($B(OCH_3)_3$) using a boron-free glass, Vycor, or fused silica distillation apparatus. It is usually sufficient that the distillation flask be made of a boron-free composition. The receiving vessel should contain a little dilute NaOH solution and be trapped with a bubbler (such as those used in wine making) to prevent the loss of uncondensed ester. Water retards the formation and distillation of methyl borate, so it is necessary to restrict its use in the sample dissolution if the sample is to be distilled immediately. Steel and many iron-, nickel-, and cobalt-base alloys can be dissolved in a $HClO_4/H_3PO_4$ mixture under reflux for this purpose.

The presence or suspicion of the presence of insoluble boron compounds requires special treatment. The best approach is to distill the soluble boron, then filter the solution remaining in the distillation flask, ignite the residue [in the presence of Na_2CO_3 or $Ca(OH)_2$], and then fuse it with Na_2CO_3. The fusion is leached in $HClO_4/H_3PO_4$ and then also distilled. Each distillation requires the addition of two separate portions of HPLC-grade methanol, the first being distilled completely before the flask is cooled and the second portion added and distilled.

Fluorine

The classical Willard-Winter steam distillation of fluoride still finds occasional use for slags and fluxes. If the sample is very finely divided and contains no readily oxidizable substances, it may be weighed directly into the distillation flask, followed by 2:1 $HClO_4:H_2O$, and directly steam distilled. Otherwise it should be fused, or ignited then fused, with Na_2CO_3 and leached with dilute $HClO_4$ in the distillation flask.

Germanium

The volatility of $GeCl_4$ (b.p. 83.1°C) allows the separation of this element from most others. Using chlorine gas and concentrated HCl, germanium can be distilled away from arsenic, antimony, tin, selenium, and tellurium, all of which also form volatile chlorides. To separate germanium from arsenic, it is necessary to ensure that arsenic is in the +V oxidation state. A train of interconnected, iced, water-filled collection vessels is required to prevent loss of the distillate.

Nitrogen

The time-honored technique of "Kjeldahl nitrogen determination" is hardly ever applied to metals any longer now that very reliable inert gas fusion instruments are commonplace. The classic procedure involved digestion of the test portion in H_2SO_4, then adding strong caustic and steam distilling the ammonia that formed. The collected ammonia was frequently mixed with Nessler's reagent (a solution of KI, $HgCl_2$, and KOH), which was then measured spectrophotometrically. One application that still remains for this approach is the determination of combined nitrogen. Here, the technique is applied to the ester-halogen insoluble residue from steels.

Osmium

Osmium can be distilled away from a solution of the platinum group metals as OsO_4. The sample is typically fused in sodium peroxide, and the cooled melt is leached in water and then transferred to a distillation flask. Nitric acid is added to produce a 10% (v/v) solution, and the osmium tetroxide is distilled out. The analyte is caught in SO_2-saturated 1:1 $HCl:H_2O$.

Selenium

On rare occasions, selenium is distilled as $SeCl_4$ using the apparatus described under antimony above. Using HCl gas in place of inert gas, it distills out of dilute H_2SO_4 at 300 to 330°C, leaving tellurium behind. If arsenic, antimony, germanium, or tin are present in the sample and they have not been previously removed, they will accompany the selenium.

Sulfur

So-called "evolution-sulfur" methods based on the aqueous acid formation and collection of H_2S gas were once an important means of routine sulfur analysis. Today the technique has returned in a new form for the determination of trace levels of the analyte in steel by spectrophotometric measurement with methylene blue. However, the method is not widely employed. The older approach in which the evolved H_2S was collected in a zinc sulfate/ammonium hydroxide solution that is acidified and titrated with standard iodine solution can still be useful for some sulfide ores and other high-sulfur materials.

Tin

After first arsenic, then antimony, have been distilled from the sample solution as described above under those entries, the distillation flask is cooled to 140°C and a 3:1 HCl:HBr mixture is introduced slowly dropwise through the dropping funnel while maintaining 140°C and a gentle flow of inert gas. Distillation is complete when about 50 mL of the mixed acids have been added.

FIRE ASSAY

This entry, unfortunately, must take on the clear character of a "cop-out" since the author has no practical experience in this important and rather complex field. Fire assay has much more of metallurgical art than chemical science in it. Yet, for the assay of gold and silver ores and bullion, it is generally accepted as the most accurate technique in expert hands. Fire assay methods have also been applied to the determination of the platinum group metals, but in this area they are less widely utilized. Fire assay techniques are highly empirical and operator sensitive. Success is affected by factors like heating rate as well as final temperature. Considerable training is required to master the fine points of a good assay. The important classical texts on fire assay include: O. C. Shepherd and W. F. Dietrich, *Fire Assaying* (McGraw-Hill, New York, 1940) and E. E. Bugbee, *A Textbook of Fire Assaying*, 3rd ed. (John Wiley & Sons, New York, 1940). Also, F. E. Beamish,

TABLE 9-1—Selected miscellaneous separations.

Separation	Typical Analytes Isolated	Typical Interferences Removed
Mercury cathode	Alkali metals, alkaline earths, rare earths, Al, Ti, Zr, Hf, B	Fe, Co, Ni, Cu, Zn, Cd, In, Sn, platinum group, Ag, Au, Hg, Tl, Bi, Ga, Ge
Chromyl chloride volatilization	Fe, Co, Ni, many others	Cr
Ether extraction from 6 *M* HCl	Al, many others	Fe, Mo
Chloride system anion exchange	Ni, Co, Fe	Analytes separated from each other
Fire assay	Ag, Au	Fe, Cu, other base metals

The Analytical Chemistry of The Noble Metals (Pergamon Press, Oxford, 1966) contains a large section on the subject.

The fire assay process in its most simplified form involves a reducing fusion of finely divided ore with sodium carbonate, sodium tetraborate, silicon dioxide, lead monoxide, and some form of carbon (or, in assayer's terms: soda ash, borax, silica, litharge, and flour). Part of the PbO is reduced to lead, which selectively collects gold and silver, leaving behind a slag that is chipped away when the melt is cooled. The lead button is then placed on a special preheated shallow porous dish made of bone ash [90% $Ca_3(PO_4)_2$] or MgO (called a *cupel*) and fired in a forced draft furnace.

The lead oxidizes and soaks into the cupel carrying metal oxide impurities with it. When the last of the lead is removed in this way (sometimes with a flash of light due to the release of latent heat of fusion), a *doré bead* of pure gold and silver is left on the dish. For bullion, this "cupellation" step is applied directly by wrapping the metal test portion in lead foil. If the samples do not contain more silver than gold, the ratio must be adjusted before cupellation by adding silver; this process is known as *inquartation*. The doré bead is weighed and then rolled out into a thin coil with a small rolling mill. This coil is then *parted* by heating just below the boiling point in dilute nitric acid to dissolve the silver. The insoluble residue is gold, which is then weighed. A *proof* is a synthetic standard taken through the entire fire assay process that is used to empirically correct the results on the unknown sample.

Table 9-1 summarizes a few common miscellaneous separations.

REFERENCES

Mercury Cathode

Center, E. J., Overbeck, R. C., and Chase, D. L., *Industrial and Engineering Chemistry, Analytical Edition*, Vol. 23, No. 8, 1951, pp. 1134–1138.

Lundell, G.E.F. and Hoffman, J. I., *Outlines of Methods of Chemical Analysis*, John Wiley & Sons, New York, 1938, pp. 94–99.

Parks, T. D., Johnson, H. O., and Lykken, L., *Industrial and Engineering Chemistry, Analytical Edition*, Vol. 20, No. 2, 1948, pp. 148–151.

Also: Instruction Manual for the Dyna-Cath (Eberbach Corp.)

Solvent Extraction

Annual Book of ASTM Standards, Vol. 03.05, American Society for Testing and Materials, Philadelphia, 1993, Designations E 35, E 37, E 40, E 107, E 120, E 350.

Annual Book of ASTM Standards, Vol. 03.06, American Society for Testing and Materials, Philadelphia, 1993, Designations E 396, E 478.

Burke, K. E., *Analyst*, Vol. 97, 1972, pp. 19–28.

Burke, K. E., *Applied Spectroscopy*, Vol. 28, No. 3, 1974, pp. 234–237.

Burke, K. E., *Talanta*, Vol. 21, 1974, pp. 417–423.

Cheng, K. L., Ueno, K., and Imamura, T., *CRC Handbook of Organic Analytical Reagents*, CRC Press, Boca Raton, FL, 1982.

Collins, T. A. and Kanzelmeyer, J. H., *Analytical Chemistry*, Vol. 33, No. 2, 1961, pp. 245–247.

Day, R. A. and Underwood, A. L., *Quantitative Analysis*, 2nd ed., Prentice-Hall, Englewood Cliffs, NJ, 1967, pp. 392–412.

Donaldson, E. M., *Some Instrumental Methods for the Determination of Minor and Trace Elements in Iron, Steel, and Non-ferrous Metals and Alloys*, Monograph 884, CanMet, Ottawa, Canada, 1982.

Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 134–137.

Hynek, R. J. and Wrangell, L. J., *Analytical Chemistry*, Vol. 28, No. 10, 1956, pp. 1520–1527.

Machlan, L. A. and Hague, J. L., *Journal of Research of the National Bureau of Standards*, Vol. 59, No. 6, 1957, pp. 415–420.

McKaveney, J. P., *Analytical Chemistry*, Vol. 40, No. 8, 1968, pp. 1276–1279.

Morrison, G. H., *Industrial and Engineering Chemistry, Analytical Edition*, Vol. 22, No. 11, 1950, pp. 1388–1393.

Morrison, G. H. and Freiser, H., *Solvent Extraction in Analytical Chemistry*, John Wiley & Sons, New York, 1957.

Ross, W. J. and White, J. C., *Analytical Chemistry*, Vol. 33, No. 3, 1961, pp. 424–427.

Ion Exchange

Annual Book of ASTM Standards, Vol. 3.05, American Society for Testing and Materials, Philadelphia, 1993, Designations E 34, E 350.

Bandi, W. R., Buyok, E. G., Lewis, L. L., and Melnick, L. M., *Analytical Chemistry*, Vol. 33, No. 9, 1961, pp. 1275–1278.

Bottei, R. S. and Trusk, B. A., *Analytica Chimica Acta*, Vol. 37, 1967, pp. 409–412.

Dixon, E. J. and Headridge, J. B., *Analyst*, Vol. 89, 1964, pp. 185–204.

Faris, J. P., *Analytical Chemistry*, Vol. 32, No. 4, 1960, pp. 520–522.

Hague, J. L., Brown, E. D., and Bright, H. A., *Journal of Research of the National Bureau of Standards*, Vol. 53, No. 4, 1954, pp. 261–262.

Hague, J. L. and Machlan, L. A., *Journal of Research of the National Bureau of Standards*, Vol. 62, No. 1, 1959, pp. 11–19.

Hague, J. L. and Machlan, L. A., *Journal of Research of the National Bureau of Standards*, Vol. 65A, No. 1, 1961, pp. 75–77.

Kallmann, S., Oberthin, H., and Liu, R., *Analytical Chemistry*, Vol. 34, No. 6, 1962, pp. 609–613.

Kallmann, S. and Oberthin, H., *Analytical Chemistry*, Vol. 37, No. 2, pp. 280–283.

Kingston, H. M., Barnes, L. L., Brady, T. J., Rains, T. C., and Champ, M. A., *Analytical Chemistry*, Vol. 50, No. 14, 1978, pp. 2064–2070.

Koster, G. and Schmuckler, G., *Analytica Chimica Acta*, Vol. 38, 1967, pp. 179-184.

Kraus, K. A. and Moore, G. E., *Journal of the American Chemical Society*, Vol. 75, 1953, p. 1460.

Kraus, K. A. and Nelson, F., *ASTM Special Technical Publication No. 195*, American Society for Testing and Materials, Philadelphia, 1956, p. 27.

Lewis, L. L. and Straub, W. A., *Analytical Chemistry*, Vol. 32, No. 1, 1960, pp. 96–99.

Machlan, L. A. and Hague, J. L., *Journal of Research of the National Bureau of Standards*, Vol. 66A, No. 6, 1962, pp. 517–520.

Nelson, F., Rush, R. M., and Kraus, K. A., *Journal of the American Chemical Society*, Vol. 82, 1960, p. 339.

Rieman III, W. and Walton, H. F., *Ion Exchange in Analytical Chemistry*, Pergamon Press, Oxford, 1970.

Strelow, F. W. E., Rethemeyer, R., and Bothma, C. J. C., *Analytical Chemistry*, Vol. 37, No. 1, 1965, pp. 106–110.

Strelow, F. W. E. and Bothma, C. J. C., *Analytical Chemistry*, Vol. 39, No. 6, 1967, pp. 595–599.

Strelow, F. W. E., *Analytical Chemistry*, Vol. 50, No. 9, 1978, pp. 1359–1361.

Van Nostrand's Scientific Encyclopedia, 4th ed., D. Van Nostrand, Princeton, NJ, 1968.

Also: *Ion Exchange Manual* (Bio-Rad Laboratories) and catalog of Bio-Rad Laboratories.

Distillation/Evolution

Annual Book of ASTM Standards, Vol. 03.05, American Society for Testing and Materials, Philadelphia, 1993, Designations E 46, E 54.

Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. L., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons , New York, 1953, pp. 70–73, 260–277, 289, 298–299, 330, 333, 354, 372, 374, 742, 756, 762 (pp. 339–383 by R. Gilchrist).

Fire Assay

Annual Book of ASTM Standards, Vol. 03.06, American Society for Testing and Materials, Philadelphia, 1993, Designation E 1335.

Bennett, V. I., *ASTM Standardization News*, November 1988, pp. 62–64.

Beamish, F. E., *The Analytical Chemistry of the Noble Metals*, Pergamon Press, Oxford, 1966, pp. 162–248.

Bugbee, E. E., *A Textbook of Fire Assaying*, 3rd ed., John Wiley & Sons, New York, 1940.

Shepherd, O. C. and Dietrich, W. F., *Fire Assaying*, McGraw-Hill, New York, 1940.

MNL25-EB/Mar. 1996

10

The Separation of the Elements

We have just completed a two-chapter survey of the major categories of inorganic separation techniques. Admittedly, the survey lacked some rigor in omitting recently developed techniques such as ion chromatography, high-performance liquid chromatography, capillary electrophoresis, and other instrumental approaches whose value to metals analysis is either unestablished or inchoate. Since these are usually inextricable from an associated measurement device, they are more properly treated in Part IV. The remainder of the field having been discussed, it is now appropriate to attempt to cross-correlate some of this information with the specific analytes. The goal here is to provide a brief glimpse at some of the aqueous chemistry of each element as it applies to some of the more useful analytical separations.

For the first time up to this point, references will be numerically indexed to provide ready access to source materials for most of the topics covered. The reader is encouraged to consult these sources before embarking on an unfamiliar path suggested by the text. In addition, the book-length works referenced in the previous two chapters should be used to provide supplementary information. Fifty-six elements will each be placed in the spotlight for a few moments, and an additional 22 will later be touched upon even more briefly, making 78 in all. For obvious reasons, the remainder have been omitted completely—the noble gases, the "light" unstable elements, and the transuranic elements. Of these inert or radioactive elements, only a few have any potential for aqueous analytical separations. And those applications are too specialized for our purposes here.

ALUMINUM

The complete separation of aluminum from a complex alloy matrix is probably the most difficult metals analysis task that is routinely performed. The only aqueous oxidation state is +III, the Al^{3+} ion being coordinated with six water molecules. Aluminum exhibits amphoteric behavior; its hydroxide, $Al(OH)_3$, is thus soluble in excess strong caustic, forming aluminates such as $NaAlO_2$. Precipitation of $Al(OH)_3$ with ammonium hydroxide requires careful pH control and is essentially complete at the methyl red transition just below pH 7 (pink to yellow) [*1*]. In strong caustic, aluminum accompanies vanadium, molybdenum, tungsten, and other elements in the filtrate, although it may be occluded in massive precipitates of nickel or magnesium. The mercury cathode removes a host of elements from aluminum, while ether extraction from 6 *M* HCl removes iron (III), molybdenum, and gallium, leaving aluminum in the aqueous phase [*2*].

The principal organic precipitant for aluminum is 8-hydroxyquinoline, which forms a yellow floc that can be dried and weighed as such or ignited to Al_2O_3 and weighed [*3*]. Traces of aluminum can be extracted with the same reagent into chloroform [*4*], but residues of iron and other contaminants must be first scrupulously removed or thoroughly masked if this separation is to serve as the basis of a spectrophotometric measurement of aluminum. Among the more troublesome elements for aluminum separation are beryllium, gallium, and zinc, which undergo many similar reactions. However, 8-hydroxyquinoline will isolate aluminum from beryllium [*5*], cupferron can be used to precipitate gallium [*6*], and 8-hydroxyquinaldine will precipitate zinc but not aluminum [*7*].

ANTIMONY

The most important oxidation states for antimony are the +III and +V (−III being exhibited in the unstable gaseous stibine, SbH_3). Only the +III state can take the form of a cation (Sb^{3+}), but even it is more frequently encountered as the oxyanion, SbO^+ (antimonyl ion). An important separation is based on the distillation of $SbCl_3$ at around 200°C, although arsenic will accompany it unless it is removed first [*8*]. Traces of antimony quantitatively coprecipitate with iron in an ammonium hydroxide separation. Antimony sulfide precipitates from acid solution and redissolves in basic sulfide solution, placing it among the so-called "arsenic group." Antimony (V) can be extracted with ethyl acetate from 1.5 *M* HCl containing citric and oxalic acids [*9*]. The principal difficulty with this element is its tendency to hydrolyze as a hydrous oxide. Complexing agents such as oxalate or tartrate prevent this effect.

ARSENIC

Arsenic shows the same oxidation states as antimony but exhibits no cation. The +III oxidation state is represented by arsenite ion (AsO_3^{3-}) and the +V oxidation state by arsenate ion (AsO_4^{3-}). Arsine gas (AsH_3), somewhat more stable than stibine, represents the -III state. Arsenic can be isolated by distillation as $AsCl_3$ from dilute sulfuric acid solution at around 100°C (only germanium, if not previously removed, accompanies it) [*10*]. The sulfide precipitates in acid solution and dissolves in basic sulfide solution. Trace amounts of arsenic are quantitatively carried down with iron in an ammonium hydroxide precipitation.

Silver arsenate precipitation in the presence of fluoride ion in weakly basic solution is an alternative to distillation for separating arsenic from antimony [*11*]. The generation of arsine gas and its collection in a pyridine solution of silver diethyldithiocarbamate is the basis of an important spectrophotometric method [*12,13*]. Arsenic (V) can be precipitated with magnesia mixture ($MgCl_2 + NH_4Cl + NH_4OH + H_2O$) from ammoniacal solution, the isolate ($MgNH_4AsO_4{\cdot}6H_2O$) generally being ignited to $Mg_2As_2O_7$ [*14*].

BARIUM

Barium, the heaviest but one of the alkaline earths (the Group IIA elements), occurs in solution as Ba^{2+} ion. Its most important separation is precipitation as the sulfate. The particles of $BaSO_4$ are very fine, requiring Ostwald ripening and other precautions for quantitative retention. For separation from calcium and strontium, precipitation of barium as the chromate is the preferred method [*15*]. The mercury cathode can be used to separate out many elements from perchloric acid solution, leaving barium (and the other alkaline earths) untouched. A sodium carbonate fusion leached in neutral water yields an insoluble precipitate of $BaCO_3$; the other alkaline earths behave similarly. A yellow precipitate forms with ethylmethyl picrate that separates barium from calcium and strontium [*16*]. A precipitate forms with ammonium oxalate and with diammonium phosphate, but neither is suitable for quantitative work. Chloranilic acid precipitates barium along with calcium and strontium.

BERYLLIUM

This element, which has the smallest "crystallographic" radius of the Group IIA series as Be^{2+} ion in a lattice solid, also has the largest hydrated radius as $(Be(H_2O)_4)^{2+}$ ion in aqueous solution. Like aluminum, it tends to form a protective oxide during acid dissolution of the metal. It also behaves amphoterically, the hydroxide dissolving in strong base to form beryllate ion, $Be(OH)_4^{2-}$. Beryllium shows a strong tendency to form covalent bonds.

Beryllium is not plated by the mercury cathode, which allows its separation from the transition metals and other elements. It does not precipitate with 8-hydroxyquinoline, which allows its separation from aluminum. And it does not precipitate with cupferron, which allows its separation from zirconium, hafnium, titanium, and vanadium, among others. A sodium hydroxide separation places beryllium in the filtrate.

An ammonium hydroxide separation (pH 8.5) is used to precipitate beryllium after its isolation from other elements [*17,18*]. In the presence of EDTA, KCl, and NH_4OH (pH 9.4), butyric acid forms an ion association complex with beryllium that extracts into chloroform, leaving iron (III), copper (II), and aluminum in the aqueous phase [*19,20*].

BISMUTH

Bismuth exhibits the +III oxidation state in a series of complex cations, such as $(Bi_6(OH)_{12})^{6+}$. The +V oxidation state is usually seen only in the oxidizing "bismuthate" reagent. Bismuth may be separated from lead, zinc, copper, and cadmium by precipitation as bismuth oxybromide (BiOBr) [*21*]. The sulfide precipitates from acid solution and does not redissolve in basic sulfide solution, placing bismuth in the "copper group." Bismuth appears in the insoluble residue when a sodium carbonate fusion is leached in neutral water. It can be precipitated with 8-hydroxyquinoline from acetic acid/acetate solution and also by cupferron from dilute HCl solution [*22*].

The cupferrate can also be extracted with chloroform [*23*]. Treatment with ammonium hydroxide and hydrogen peroxide will cause the precipitation of a hydrated bismuth oxide. An important separation is based on the precipitation of bismuth as $BiPO_4$ with $(NH_4)_2HPO_4$ [*24*]. Several solvent extraction systems will isolate traces of bismuth, including dithizone/chloroform [*25*], diethyldithiocarbamate/carbon tetrachloride [*26*], and TOPO/iodide/ MIBK [*27*].

BORON

The only stable oxidation state of boron in aqueous solution is +III. It has an exceedingly complex chemistry with a pronounced tendency to form rings. Such ring structures even form in aqueous solutions of simple borates. Boron also forms a number of volatile compounds, including the halides, BF_3, BCl_3, and BBr_3, which are useful for the element's elimination from aqueous solutions, and the methyl borate ester, $B(OCH_3)_3$, which is the basis for an important distillation separation. The methyl borate is distilled out of strong acid solution and collected in dilute caustic or limewater, where it is saponified: [$B(OCH_3)_3 + 3H_2O \rightarrow 3CH_3OH + B(OH)_3$ and $H_3BO_3 + NaOH \rightarrow NaBO_2 + 2H_2O$] [*28*].

A mixed-bed ion exchange separation that removes both matrix cations and acid dissolution anions was developed for the mannitol complex pH titration procedure [*29*]. Boron is not removed by the mercury cathode, and thus the separation is ideal for isolating boron for ICP/OES determination. However, that separation is no help in the presence of tungsten, which interferes on the 2496 Å boron line. In that case, the methyl borate distillation is called for. Boron can be extracted as the fluoride from cold solutions using various chlorinated solvents and reagents such as tetraphenylarsonium chloride [*30*] and methylene blue [*31*].

CADMIUM

Cadmium exhibits only the +II state. Its chemical behavior is similar to that of zinc except that it shows no amphoteric reactions. Cadmium is a "copper group" element—it precipitates in acid sulfide and does not redissolve in basic sulfide. Its soluble ammonium complex places it in the filtrate in an ammonium hydroxide separation. It precipitates with sodium hydroxide (and does not redissolve in excess caustic). It precipitates with 8-hydroxyquinoline (out of acetic acid/acetate solution) and with chloranilic acid. It can be electroplated onto a platinum gauze electrode from an alkaline solution containing cyanide [*32*]. Traces of cadmium can be extracted with dithizone/chloroform [*33*] or with diethyldithiocarbamate/carbon tetrachloride [*34*].

CALCIUM

Like all the alkaline earth elements, calcium shows only the +II oxidation state. Its carbonate and sulfate are less soluble than those of magnesium, but more soluble than those of strontium and barium. Like magnesium, but unlike the rest of the group, it is a soluble complex former. Calcium (and the other group IIA elements) are readily isolated with the mercury cathode. Calcium may be separated from magnesium by ion exchange on strongly basic anion exchange resin using ammonium citrate and citric acid eluents [*35*] or by a double precipitation of calcium with ammonium oxalate [*36*]. A rapid colorimetric method is based on the decrease in color of chloranilic acid after it is used to precipitate calcium, but most matrix elements must be low or absent [*37*]. Today, except for the mercury cathode approach, calcium is seldom separated since good instrumental approaches are available.

CERIUM

This first element of the lanthanide series manifests the characteristic rare earth oxidation state +III and also one higher stable state (quite uncharacteristic): +IV. Thus, cerium has an active redox chemistry. The ceric/cerous couple's half-cell potential differs with the acid medium employed, indicating mechanisms that involve coordination of the acid anion. Cerous ion (Ce^{3+}) is colorless, while ceric ion (Ce^{4+}) is orange/red in aqueous solution. Cerium can be oxidized to the +IV state with persulfate, then precipitated with potassium iodate to separate it from the other rare earths. Thorium, zirconium, and hafnium accompany cerium unless they have been previously removed [*38*].

Like the other rare earths, cerium is precipitated by ammonium hydroxide, by sodium hydroxide, by hydrofluoric acid, and by ammonium oxalate. Like them as well, it is efficiently isolated using the mercury cathode. A popular ICP/OES emission line (4186 Å) has a serious zirconium interference that lends itself to an extraction with 8-hydroxyquinoline/chloroform from an appropriately masked ammoniacal solution. The procedure was originally applied to the spectrophotometric determination of cerium in cast iron [*39*].

CESIUM

Cesium is the heaviest stable alkali metal. Like all of Group IA it shows only the +I oxidation state, and most of its compounds are ionically bonded. The metal reacts with explosive violence with water. Solutions of cesium yield a characteristic red/violet flame test (doublet at 4555 and 4593 Å). Cesium can be separated (along with potassium and rubidium) by precipitation with perchloric acid. Sodium, lithium, and all other metals will be found in the filtrate. Sodium tetraphenylborate will precipitate cesium, potassium, and rubidium as well [*40*]. A related compound, tetra(p-fluorophenyl)borate, will precipitate rubidium and cesium, but not potassium [*41*]. Crown polyethers are cyclic polymers with a ring structure composed of five, six, seven, or eight oxygen bridges. The central hole of certain of these compounds matches the size of the "crystallographic" cesium ion, allowing its extraction into a solvent such as chloroform [*42*].

CHROMIUM

Chromium shows a complex aqueous redox chemistry. Chromous ion, Cr^{2+}, is blue and unstable. It is readily oxidized to the stable, green chromic ion, Cr^{3+}. The +VI state is represented by chromate, CrO_4^{2-} (yellow) in basic solution ($pH > 6$) and in strong acid ($pH < 1$, where it exists as $H_2Cr_2O_4$). Between pH 2 and 6, chromate is in equilibrium with dichromate, $Cr_2O_7^{2-}$ (orange-red). Addition of hydrogen peroxide to acidic chromium (VI) solutions produces a flash of the dark blue peroxochromate that quickly fades to Cr^{3+} green.

The most important separation of chromium is its elimination from solution by the evolution of volatile chromyl chloride (CrO_2Cl_2)—a bromine-like liquid that boils at 117°C. It is formed by the reaction of chloride ion with a fuming perchloric acid solution of the chromium-bearing sample. It is seldom necessary to isolate chromium for its determination. In addition to the evolution of CrO_2Cl_2, there are many other means for its removal. Chromium appears in the filtrate after a sodium peroxide fusion/water leach. Chromium (III) precipitates with ammonium hydroxide and with sodium hydroxide, but chromium (VI) does not. Silver, mercury (I), barium, and lead all form insoluble chromates. Chromium is removed slowly on the mercury cathode.

COBALT

Cobalt has two common aqueous oxidation states, +II and +III, as evinced by pink cobaltous ion, Co^{2+}, and blue cobaltic ion, Co^{3+}, respectively. Of these, the +II state is favored in the absence of complexing species. The +III state is reduced by water. In the presence of ammonium hydroxide, however, the +III state is stable.

Separation of cobalt from iron or aluminum with ammonium hydroxide is never quantitative due to inclusion of cobalt in the precipitate. However, a zinc oxide suspension can make this separation cleanly if the amount of cobalt is not excessive [*43*]. Alpha-nitroso-beta-naphthol will precipitate cobalt from dilute HCl solution, but, except for nickel, the cobalt must be relatively matrix-free [*44*].

Cobalt can be very well separated from iron, nickel, and many other elements using chloride system anion exchange on a strongly basic resin like Bio-Rad AG 1-X8 [*45*]. The element plates well electrolytically onto a platinum gauze electrode from dilute ammonium hydroxide solution [*46*] and is removed efficiently on the mercury cathode. In the presence of thiocyanate and ammonium fluoride, the blue cobalt-tetraphenylarsonium ion association complex will extract into chloroform [*47*].

COPPER

Copper (I), which is colorless in solution, does not long persist in the presence of water (except as insoluble compounds like CuI). Copper (II) is blue as $(Cu(H_2O)_6)^{2+}$ and becomes darker blue as the ammonia complex. Copper (II) sulfide precipitates from acid solution and does not redissolve in basic sulfide solution. Sodium hydroxide precipitates $Cu(OH)_2$, while an ammonium hydroxide treatment forms the soluble ammonia complex.

Addition of a reducing agent like sulfurous acid produces Cu^+ and allows the precipitation of either the thiocyanate or the iodide. Copper can be separated from nickel, iron, and zinc by chloride system anion exchange, but in the presence of cobalt extreme care is required to obtain a clean separation [*48*]. Copper can be easily removed with the mercury cathode, and it plates well on platinum electrodes from dilute sulfuric and nitric acid solution [*49,50*]. Reduction to Cu^+ with hydroxylamine hydrochloride allows the formation of the neocuproine (2,9-dimethyl-1,10-phenanthroline) complex, which extracts into chloroform [*51*].

EUROPIUM

Element 63, near the middle of the lanthanide series, shows some redox chemistry that is lacking for most of the other rare earths (except cerium). Besides the expected +III state, exhibited by pale pink europic ion, Eu^{3+}, there is also a somewhat stable +II state, exhibited by colorless europous ion, Eu^{2+}. Advantage is taken of this property by passing a dilute HCl solution of the rare earths through a Jones Reductor (Zn-Hg amalgam) column. Europous ion forms on the column and is collected in standard ferric sulfate solution. The ferrous sulfate formed is then titrated. The less stable Sm^{2+} and Yb^{2+} do not form in a Jones Reductor and thus do not interfere [*52*].

GALLIUM

Gallium, like aluminum, shows only the +III oxidation state. It melts at 29.8°C and boils at 2070°C, thus showing the widest liquid range of any element. It undergoes many of the same reactions as aluminum and, like that element, exhibits amphoteric behavior [$Ga(OH)_3$ (i) + $NaOH \rightarrow NaGaO_2$ (s) + H_2O]. Gallium thus accompanies aluminum, beryllium, molybdenum, tungsten, chromium (VI), and vanadium in the sodium hydroxide filtrate.

Gallium can be extracted from 6 *M* HCl with ether, although traces of indium will accompany it. Iron will remain in the aqueous phase if it is first reduced by passing the solution through a silver metal reductor column. Once separated and in aqueous solution, ammonium hydroxide is an effective precipitant for gallium. The residue can then be ignited to the oxide for gravimetry.

Cupferron can be used to precipitate gallium in the presence of aluminum and indium, while 8-hydroxyquinoline will precipitate gallium in the presence of vanadium, tungsten, and molybdenum. Special care must be taken in both instances to ensure complete recovery and complete separations [*53*]. In the absence of oxidizing agents, potassium ferrocyanide will precipitate gallium (as well as zinc, zirconium, hafnium, and indium). The mercury cathode will serve to remove gallium, leaving aluminum in the electrolyte.

GERMANIUM

Germanium has a +II oxidation state, but the analytical chemist usually encounters the +IV state. It is a member of the "arsenic group" of sulfides, precipitating in acid sulfide solution and dissolving in basic sulfide solution. The chloride, $GeCl_4$, is volatile (b.p. 83.1°C), being easily distilled from the sample matrix, including elements like arsenic, tin, and antimony, whose chlorides distill at higher temperatures. Germanium is removed on the mercury cathode. It can also be extracted from 9 *M* HCl into carbon tetrachloride, then complexed by an alcoholic solution of phenylfluorone in the organic phase and measured spectrophotometrically [*54*].

GOLD

The +III oxidation state is nearly always encountered, although +I occurs in certain stable cyanide complexes. Gold is always complexed in aqueous solutions. Gold (III) extracts from 2 *M* HBr or 2 *M* HCl into isopropyl or ethyl ether. It is frequently separated as the metal, reduced from aqueous solution by sodium nitrite, ferrous sulfate, sulfur dioxide, or hydroquinone. It is part of the "arsenic group," precipitated by acid sulfide and soluble in basic sulfide. It precipitates with ammonium oxalate and with tetraphenylarsonium chloride. The umpire methods for gold assay are the ancient fire assay procedures.

INDIUM

Only the +III state is commonly encountered in aqueous solutions. Indium precipitates with ammonium hydroxide. It will precipitate with ammonium oxalate at pH 8 and with diammonium phosphate from ammoniacal solution. The sulfide precipitates from dilute acid solution (pH 2 to 3). Lead can be removed from indium by precipitation of $PbSO_4$. Indium can be extracted from a 1.5 *M* HI solution into ethyl ether [*55*]. The element is removed by the mercury cathode.

IRIDIUM

This platinum group metal has several well-defined aqueous oxidation states, +III and +IV being the most significant analytically. The +I and +VI occur in special complexes. It forms no volatile oxides or aqueous oxyanions, as osmium and ruthenium do. It is a member of the "arsenic group," the precipitated acid sulfide redissolving in basic sulfide. It can be precipitated with 2-mercaptobenzothiazole [*56*], but its separation from the platinum group elements is complex [*57*].

IRON

While the +IV and +VI occur in compounds, only the +II and +III states have an aqueous chemistry. Ferrous ion, Fe^{2+}, forms pale green complexes, while ferric ion, Fe^{3+}, is often seen as the bright yellow $FeCl_4^-$ ion. Iron is removed from solution easily on the mercury cathode. It extracts as Fe (III) from 6 *M* HCl into ethyl ether and precipitates with ammonium hydroxide and with sodium hydroxide. Cupferron precipitates the +III ion completely, but the +II ion only partially. Iron does not precipitate with acid sulfide, but will precipitate with the basic sulfide elements. Iron can be separated cleanly from nickel and chromium (VI) by an ammonium hydroxide precipitation, but traces of cobalt and copper will accompany the precipitate. Chloride system anion exchange is necessary to completely separate iron from cobalt and copper. Many procedures for iron determination, however, do not require a rigorous separation.

LANTHANUM

Lanthanum, strictly speaking, is not a lanthanide (just as scandium and yttrium are not). It is included here as representative of the properties of the rare earths (which we take to include all 17 elements). Typical of the series, only the +III oxidation state is exhibited. Like all the +III rare earths, lanthanum forms a precipitate with ammonium hydroxide, with sodium hydroxide, with hydrofluoric acid, and with oxalic acid. A water-leached sodium carbonate fusion leaves lanthanum in the insoluble residue. And electrolysis on the mercury cathode leaves it in the electrolyte solution. Ion exchange is a viable means to separate the entire series, which elute in reverse order due to the so-called "lanthanide contraction"—the ionic radius of the lanthanides *decreases* with increasing atomic number.

LEAD

The aqueous chemistry of lead involves the +II state almost exclusively, although +IV compounds exist. Precipitation by sulfate results in a separation that is not absolutely quantitative due to the solubility of $PbSO_4$, but which serves for all but the most accurate work [*58*]. Lead also precipitates as the chromate and as the molybdate. Traces of lead can be extracted with dithizone/chloroform from a medium of ammonium hydroxide, cyanide, and sulfite [*59,60*] and by TOPO/MIBK from a medium of hydrochloric acid, iodide, and ascorbic acid [*61*]. Lead can be separated by chloride system anion exchange [*62*]. On the mercury cathode, it is quantitatively removed from the electrolyte but not quantitatively deposited in the mercury. In electrogravimetry, it can be quantitatively deposited as PbO on the platinum anode.

LITHIUM

Li^+ is a very small ion, which explains the fact that its compounds with small anions are stable but those with large anions are unstable. Like all the alkali metals, only the +I state occurs. It produces a crimson flame test due to its emission line at 6708 Å. The chloride is soluble in ether/alcohol mixtures and in acetone, while the chlorides of the other alkali metals are not [*63*]. However, usually no attempt is made to separate it. Like the other alkali metals, it is not plated on the mercury cathode.

MAGNESIUM

Magnesium shows only the +II state typical of the alkaline earth metals. It precipitates from ammoniacal solution with 8-hydroxyquinoline. It also precipitates with diammonium phosphate and with sodium hydroxide. The phosphate separation allows its isolation from aluminum, zinc, iron, and tin. Like the other alkaline earth metals, it is not plated on the mercury cathode. The 8-hydroquinolate can be extracted into chloroform [*64,65*]. When a sodium carbonate fusion is leached in neutral water, magnesium appears in the insoluble residue. Magnesium can be separated from calcium, strontium, and barium by anion exchange using a citrate system [*66*].

MANGANESE

This element shows a number of oxidation states, but some are characteristic of only a few common compounds. The +II state is represented by manganous ion, Mn^{2+}, which is pale pink and quite stable. The +III state (manganic ion, Mn^{3+}) is rarely seen, being readily reduced to Mn^{2+} or dividing into MnO_2 and Mn^{2+}. The +IV state is represented by the water-insoluble MnO_2. The +VI state only forms in basic oxidizing media (dark green manganate ion, MnO_4^{2-}). The +VII state is the familiar dark purple permanganate ion, MnO_4^-. Manganese is removed incompletely on the mercury cathode. If present in large amount, it may precipitate as MnO_2 in the electrolysis cell but can be redissolved with a few drops of sulfurous acid.

Other techniques for removing manganese include intentional precipitation of MnO_2 from acid solution with potassium bromate [*67*] and precipitation of NH_4MnPO_4 with diammonium phosphate from ammoniacal solution [*68*]. Manganese does not precipitate with ammonium hydroxide, but may contaminate the ammonia precipitate if the solution is boiled too long or allowed to stand too long before filtration. Manganese does precipitate with sodium hydroxide and in basic sulfide media. In general, however, methods for manganese do not require its isolation.

MERCURY

The +II state (mercuric ion, Hg^{2+}) is stable and commonly encountered and the +I state (mercurous ion, Hg_2^{2+}) somewhat less so. No oxide, hydroxide, or sulfide of the +I state can be isolated, although the halides are stable. The equilibrium between these two oxidation states is often complex, especially in the presence of metallic mercury. Mercury (II) is a member of the "copper group," precipitating in both acid and basic sulfide media. HgS is the only acid sulfide that is insoluble in nitric acid. Mercurous chloride can be precipitated from hydrochloric acid solution by reduction with phosphorous acid, although Hg_2Cl_2 proves to be somewhat soluble.

It is relatively easy to reduce mercury to the metal with reducing agents like hydrazine or hypophosphorous acid. Both the metal and $HgCl_2$ are volatile (Hg: b.p. 357°C; $HgCl_2$: b.p. 302°C). Mercury plates out on the mercury cathode. The iodate, chromate, and oxalate are insoluble. Mercury can be extracted as a diethyldithiocarbamate [*69*] or a dithizone [*70*] chelate into carbon tetrachloride.

MOLYBDENUM

Molybdenum can occur in eight different oxidation states, but only three are ordinarily encountered in aqueous solutions: the +III state in ions like $MoCl_6^{3-}$; the +V in ions like $MoOCl_5^{2-}$; and the +VI in molybdate ion, MoO_4^{2-}, and its polymeric forms. The principal (nearly specific) precipitant for molybdenum is alpha-benzoinoxime. Only tungsten accompanies molybdenum (it does not precipitate completely in the absence of molybdenum). Molybdenum also precipitates with 8-hydroxyquinoline. Molybdenum is part of the "arsenic group," precipitating in acid sulfide solution and redissolving in basic sulfide solution. A sodium carbonate fusion followed by leaching with neutral water places molybdenum in the filtrate. It also appears in the filtrate in ammonium hydroxide and sodium hydroxide separations.

Removal on the mercury cathode is difficult and must usually be regarded as incomplete. Molybdenum is, however, completely extracted from 6 *M* HCl with ethyl ether. Both lead molybdate and silver molybdate are insoluble and can be used to separate the element [*71*]. Molybdenum is very effectively isolated by chloride/fluoride system anion exchange. Using this technique, clean separations from tungsten, niobium, and tantalum are achieved [*72*]. Molybdenum may be extracted away from traces of tungsten with toluene-3,4-dithiol/chloroform (prior to the reduction of tungsten and its extraction with the same reagent into butyl acetate) [*73*].

NICKEL

Despite some confusion in the older literature, there appears to be little basis for the occurrence of the +III state of nickel in aqueous solution. Thus the +II is the only oxidation state that need ordinarily concern the metals analyst. Dimethylglyoxime is a near specific precipitant for nickel from ammoniacal citrate solution (palladium partially accompanies nickel under these conditions and precipitates completely from dilute acid solution). Tendencies toward coprecipitation by elements like cobalt, iron, and copper can be handled by oxidation or complexation. Certain elements like zinc, copper, cobalt, and manganese consume reagent, and their presence requires an excess [*74*].

The nickel dimethylglyoximate can also be extracted into chloroform for spectrophotometric measurement. It is more sensitive when the extraction is preceded by oxidation with bromine, iodine, or persulfate, but requires rigorous control of conditions in this case. Traces of nickel are best extracted with the related compound, furildioxime [*75*]. Nickel precipitates with sodium hydroxide and appears in the filtrate in an ammonium hydroxide separation. Once the acid sulfide elements have been removed, nickel will precipitate with basic sulfide. It is easily removed on the mercury cathode and easily separated from iron and cobalt by chloride system anion exchange [*76*].

NIOBIUM

Niobium typically exhibits the +V oxidation state in aqueous solutions of HF, taking forms such as $NbOF_5^{2-}$ or NbF_6^-, depending on the free HF concentration. Niobium can be cleanly separated from tungsten, molybdenum, and tantalum by chloride/fluoride system anion exchange [*77,78*]. Niobium yields precipitates with ammonium hydroxide and with dilute sodium hydroxide. However, after a potassium carbonate fusion and a neutral water leach, niobium appears in the filtrate. The element precipitates with cupferron from dilute acid solution—a technique that serves best as a "finishing" isolation after some preliminary cleanup of the solution. Small amounts of niobium are best precipitated with cupferron in the presence of a carrier such as zirconium or hafnium. Niobium can be hydrolyzed quantitatively as the hydrous oxide by fuming the solution in perchloric acid, adding sulfurous acid to the cooled, diluted solution, and boiling. The mercury cathode does not plate niobium, but it tends to hydrolyze, and some is lost in subsequent filtration of the electrolyte.

OSMIUM

This platinum group element most closely resembles ruthenium in its properties (for example, both form volatile tetroxides). The most common oxidation state is the +IV in which the $OsCl_6^{2-}$ ion is encountered. The +VI is represented by osmate ion, $OsO_2(OH)_4^{2-}$, and the +VIII by the volatile OsO_4 compound (b.p. 130°C). The distillation of the tetroxide from nitric acid solution is the most important means of separation. The distillate is collected in SO_2-saturated 1:1 HCl:H_2O and then precipitated as hydrous OsO_2 with sodium bicarbonate. The filtered and ignited osmium dioxide, in turn, can be reduced to osmium metal by annealing in hydrogen [*79*]. Osmium is a "copper group" metal, forming brownish-black precipitates in both acid sulfide and basic sulfide media. Reddish-brown $Os(OH)_4$ forms with either sodium hydroxide or ammonium hydroxide. Osmium is completely removed on the mercury cathode even though it is partially volatilized and partially plated.

PALLADIUM

Like platinum, palladium exhibits the +II and the +IV oxidation states, but the two metals differ in the relative importance of the two states in their aqueous chemistry. With palladium, the +II state, as evinced by such ions as yellow $PdCl_4^{2-}$, is dominant. Dimethylglyoxime is nearly a specific precipitant for palladium, producing a yellow precipitate from very dilute HCl [*80*]. The related compound, furildioxime, is more sensitive than dimethylglyoxime for solvent extraction of traces [*81*]. Iodide will react with palladium to form black insoluble palladous iodide, PdI_2. Both sodium hydroxide and ammonium hydroxide yield curious brown and red (respectively) precipitates of complex or uncertain stoichiometry that redissolve in excess reagent. Palladium is removed on the mercury cathode. Palladium can be chemically reduced to the metal with hydrazine sulfate or formic acid or by hydrogen annealing of an ignited oxide residue.

PHOSPHORUS

Phosphorus forms primarily covalent bonds, and thus its aqueous chemistry is nearly exclusively that of oxyanions. The -III state is represented by gaseous phosphine, PH_3, the +III state by the low boiling phosphorus trihalides, and the +V state by phosphate ion, PO_4^{3-}. There are numerous other oxidation states. Phosphorus is quantitatively coprecipitated with iron in an ammonium hydroxide separation. It is found in the filtrate of sodium hydroxide precipitations. Zirconium ion can be used to precipitate phosphorus as zirconium phosphate, which can be filtered, ignited, and fused with sodium carbonate. But the principal means of phosphorus isolation is by precipitation as ammonium phosphomolybdate $[(NH_4)_3PO_4{\cdot}12MoO_3]$, which may be titrated with standard base or dried and weighed as the monohydrate [*82,83*]. Precipitation with magnesia mixture ($MgCl_2$ and NH_4Cl) under ammoniacal conditions isolates the element as magnesium ammonium phosphate, which allows its separation from tungsten, molybdenum, and vanadium [*84,85*]. Phosphorus has been isolated by ion exchange using organic resins or alumina [*86*].

PLATINUM

The +II and the +IV oxidation states are typical. The former is rare in aqueous solution, but is represented by $PtCl_4^{2-}$ (chloroplatinous ion); the latter is represented by many complexes including the red $PtCl_6^{2-}$ (chloroplatinic ion). Reduction to the metal is possible with a number of reducing agents: stannous chloride in acid solution yields red colloidal platinum, and formaldehyde in basic solution yields platinum black. The acid sulfide is dark brown and soluble in basic sulfide solution. Precipitation of the sparingly soluble, yellow ammonium chloroplatinate, $(NH_4)_2PtCl_6$, is sometimes employed as a first separation. The other members of the platinum group may be precipitated away from platinum by oxidizing the hot acid solution with bromate and neutralizing with a hydroxide (osmium and ruthenium are usually distilled off first) [*87*]. Platinum, like the other platinum group metals, is plated on the mercury cathode.

POTASSIUM

As with all the alkali metals, only the +I state occurs. The structure and properties of potassium compounds closely resemble the analogous ammonium compounds. Potassium can be precipitated as the perchlorate [*88*], as the chloroplatinate [*89*], as the periodate [*90*], and as the tetraphenyl borate [*91*]. It is not plated on the mercury cathode. Certain crown polyethers will allow the extraction of potassium ion into solvents like chloroform [*92*]. Potassium is usually determined without separation by atomic absorption or optical emission techniques.

RHENIUM

Rhenium (like the radioactive element technicium with which it shares many properties) shows the +VII oxidation state in both a volatile oxide (Re_2O_7) and an oxyanion (perrhenate ion, ReO_4^-). The +IV state is also common in aqueous solution, as exemplified by blue-green $ReCl_6^{2-}$, which tends to hydrolyze, and ReF_6^{2-}, which does not. Rhenium can be evolved away from the sample matrix by cautious dropwise additions of HNO_3 to a fuming sulfuric acid solution. Strongly basic anion exchange resin will retain rhenium from 10% (w/v) sodium hydroxide solution, but allow molybdenum to elute [*93*].

In the chloride/fluoride anion exchange system, rhenium can be separated from tungsten, molybdenum, niobium, and tantalum, being finally eluted with noncomplexing 10% perchloric acid [*94*]. Rhenium forms precipitates with tetraphenylarsonium chloride, with nitron, and with sulfide (in both acid and basic solution) [*95*]. Significantly, it does *not* precipitate with alpha-benzoinoxime, allowing a separation from molybdenum (with which it occurs in ores).

RHODIUM

The +III oxidation state is nearly the only one encountered in aqueous solution, as shown by the yellow $Rh(H_2O)_6^{3-}$ ion. The +I state occurs in certain complexes. Rhodium is placed in the "copper group," its acid and basic sulfides being both insoluble. Ignition of the sulfide residue in hydrogen allows the reduced metal to be weighed. The separation of rhodium from the other platinum group metals is complex but feasible. After osmium and ruthenium are distilled off, palladium, rhodium, and iridium are precipitated as hydrous oxides with bromate and bicarbonate, leaving platinum in the filtrate. Then palladium is precipitated with dimethylglyoxime. Finally rhodium is precipitated with titanous chloride, leaving iridium in the filtrate [*96*]. A separation of rhodium and iridium is also possible with sodium nitrite in a sodium carbonate medium. Addition of sulfide to the acidified solution will precipitate dark brown rhodium sulfide [*97*].

RUBIDIUM

As an alkali metal rubidium exhibits only the +I oxidation state. The ionic radius of Rb^+ ion is similar to that of Tl^+. The red-violet color it imparts to a flame is similar to that of potassium, showing emission doublets at 4202/4215 Å and 7811/7950 Å. It precipitates with perchlorate, chloroplatinate, and tetraphenyl borate (as do potassium and cesium). It also precipitates with tetra(*p*-fluorophenyl) borate (accompanied by cesium only) [*98*]. Rubidium can also be extracted into chloroform with crown polyethers [*99*].

RUTHENIUM

Unlike osmium (which it resembles), ruthenium's most commonly encountered oxidation state is the +III, exemplified by $Ru(H_2O)_6^{3+}$. The volatile tetroxide, RuO_4, represents the +VIII oxidation state. Both the ruthenate ion RuO_4^{2-} (+VI) and the perruthenate ion RuO_4^- (+VII) are known. The primary means of separation is the distillation of RuO_4, which is usually performed after osmium is removed by distillation. The remaining solution is evaporated to dryness with HCl to expel NO_x gases, sulfuric acid is added, and the solution is taken to fumes of SO_3 and then distilled with sodium bromate. The ruthenium distillate is collected in HCl saturated with SO_2 [*100*]. Ruthenium is a "copper group" element, its acid sulfide and its basic sulfide being insoluble.

SELENIUM

Like the other members of group VIB selenium exhibits −II, +IV, and +VI oxidation states. The +IV is commonly seen in aqueous solution as SeO_3^{2-} and $HSeO_3^-$ ions, the +VI as H_2SeO_4, $HSeO_4^-$, and SeO_4^{2-}. Gaseous H_2Se represents the −II state. Selenium is commonly separated as the element, reduced with hydrazine sulfate, sulfurous acid, stannous chloride, or hydroxylamine hydrochloride. It accompanies iron in the precipitation with ammonium hydroxide. As a member of the "arsenic group," the +IV element precipitates with acid sulfide and redissolves in basic sulfide solution. Selenium can be extracted with 3,3′-diaminobenzidine into toluene as the piazselenol complex that can be measured spectrophotometrically [*101*]. If selenium must be separated from tellurium, it should be precipitated as the red elemental form with SO_2 or hydroxylamine hydrochloride. Under such mild reducing conditions, tellurium does not precipitate [*102*].

SILICON

The metals analyst usually sees silicon in the +IV oxidation state, either as the oxide, SiO_2, or as a silicate such as $SiO_2(OH)_2^{2-}$. In fact, silicon chemistry is very complex , the element forming rings and chains with oxygen, as well as other complex structures that include other species. Silicon is separated by precipitation and dehydration of SiO_2. It is also volatilized away from the sample matrix as hydrofluosilicic acid, H_2SiF_6, or silicon tetrafluoride, SiF_4. In the time-honored dehydration gravimetric procedure, boron accompanies the SiO_2, although it is rarely a significant source of error. The so-called double dehydration procedure takes two distinct forms—in one the filtrate is dehydrated to incorporate losses for high levels, and in the other the residue is reprocessed to exclude contaminants. Sometimes it is necessary to substitute dehydrating acids due to the sample matrix; thus, $HClO_4$ is used in place of H_2SO_4 if elements that form insoluble sulfates are present. Silicon forms a heteropoly acid with molybdate, which can be extracted with butyl alcohol for spectrophotometric measurement.

SILVER

Silver shows only the +I oxidation state in ordinary aqueous chemistry. Precipitation with chloride allows separation from most elements except lead, mercury (I), thallium (I), and large amounts of bismuth and antimony. Silver precipitates with sodium hydroxide, but is soluble in ammonium hydroxide. It can be electrolytically plated from oxalate or persulfate solution. Both the acid sulfide and the basic sulfide are insoluble. Traces of silver are extracted from iodide/ascorbic acid with TOPO/MIBK [*103*]. The precipitated chloride is photosensitive and must be protected from light.

SODIUM

Only the +I state occurs. Sodium can be separated by cation exchange and is often determined by ion chromatography. It is retained in the electrolyte in mercury cathode electrolysis, affording a convenient means of removing extraneous matrix elements. Precipitation as sodium zinc uranyl acetate was a classic procedure for many years. The compound is sparingly soluble in water, but less so in alcohol. Flame emission, flame AA, and ICP/OES are good approaches for sodium, generally requiring no separations.

STRONTIUM

Like the other alkaline earth elements, only the +II state is seen with strontium. The sulfate is insoluble, but not to the degree of $BaSO_4$. It can be separated from barium and magnesium by precipitation as the oxalate. Like the other alkaline earths, it does not plate out on the mercury cathode. When a sodium carbonate fusion is leached in neutral water, strontium is found in the precipitate. Precipitation with 8-hydroxyquinoline from ammoniacal solution is questionable, some reports suggesting that the separation is incomplete.

SULFUR

We see sulfur in its +VI state as sulfuric acid, H_2SO_4,; in its +IV state as sulfite ion, SO_3^{2-} (there is reason to believe that sulfurous acid, H_2SO_3, although popularly recognized, does not actually exist as such); and in its −II state as H_2S gas. Sulfur is included here because, unlike carbon, it exhibits some useful solution inorganic analytical chemistry. For example, it can be precipitated as barium sulfate. In this separation, typically sulfur is oxidized with bromine water, then iron is reduced with aluminum metal in dilute acid solution prior to the addition of barium chloride solution. Hydrogen sulfide can be evolved by treatment of the finely divided test portion with acid, the gas being collected and measured. Sulfate can also be separated by ion exchange on a column of activated alumina [*104*]. Today most sulfur determinations are performed by instrumental techniques in which the solid sample is hot extracted in oxygen.

TANTALUM

The +V state is usually observed in aqueous solution; it takes forms such as TaF_6^- and TaF_7^{2-}. Like niobium, but to an even greater degree, tantalum shows a tendency to hydrolyze in acid solution in the absence of fluoride, oxalate, or some other complexing agent. Tantalum is most effectively separated from elements such as titanium, molybdenum, niobium, and rhenium by chloride/fluoride system anion exchange [*105,106*]. Precipitation with cupferron followed by ignition to Ta_2O_5 is commonly employed after ion exchange.

Tantalum can also be intentionally hydrolyzed as the hydrous oxide by fuming with perchloric acid, adding sulfurous acid to the cooled, diluted solution, and boiling for several minutes. Tantalum also precipitates with ammonium hydroxide and with dilute sodium hydroxide, but it is (at least partially) found in the filtrate of a water-leached potassium carbonate fusion. Tantalum does not plate out on the mercury cathode, but it is very likely to hydrolyze in most electrolyte media used.

TELLURIUM

Tellurium occurs in the +IV state as, for example, $TeCl_6^{2-}$ ion and in the +VI state as tellurates such as $TeO_2(OH)_4^{2-}$. H_2Te gas is not stable, but the -II state occurs in telluride salts. Tellurium is normally separated by reduction to the elemental form. This process requires a strong reducing agent such as hydrazine sulfate or sodium hypophosphite. If arsenic is present, it is removed first either by distillation or by precipitation as the element by means of a reducing agent too mild to precipitate tellurium [*107*]. Traces of tellurium (and selenium) are quantitatively coprecipitated with iron in an ammonium hydroxide separation. Tellurium, like selenium, is a member of the "arsenic group," precipitating in acid sulfide solution but not in basic sulfide solution.

THALLIUM

Unlike the other members of Group IIIB that exhibit only a +III oxidation state, thallium shows both the +I and +III states. And the +I state (as thallous ion, Tl^+) is significantly more stable than the +III state (as thallic ion, Tl^{3+}). Thallium imparts an emerald-green color to a colorless flame due to an emission line at 5350 Å. It can be extracted as Tl (III) into ethyl ether from 6 *M* HCl [*108*]. Black thallium (I) sulfide will precipitate from weak acid or basic sulfide solution. Chromate, chloride, and iodide each form insoluble precipitates with thallium (I). Ammonium hydroxide and sodium hydroxide both form the brown precipitate $Tl(OH)_3$ with thallium (III), but no precipitate forms in either case with thallium (I). Traces of thallium can be extracted from iodide/ascorbic acid solution with TOPO/MIBK [*109*].

THORIUM

The +IV oxidation state is the only state observed in aqueous solution. This is untypical of the actinides, where +III tends to be the dominant state. The precipitation with oxalate from dilute acid solution is a principal means of separation from most elements, including zirconium and titanium [*110*]. However, it affords no isolation from the rare earths. Mercury cathode electrolysis similarly serves to separate thorium from many elements since it does not plate, but the rare earths, titanium, and zirconium accompany it. Precipitation of thorium iodate, $Th(IO_3)_4$, leaves the lanthanides in solution (but titanium and zirconium precipitate). Thorium precipitates with ammonium hydroxide, with sodium hydroxide, and with hydrofluoric acid. Ion exchange separations are also known [*111,112*].

TIN

Tin is the only Group IVB element with an active redox chemistry. The +IV state is stable but with a marked tendency to hydrolyze as the hydrous form of SnO_2. The +II state acts as a reducing agent in chloride solution ($SnCl_3^- + 3Cl^- \rightarrow SnCl_6^{2-} + 2e^-$). Tin is a member of the "arsenic group"—its acid sulfide precipitates, but dissolves in basic sulfide solution. Tin can be separated by distillation at 140°C with HCl/HBr. Arsenic and antimony are generally each first removed by means of previous distillation procedures [*113*].

Tin is precipitated by ammonium hydroxide, but it appears in the filtrate of a sodium hydroxide separation. In the absence of iron (which contaminates the precipitate), a simple oxidizing hydrolysis with nitric acid will produce insoluble metastannic acid (H_2SnO_3) that can be ignited to SnO_2. Tin can also be precipitated with cupferron. Traces of tin may be extracted from iodide/ascorbic acid solution with TOPO/MIBK [*114*] and from chloride/sulfate solution with TEHPO/cyclohexane [*115*].

TITANIUM

The aqueous chemistry of this element is primarily that of the +IV oxidation state, although many other states occur. The +IV state is seen as TiF_6^{2-}, $TiCl_6^{2-}$, and in oxychloro complexes like $TiO_2Cl_4^{4-}$. The purple +III state is primarily represented by the reducing agent titanous chloride, $TiCl_3$, although $Ti(H_2O)_6^{3+}$ will form whenever the metal is dissolved in either sulfuric or hydrochloric acid. Titanium precipitates with ammonium hydroxide and also with sodium hydroxide. It is found in the insoluble residue when a cooled carbonate fusion has been water leached.

Titanium forms a lemon-yellow precipitate with cupferron. It is not plated on the mercury cathode. The chloride/fluoride anion exchange system will separate titanium from molybdenum, niobium, tantalum, and rhenium, but not from tungsten, zirconium, hafnium, and vanadium, which elute with it [*116,117*]. Tungsten and vanadium are placed in the filtrate in a sodium hydroxide separation, and zirconium and hafnium can be precipitated with *p*-bromomandelic acid or with diammonium phosphate in the presence of hydrogen peroxide. Some chemical methods for titanium do not require much or any separation.

TUNGSTEN

Like molybdenum, tungsten can exist in many oxidation states, but only the +III, the +V, and the +VI are commonly encountered in aqueous solution. Of these, the +VI is the most important; it is represented by tungstate ion, WO_4^{2-} in basic solution and by various polymeric forms in dilute acid. In strong acid in the absence of complexing species, the hydrous oxide $WO_3 \cdot 2H_2O$ precipitates. Tungsten is quantitatively precipitated as the hydrous oxide by fuming in perchloric acid, cooling, then adding HCl, hot water, and cinchonine to the solution. Other approaches to the acid hydrolysis of tungsten trioxide are also possible [*118*], but in all cases the ignited residue is impure. When employed as a gravimetric finish, the weighed oxide is always treated with sodium hydroxide and ammonium hydroxide in a series of operations; then the impurities are weighed and used to correct the result.

Tungsten is quantitatively coprecipitated with molybdenum by alpha-benzoinoxime. It does not completely precipitate in the absence of molybdenum. Tungsten appears in the filtrate of a sodium hydroxide separation and in the filtrate of a water-leached carbonate fusion. Chloride/fluoride system anion exchange allows the separation of tungsten from molybdenum, niobium, tantalum, and rhenium, but titanium, vanadium, zirconium, and hafnium accompany the tungsten fraction. Tungsten is not separated on the mercury cathode, but some is likely to hydrolyze. The chelate that forms with toluene-3,4-dithiol can be extracted into butyl or amyl acetate (after molybdenum has first been removed by extraction under different conditions with the same reagent) [*119,120*].

URANIUM

The +III, +IV, and +VI oxidation states are observed in aqueous solution. They are represented, respectively, by U^{3+} ion, which is reddish-brown, U^{4+} ion, which is green, and UO_2^{2+} (uranyl) ion, which is yellow. This order also represents increasing stability. The uranyl ion is easily formed by oxidation of U^{4+}, but, once formed, it is difficult to reduce. In the absence of vanadium and carbonates, sodium hydroxide and ammonium hydroxide are both useful precipitants for uranium. In the presence of either, both separations fail. Special care is required, therefore, in reagent selection and to prevent the excessive absorption of atmospheric CO_2 [*121*]. Ammonium carbonate, on the other hand, quantitatively places uranium in the filtrate, allowing its separation from iron, aluminum, and other elements. Cupferron precipitates uranium (IV) but not uranium (VI). Uranium does not plate out on the mercury cathode. Extraction is feasible from a nitric acid solution containing a nitrate salt using ethyl ether [*122*]. Many other solvent extraction [*123*] and ion exchange [*124*] procedures have been used.

VANADIUM

Vanadium has a very complex aqueous chemistry, exhibiting the +II, +III, +IV, and +V oxidation states. The +II state (violet V^{2+} ion) is unstable to air oxidation. The +III state is exemplified by vanadic ion, V^{3+}, which is blue. The most stable state is the +IV, as shown by blue VO^{2+} ion and by many other oxycations and oxyanions. The +V state is illustrated by vanadyl ion, VO_2^+, which is light yellow, and vanadate (VO_4^{3-}) and metavanadate (VO_3^-), which are orange. The latter two ions are phenomena of basic solutions. In fact, the actual species that occur in solution for each oxidation state are often considerably more complex than this picture provides. Vanadium occurs in the filtrate of a sodium hydroxide separation. It is also frequently separated from iron by a sodium hydroxide/sodium peroxide precipitation, where it again appears in the filtrate. It quantitatively accompanies iron in an ammonium hydroxide precipitation, but, in the absence of iron or aluminum, it does not precipitate. Vanadium is not plated on the mercury cathode. Vanadium (V) precipitates with cupferron. In a chloride/fluoride anion exchange separation, vanadium accompanies the titanium, tungsten, zirconium, and hafnium.

ZINC

In aqueous solution under ordinary conditions, only the +II oxidation state is seen. Zinc is amphoteric, the precipitated hydroxide dissolving in excess base to form the zincate ion [ZnO_2^{2-}, or, more correctly, $Zn(OH)_4^{2-}$]. Zinc sulfide precipitates from dilute acid solution (pH 2 to 3) once the "acid sulfide group" has been removed and also from basic sulfide solution. It appears in the filtrates of both ammonium hydroxide and sodium hydroxide separations, although it tends to adsorb on the surface of chromium (III) and iron precipitates. Insoluble zinc carbonate appears in the residue from the water leach of a carbonate fusion.

Precipitation with diammonium phosphate is sometimes employed. The precipitate can be ignited to $Zn_2P_2O_7$ [*125*]. Copper is conveniently removed by plating it on a platinum electrode from dilute nitric acid/sulfate solution or by ionic displacement on granules of lead from a boiling sulfate solution. Zinc and aluminum are both precipitated from dilute acid by 8-hydroxyquinoline, but only zinc precipitates with the derivative, 8-hydroxyquinaldine. Dithizone extraction with carbon tetrachloride from an appropriately masked solution is effective for traces of zinc [*126*]. Zinc can be separated by chloride system anion exchange, using very dilute HCl [*127*].

ZIRCONIUM

Zirconium exhibits nearly the same atomic and ionic radii as hafnium (due to the effect of the "lanthanide contraction," discussed briefly below). In consequence, the aqueous chemistry of these two elements is nearly identical. The only important oxidation state is the +IV, which takes the form of the zirconyl ion (usually written ZrO^{2+}). There is a tendency to form strong soluble complexes with sulfate ion. *p*-Bromomandelic acid is a specific precipitant for zirconium (and hafnium), but is usually applied after some preliminary separations. Weighing the mixed Zr + Hf *p*-bromomandelates, igniting to the oxides, and reweighing can be used to estimate the relative concentrations of the two elements [*128*].

Zirconium precipitates with cupferron, with ammonium hydroxide, and with sodium hydroxide. In a water-leached carbonate fusion, it is found in the insoluble residue. It is not plated out on the mercury cathode, and it does not precipitate with hydrofluoric acid or with oxalate. It *does* precipitate with diammonium phosphate from dilute sulfuric acid containing a little hydrogen peroxide—a procedure that yields a clean separation from titanium [*129*]. Traces of zirconium can be extracted from 7 *M* nitric acid with TOPO/cyclohexane [*130*]. Zirconium accompanies the tungsten, titanium, and vanadium fraction in chloride/fluoride anion exchange.

OTHER ELEMENTS

We are not quite finished because we have skipped over some elements that require a few words. The *halogens* are sometimes determined in metals analysis labs in water and process solutions; fluorine in slags and chlorine in titanium are also common requests. The halogens all occur in aqueous solution in the -I oxidation state. The +V and +VII states are also common for chlorine, bromine, and iodine. The -I state is shown by the free anions: F^-, Cl^-, Br^-, and I^-; the +V state by chlorate (ClO_3^-), bromate (BrO_3^-), and iodate (IO_3^-); and the +VII state by perchlorate (ClO_4^-), perbromate (BrO_4^-), and periodate (IO_4^-). *Fluorine* is commonly separated by some version of the classical Willard-Winter distillation in which steam is used to expel H_2SiF_6 from sulfuric or perchloric acid solution [*131*]. The element is similarly expelled as an interference (as SiF_4) by fuming with sulfuric or perchloric acid. *Chlorine*, *bromine*, and *iodine* are commonly precipitated as light-sensitive silver compounds.

Hafnium undergoes all the same chemistry as zirconium, but the two elements can be separated by ion exchange using a sulfuric acid system and a strongly basic anion exchange resin [*132*]. The reason for the similarity of the chemistry of these two elements derives ultimately from the "lanthanide contraction," a term that describes the regular *decrease* in atomic radius with *increasing* atomic number for the third transition series. Lanthanum (Atomic No. 57) thus has the largest radius, and lutetium (Atomic No. 71) has the smallest radius. Hafnium (Atomic No. 72), as a result, has an unexpectedly small radius that proves to be nearly identical to that of zirconium (Atomic No. 40).

Another result of the lanthanide contraction is that the lanthanides elute "backwards" in many ion exchange schemes. The lanthanide contraction effect derives ultimately from the decrease in nuclear shielding by the 4f shell electrons with each rise in atomic number. Beyond this difference, the rare earths are remarkably similar in chemical properties. Scandium, yttrium, and lanthanum are not "lanthanides" *per se* but share enough chemistry to be included in the "rare earths." The +III oxidation state is dominant throughout the series, with only cerium (+IV), europium (+II), samarium (+II), and ytterbium (+II) exhibiting alternative states. We have already discussed the first two of this subset, and both Sm^{2+} (red) and Yb^{2+} (yellow) are unstable in aqueous solution.

The rare earths (for our purposes *scandium*, *yttrium*, *lanthanum*, *cerium*, *praseodymium*, *neodymium*, *promethium* (radioactive), *samarium*, *europium*, *gadolinium*, *terbium*, *dysprosium*, *holmium*, *erbium*, *thulium*, *ytterbium*, and *lutetium*) all undergo the separation reactions described above under "Lanthanum." There is an interesting regular order to the colors of the free ions in aqueous solution. Thus, La^{3+}, Ce^{3+}, Gd^{3+}, Yb^{3+}, and Lu^{3+} are colorless; Pr^{3+}, and Tm^{3+} are green; Nd^{3+} and Er^{3+} are violet; Eu^{3+} and Tb^{3+} are pink; and Sm^{3+}, Dy^{3+}, and Ho^{3+} are yellow.

Finally, we have *carbon*, *oxygen*, *nitrogen*, and *hydrogen*, which are all critical to metals analysis work, but which are seldom treated by aqueous chemical techniques (we have discussed sulfur previously). These elements are typically determined by hot extraction techniques (as is sulfur). Nitrogen by the Kjeldahl approach—in which NH_3 is steam distilled from a strong caustic solution of the sample—is now only rarely employed. Carbon and sulfur are reacted with oxygen by melting the solid sample in a high-frequency induction field in a flowing stream of oxygen. Carbon dioxide is either absorbed in Ascarite (NaOH on alumina) and weighed, or measured by thermal conductivity or infrared absorption. Sulfur dioxide may be titrated with iodate or measured by thermal conductivity or IR absorption. Nitrogen, oxygen, and hydrogen are evolved thermally in a flowing inert gas stream and measured by thermal conductivity or, sometimes, mass spectrometry. In some instruments, oxygen is measured by the IR absorption of its reaction products with carbon (CO and/or CO_2).

ENVOI

This chapter has provided a sketchy overview of the separations that can be useful in isolating and concentrating elemental analytes. It is not exhaustive nor complete in its treatment of the subject. The trained analyst must remain flexible and scour the literature for alternate approaches that suit a specific problem. There are many paths through a maze, and the familiar turn is not always the correct one.

REFERENCES

NOTE, In addition to the following reference list, these additional sources were used extensively throughout this chapter: Cotton, F. A. and Wilkinson, G., *Advanced Inorganic Chemistry*, 3rd ed., Interscience Publishers, New York, 1972; Wagner, W., Hull, C. J., and Markle, G. E., *Advanced Analytical Chemistry*, Reinhold, New York, 1956; *Lange's Handbook of Chemistry*, 11th ed., J. A. Dean, Ed., McGraw-Hill, New York, 1973; *Bio-Rad Ion Exchange Manual*, Bio-Rad Laboratories, Richmond, CA, 1982.

[*1*] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 500–505.

[2] Morrison, G. H. and Freiser, H., *Solvent Extraction in Analytical Chemistry*, John Wiley & Sons, New York, 1957, pp. 127–131.

[3] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 507–511.

[4] Gentry, C. H. R. and Sherrington, L. G., *Analyst*, Vol. 71, 1946, p. 432.

[5] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 519–520.

[6] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, p. 490.

[7] Merritt, L. L. and Wolker, J. K., *Industrial and Engineering Chemistry, Analytical Edition*, Vol. 16, 1944, p. 387.

[8] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 70–75.

[9] *Standard Methods of Chemical Analysis*, Vol. 1, 6th ed., N. H. Furman, Ed., Robert E. Krieger Publishing Co., Malabar, FL, pp. 89–90.

[10] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 70–74.

[11] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, p. 264–265.

[12] Bode, H. and Hachmann, K., *Fresenius' Zeitschrift für analytische Chemie*, Vol. 229, 1967, p. 261.

[13] Bode, H. and Hachmann, K., *Fresenius' Zeitschrift für analytische Chemie*, Vol. 241, 1968, p. 18.

[14] *Standard Methods of Chemical Analysis*, Vol. 1, 6th ed., N. H. Furman, Ed., Robert E. Krieger Publishing Co., Malabar, FL, pp. 113–114.

[15] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 618–619.

[16] Caley, E. R. and Moore, C. E., *Analytical Chemistry*, Vol. 26, 1954, p. 939.

[17] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 518–523.

[18] *Standard Methods of Chemical Analysis*, Vol. 1, 6th ed., N. H. Furman, Ed., Robert E. Krieger Publishing Co., Malabar, FL, pp. 163–166.

[19] Sundaram, A. K. and Banerjee, S., *Analytica Chimica Acta*, Vol. 8, 1953, p. 536.

[20] Banerjee, S., Sundaram, A. K., and Sharma, H. D., *Analytica Chimica Acta*, Vol. 10, 1954, p. 256.

[21] *Standard Methods of Chemical Analysis*, Vol. 1, 6th ed., N. H. Furman, Ed., Robert E. Krieger Publishing Co., Malabar, FL, p. 194.

[22] Silverman, L. and Schideler, M., *Analytical Chemistry*, Vol. 26, 1954, p. 911.

[23] Sandell, E. B., *Colorimetric Determination of Traces of Metals*, 3rd ed., Interscience Publishers, New York, 1959, p. 342.

[24] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 238–239.

[25] Haddock, L. A., *Analyst*, Vol. 59, 1934, p. 163.

[26] Cheng, K. L., Bray, R. H., and Melsted, S. W., *Analytical Chemistry*, Vol. 27, 1955, p. 24.

[27] Burke, K. E., *Analyst*, Vol. 97, 1972, p. 19.

[28] *Annual Book of ASTM Standards*, Vol. 03.05, American Society for Testing and Materials, Philadelphia, 1993, Designation E 350.

[29] Wolszon, J. D., Hayes, J. R., and Hill, W. H., *Analytical Chemistry*, Vol. 29, 1957, p. 829.

[30] Coursier, J., Hure, J., and Platzer, R., *Analytica Chimica Acta*, Vol. 13, 1955, p. 379.

[31] Matsuo, T. in *Bunseki Kagaku*, Vol. 21, 1972, p. 671.

[32] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 257–258.

[33] *Standard Methods of Chemical Analysis*, Vol. 1, 6th ed., N. H. Furman, Ed., Robert E. Krieger Publishing Co., Malabar, FL, pp. 254–256.

[34] Bode, H., *Zeitschrift für analytische Chemie*, Vol. 144, 1955, p. 165.

[35] Kraus, F. N. and Kraus, K. A., *Journal of the American Chemical Society*, Vol. 77, 1955, p. 801.

[36] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 622–626.

[37] *Standard Methods of Chemical Analysis*, Vol. 1, 6th ed., N. H. Furman, Ed., Robert E. Krieger Publishing Co., Malabar, FL, p. 267.

[38] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 555–556.

[39] Westwood, W. and Mayer, A., *Analyst*, Vol. 73, 1948, p. 275.

[40] Flaschka, H. and Barnard, Jr., A. J., "Tetraphenylboron (TPB) as an Analytical Reagent," *Advances in Analytical Chemistry and Instrumentation*, Vol. I, C. N. Reilly, Ed., Interscience Publishers, New York, 1960.

[41] Moore, C. E., Cassaretto, F. P., Posvic, H., and McLafferty, J. J., *Analytica Chimica Acta*, Vol. 35, 1966, p. 1.

[42] Cheng, K. L.,Ueno, K., and Imamura, T., *CRC Handbook of Organic Analytical Reagents*, CRC Press, Boca Raton, FL, 1982, pp. 127–138.

[43] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, p. 83 (Footnote 48) and p. 418 (Footnote 2).

[44] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 421–423.

[45] Lewis, L. L. and Straub, W. A., *Analytical Chemistry*, Vol. 32, 1960, p. 96.

[46] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, p. 419.

[47] Morrison, G. H. and Freiser, H., *Solvent Extraction in Analytical Chemistry*, John Wiley & Sons, New York, 1957, p. 203.

[48] Lewis, L. L. and Straub, W. A., *Analytical Chemistry*, Vol. 32, 1960, p. 96.

[49] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 247–248.

[50] *Standard Methods of Chemical Analysis*, Vol. 1, 6th ed., N. H. Furman, Ed., Robert E. Krieger Publishing Co., Malabar, FL, pp. 402–404.

[51] Gahler, A. R., *Analytical Chemistry*, Vol. 26, 1954, p. 577.

[52] Foster, D. C. and Kremers, H. E., *Analytical Chemistry*, Vol. 25, 1953, p. 1921.

[53] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, p. 490.

[54] Senise, P. and Sant'Agostino, L., *Mikrochimica Acta*, 1959, p. 572.

[55] Irving, H. M. and Rossotti, F. J. C., *Analyst*, Vol. 77, 1952, p. 801.

[56] Barefoot, R. R., MacDonnell, W. J., and Beamish, F. E., *Analytical Chemistry*, Vol. 23, 1951, p. 514.

[57] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 351–363.

[58] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, p. 227.

[59] Snyder, L. J., *Analytical Chemistry*, Vol. 19, 1947, p. 648.

[60] Morrison, G. H. and Freiser, H., *Solvent Extraction in Analytical Chemistry*, John Wiley & Sons, New York, 1957, pp. 214–215.

[61] Burke, K. E., *Analyst*, Vol. 97, 1972, p. 19.

[62] *Annual Book of ASTM Standards*, Vol. 03.05, American Society for Testing and Materials, Philadelphia, 1993, Designation E 350.

[63] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 655–657.

[64] Luke, C. L. and Campbell, M. E., *Analytical Chemistry*, Vol. 26, 1954, p. 1778.

[65] Luke, C. L., *Analytical Chemistry*, Vol. 28, 1956, p. 1443.

[66] Kraus, F. N. and Kraus, K. A., *Journal of the American Chemical Society*, Vol. 77, 1955, p. 801.

[67] *Standard Methods of Chemical Analysis*, Vol. 1, 6th ed., N. H. Furman, Ed., Robert E. Krieger Publishing Co., Malabar, FL, p. 643.

[68] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 449–451.

[69] Bode, H., *Zeitschrift für analytische Chemie*, Vol. 144, 1955, p. 165.

[70] Freidenberg, H., *Analytical Chemistry*, Vol. 27, 1955, p. 305.

[71] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 311–313.

[72] *Annual Book of ASTM Standards*, Vol. 03.05, American Society for Testing and Materials, Philadelphia, 1993, Designation E 350.

[73] Machlan, L. A. and Hague, J. L., *Journal of Research of the National Bureau of Standards*, Vol. 59, 1957, p. 415.

[74] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 408–412.

[75] Cheng, K. L.,Ueno, K., and Imamura, T., *CRC Handbook of Organic Analytical Reagents*, CRC Press, Boca Raton, FL, 1982, pp. 339–348.

[76] Lewis, L. L. and Straub, W. A., *Analytical Chemistry*, Vol. 32, 1960, p. 96.

[77] Hague, J. L., Brown, E. D., and Bright, H. A., *Journal of Research of the National Bureau of Standards*, Vol. 53, 1954, p. 261.

[78] Kallmann, S. and Oberthin, H. K., *Analytical Chemistry*, Vol. 37, 1965, p. 280.

[79] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, p. 354 and pp. 371–374.

[80] *Standard Methods of Chemical Analysis*, Vol. 1, 6th ed., N. H. Furman, Ed., Robert E. Krieger Publishing Co., Malabar, FL, pp. 883–884.

[81] Menis, O. and Rains, T. C., *Analytical Chemistry*, Vol. 27, 1955, p. 1932.

[82] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 699–708.

[83] *Standard Methods of Chemical Analysis*, Vol. 1, 6th ed., N. H. Furman, Ed., Robert E. Krieger Publishing Co., Malabar, FL, pp. 814–816.

[84] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 708–709.

[85] *Standard Methods of Chemical Analysis*, Vol. 1, 6th ed., N. H. Furman, Ed., Robert E. Krieger Publishing Co., Malabar, FL, pp. 809–810.

[86] Davies, J. E., Grzeskowiak, R., and Mendham, J., *Journal of Chromatography*, Vol. 201, 1980, p. 305.

[87] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I. (and Gilchrist, R.), *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 339–383.

[88] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 663–664.

[89] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 648–650.

[90] Willard, H. H. and Boyle, A. J., *Industrial and Engineering Chemistry, Analytical Edition*, Vol. 13, 1941, p. 137.

[91] Kohler, M., *Zeitschrift für analytische Chemie*, Vol. 138, 1953, p. 9.

[92] Cheng, K. L., Ueno, K., and Imamura, T., *CRC Handbook of Organic Analytical Reagents*, CRC Press, Boca Raton, FL, 1982, pp. 127–138.

[93] Meloche, V. W. and Preuss, A. F., *Analytical Chemistry*, Vol. 26, 1954, p. 1911.

[94] Kallmann, S. and Oberthin, H. K., *Analytical Chemistry*, Vol. 37, 1965, p. 280.

[95] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 320–321.

[96] Hillebrand, W.F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I. (and Gilchrist, R.), *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 371–383.

[97] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, p. 900.

[98] Moore, C. E. Cassaretto, F. P., Posvic, H., and McLafferty, J. J., *Analytica Chimica Acta*, Vol. 35, 1966, p. 1.

[99] Cheng, K. L., Ueno, K., and Imamura, T., *CRC Handbook of Organic Analytical Reagents*, CRC Press, Boca Raton, FL, 1982, pp. 127–138.

[100] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I. (and Gilchrist, R.), *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, p. 374.

[101] Cheng, K. L., *Analytical Chemistry*, Vol. 28, 1956, p. 1738.

[102] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 334–337.

[103] Burke, K. E., *Talanta*, Vol. 21, 1974, p. 417.

[104] Nydahl, F., *Analytical Chemistry*, Vol. 26, 1954, p. 580.

[105] Hague, J. L. and Machlan, L. A., *Journal of Research of the National Bureau of Standards*, Vol. 62, 1959, p. 11.

[106] Kallmann, S. and Oberthin, H. K., *Analytical Chemistry*, Vol. 37, 1965, p. 280.

[107] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 337–338.

[108] Sandell, E. B., *Colorimetric Determination of Traces of Metals*, 3rd ed., Interscience Publishers, New York, 1959, p. 560.

[109] Burke, K. E., *Applied Spectroscopy*, Vol. 28, 1974, p. 234.

[110] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, p. 542.

[111] Strelow, F. W. E. and Bothma, C. J. C., *Analytical Chemistry*, Vol. 39, 1967, p. 595.

[112] Berman, S. S., McKinney, L. E., and Bednas, M. E., *Talanta*, Vol. 4, 1960, p. 153.

[113] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman,

J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 70–75.

[*114*] Burke, K. E., *Analyst*, Vol. 97, 1972, p. 19.

[*115*] Ross, W. J. and White, J. C., *Analytical Chemistry*, Vol. 33, 1961, p. 424.

[*116*] Hague, J. L. and Machlan, L. A., *Journal of Research of the National Bureau of Standards*, Vol. 62, 1959, p.11.

[*117*] Kallmann, S. and Oberthin, H. K., *Analytical Chemistry*, Vol. 37, 1965, p. 280.

[*118*] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 688–693.

[*119*] Bagshawe, B. and Truman, R. J., *Analyst*, Vol. 72, 1947, p. 189.

[*120*] Machlan, L. A. and Hague, J. L., *Journal of Research of the National Bureau of Standards*, Vol. 59, 1957, p. 415.

[*121*] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 466–471.

[*122*] Guest, R. J. and Zimmerman, J. B., *Analytical Chemistry*, Vol. 27, 1955, p. 931.

[*123*] Morrison, G. H. and Freiser, H., *Solvent Extraction, Analytical Chemistry*, John Wiley & Sons, New York, 1957, pp. 241–243.

[*124*] *Standard Methods of Chemical Analysis*, Vol. 1, 6th ed., N. H. Furman, Ed., Robert E. Krieger Publishing Co., Malabar, FL, pp. 1185–1189.

[*125*] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, pp. 432–433.

[*126*] Morrison, G. H. and Freiser, H., *Solvent Extraction in Analytical Chemistry*, John Wiley & Sons, New York, 1957, pp. 245–246.

[*127*] Kraus, K. A. and Moore, G. E., *Journal of the American Chemical Society*, Vol. 75, 1953, p. 1460.

[*128*] Hahn, R. B., *Analytical Chemistry*, Vol. 23, 1951, p. 1259.

[*129*] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953, p. 569–571.

[*130*] Young, J. P. and White, J. C., *Talanta*, Vol. 1, 1958, p. 263.

[*131*] *Standard Methods of Chemical Analysis*, Vol. 1, 6th ed., N. H. Furman, Ed., Robert E. Krieger Publishing Co., Malabar, FL, pp. 432–434.

[*132*] Hague, J. L. and Machlan, L. A., *Journal of Research of the National Bureau of Standards*, Vol. 65A, 1961, p. 75.

Part IV: Measurement

"A naturalist would scarce expect to see ye science of those colors become mathematicall, and yet I dare affirm that there is as much certainty in it as in any other part of Opticks."

—Isaac Newton (1642–1727)

". . . if . . . we express by the term elements *. . . the idea of the last point reached by analysis, all substances that we have not yet been able to decompose by any means are elements to us."*

—Antoine Laurent Lavoisier
Traite Elementaire de Chemie (1789)

11

Gravimetry

WE PROCEED NOW TO THE TECHNIQUES of analytical measurement, the last phase of the metals analysis process. In these five brief chapters, we will highlight some relevant details of some of the major means of "finishing" a determination. Since these subjects are rather broad, with very wide-ranging applications, we must confine examples to only a useful handful in selected areas.

Our first subject is classical gravimetry—a technique that remains valuable even though imperiled with becoming a lost art. Gravimetry is unique in both its dependence upon operator skills and its independence of primary or secondary reference materials. In few other measurement techniques does the analyst find the fate of his work so squarely in his own hands since manual dexterity and lab lore are critical to success. And, while certified reference materials are the principal means to *validate* a gravimetric analysis, they play no role in the analytical process itself. This independence from standards is one important reason that classical gravimetry remains a vital part of any comprehensive analytical laboratory.

THE TECHNIQUE OF GRAVIMETRY

In various places in the preceding chapters, we have already touched upon most of the essential manipulations that comprise a successful gravimetric determination. But it may be well to step through the process in its logical sequence here, adding a few details that have so far eluded description. We begin with the sample solution at a point at which it is ready for a final precipitation, intended to lead to a species that will be weighed. In the most common case, a reagent or reagents are added with vigorous stirring (the solution may be boiling hot or chilled to ice-cold temperatures). In some cases, it is necessary to digest the precipitated solution on a hotplate to complete the reaction or to coagulate the precipitated particles.

Typically the solution is allowed to cool and then stand at room temperature for some period of time before it is filtered. The filter paper is selected to completely retain the precipitate without undue filtration times. It is folded carefully twice, and a small corner is removed from the outer edge of the second fold. It is then opened into a conical shape and held in place in a fluted funnel. The diameter of the filter paper should be selected so at least a half inch of the funnel rim extends beyond its upper edge when it is fully seated.

Seating the paper is best accomplished by filling the funnel completely with distilled water and molding the filter paper to the funnel walls when the water is poured out. Creases and trapped air blisters (as in wallpapering) must be worked out or else the paper must be removed and discarded and the process tried again. Filter pulp (as a water suspension) may be added to the funnel and allowed to drain, forming a small plug at the apex.

The watchglass is removed and its underside is rinsed into the sample beaker. The sample solution is then poured down the vertically held stirring rod into the funnel. The liquid level in the funnel should never approach the upper edge of the filter paper. The funnel stem should touch the wall of the receiving beaker, and, in the ideal case, the funnel stem should be completely filled with liquid. When all of the sample solution has been filtered, the beaker is rinsed thoroughly with a fine spray from a wash bottle to dislodge any loose precipitate particles and the rinsings are transferred to the funnel.

The stirring rod is policed by rubbing it thoroughly with a moistened rubber policeman at the end of a glass or plastic rod. The stirring rod is then rinsed into the beaker. A small piece of moistened filter paper may be used to remove stubborn residues. The paper is then placed into the funnel. The beaker is then policed by rubbing its moistened walls vertically, then in a circular spiral motion with the rubber policeman. Particular attention to the bottom surface and the immediately adjacent areas of the walls should be given, using both back-and-forth and circular motions of the policeman. The rubber policeman should be thoroughly rinsed into the beaker.

The walls and bottom surface of the beaker should be rinsed and the solution transferred to the funnel. A small piece of moistened filter paper may be used to capture traces of residues at the underside of the beaker's pouring lip. The entire policing process may have to be repeated up to three times in critical work. It is wise to finish the process by holding the beaker at an inverted angle just above the funnel and directing a fine spray of liquid against all inner surfaces, and finally against the underside of the pouring lip.

The filtered precipitate is washed by directing a spray of liquid first above the upper edge of the paper, then just below it. The multi-folded quadrant of the filter should receive proportionately more washing per cycle than the remainder of the paper. Each washing cycle should be allowed to drain completely before the next begins. The solution used for the washing (and for the preceding beaker rinsing) and the number of washing cycles are specific to the determination. In general, however, a dilute solution of the precipitating agent or some common ion is used more frequently than plain water. In some cases washings begin with some other solution and end with plain water.

The precipitates should not be washed more than a method specifies since many are partially soluble. In general, fine crystalline and gelatinous precipitates require the most washing. Residues from perchlorate or nitrate media require especially thorough washing to prevent "popping" and possible sample loss during subsequent ignition. When the washing is complete, the paper is first detached from the funnel wall at the multi-folded quadrant. It is folded and wiped across the funnel surface using a circular upward motion. The paper and residue are placed in a tared ignition crucible with the open portion of the paper downward. If necessary, a moistened piece of filter paper is used to remove residue traces from the funnel.

The crucible is placed either directly on the hearth of a muffle furnace or on a vitreous silica tray, which is placed in a muffle furnace using appropriate long-handled tongs. The means and manner of ignition are method specific. It is important to follow procedures exactly since some residues are volatile at temperatures that can be achieved by a muffle furnace, and some precipitates are reduced to undesired species by charred filter paper. Rapid heating of wet residues can cause precipitate loss, thus sometimes the residue and paper are charred at the open muffle door, then ignited at a higher temperature in a closed muffle.

Fine precipitates may be lost if the filter paper catches fire; thus, sometimes the residue and paper are ignited in a closed high-temperature muffle or in a closed lower-temperature muffle with the door opened momentarily and periodically after the first hour. Particularly in the last-mentioned approach, but also in other ignition schemes, carbonaceous material may sometimes, remarkably, survive temperature regimes that should have destroyed it. This is caused by encapsulation by insulating refractory oxides. It is generally better to err on the side of excessive ignition times in most cases. A more risky alternative is to remove the ignited residues, stir them with a platinum wire to expose any carbon, and return them to the muffle. The risk relates to the possibility of sample loss due to dusting or ejection of particles.

When ignition is complete, the crucible is placed in a desiccator with the lid vent open. After about 15 min, the lid vent is closed and the crucible is allowed to cool completely. Cooling times depend on the total mass and the crucible material—platinum requires at least 90 min and porcelain, Vycor, and fused silica at least 150 min. When the crucible is ready to be weighed, the lid vent is carefully opened and the lid removed. The crucible is removed and handled only with clean forceps. The bottom surface of the crucible should be lightly brushed before weighing. On rare occasions an ignited residue is so highly hygroscopic that it must be removed from the desiccator and quickly transferred to a tared weighing bottle for weighing. In the case of certain fine dry residues, brushing the crucible will generate a static charge causing particles to jump out of the crucible. In this situation the bottom surface can be wiped clean by drawing it across a lint-free tissue.

There are many variations on the above scenario. Some precipitates are best filtered using suction. In these cases, a tantalum or platinum filter cone is required to support the filter paper in the funnel. There are also cases where a micropore membrane and its associated apparatus or a tared glass frit, porous porcelain, or Munroe platinum filter crucible are appropriate. In the latter three cases, the filtered residue is dried (usually at either 110 or 130°C) in a drying oven rather than ignited to an oxide. Electrogravimetric analysis is a spe-

TABLE 11-1—Selected gravimetric measurements.

Element	Precipitate as the:	Weigh as the:	Comments
Aluminum	8-Hydroxyquinolate	8-Hydroxyquinolate	Tartaric acid prevents formation of $Al(OH)_3$
Barium	Sulfate	Sulfate	Finely divided precipitate
Bismuth	Carbonate	Oxide	Weigh small amounts as BiOCl
Calcium	Oxalate	Oxide	Correct for coprecipitated Mg and Sr
Copper	Metal	Metal	Electrolytic from dilute $HNO_3 + SO_4^{2-}$
Gold	Metal	Metal	1st reduction: H_2SO_3; reprecipitation: $NaNO_2$
Lead	Sulfate	Sulfate	Correct by electrolysis of filtrate
Molybdenum	Alpha-benzoinoxime complex	Oxide	Ignition must not exceed 525°C
Nickel	Dimethylglyoximate	Dimethylglyoximate	Zn, Cu, Co, and Mn consume reagent
Niobium	Cupferrate	Oxide	Ion exchange separation from Ti, Ta, etc.
Palladium	Dimethylglyoximate	Dimethylglyoximate	Au and Se partially precipitate as elements
Platinum	Sulfide	Metal	Highest accuracy: reprecipitate with formic acid
Selenium	Element	Element	If Te present, use hydroxylamine·HCl
Silicon	Hydrous Oxide	Oxide	Dehydration with either $HClO_4$ or H_2SO_4
Silver	Chloride	Chloride	Photoreduction unless kept in the dark
Tantalum	Cupferrate	Oxide	Ion exchange separation from Ti, Nb, etc.
Tellurium	Element	Element	Reduction with H_2SO_3 + hydrazine·HCl
Titanium	Cupferrate	Oxide	Ion exchange separation from Nb, Ta, etc.
Tungsten	Hydrous Oxide	Oxide	Cinchonine used as precipitation aid
Zirconium	Phosphate	Pyrophosphate	H_2O_2 prevents precipitation of Ti

cial approach in which platinum electrodes are rinsed in water and low-residue methanol, ethanol, or acetone and dried at 110°C. The electrodes are cooled in a large desiccator before weighing and are best handled with nylon gloves. The use of a semi-microbalance, readable to five decimal places, sometimes improves analytical performance. The use of unetched and scrupulously clean beakers will greatly facilitate the policing of precipitates. The temperature controls on muffle furnaces and drying ovens should be regularly calibrated.

Since much of gravimetry is inextricably linked to separation procedures, much relevant information has already been covered in Part III. In the sections that follow, no attempt has been made to retrace this ground, and the reader should refer to Part III and especially Chapter Eight for many additional gravimetric method descriptions. See Table 11–1 for some examples of gravimetric measurements.

WEIGHING AS THE ELEMENT

Many methods have been developed in which the analyte is either chemically or electrolytically reduced to the elemental state and weighed as such. Chemical reduction is widely used for selenium and tellurium, and rhenium and certain precious metals are sometimes reduced to metals with hydrogen gas. Mercury can be chemically reduced to elemental form, filtered, and weighed, although traces are best measured as an elemental cold vapor by an AA technique. Good applied potential electrogravimetric methods are available for copper, cobalt, cadmium, and nickel. Less useful electroplating methods have been applied to tin, zinc, silver, and rhenium. Lead anodically deposited as PbO_2 is a good method, but does not strictly fit this category.

Determination of Selenium and Tellurium

Prepare a sample solution that contains 50 to 200 mg of Se + Te in 5 *M* HCl. Add 10 mL of a 25% (w/v) solution of hydroxylamine hydrochloride and heat just below boiling for 4 h. Cool and filter with suction into tared fine-porosity sintered glass crucible. Wash six times with water and twice with methanol. Dry for 1 h at 110°C, cool in a desiccator, and weigh as selenium. Transfer the filtrate to a 600-mL beaker and heat below boiling until the solution has been reduced to about 50 mL. Add 50 mL of water and bring to a boil. Add 15 mL of H_2SO_3, then 10 mL of a 15% (w/v) solution of hydrazine hydrochloride, then an additional 25 mL of H_2SO_3. Boil for 5 min, cool slightly, and then filter on a tared fine-porosity sintered glass crucible. Wash immediately with hot water six times, then twice with methanol. Dry for 40 min at 105°C, cool in a desiccator, and weigh as tellurium.

Determination of Copper (in Iron-Bearing Alloys)

(*WARNING*: Ether and its vapors are extremely flammable. Thioacetamide is a known carcinogen. Remove sources of flame and sparks and post the room with "No Smoking" signs. Use protective equipment and work in an efficient hood.)

Weigh a sample that contains 30 to 200 mg of copper (but not more than a 3-g sample) into a 250-mL beaker. Dissolve in HCl with dropwise additions of HNO_3. Evaporate to incipient dryness; cool, add 50 mL of 1:1 $HCl:H_2O$, and evaporate to approximately 15 mL. Cool to room temperature, then in an ice bath. Transfer to a 500-mL separatory funnel with chilled 1:1 $HCl:H_2O$ that has been saturated with ether (10 mL of ethyl ether in 500 mL 1:1 $HCl:H_2O$). Stopper funnel tightly and chill in an ice bath for 10 min. Add 50 mL of ethyl ether, restopper, and chill for an additional 10 min. Agitate the funnel for several seconds, then cautiously vent the stopcock; then agitate vigorously for 30 s.

Remove the stopper and allow the layers to separate. Transfer the (lower) aqueous layer to a 500-mL Erlenmeyer flask. Add 15 mL of ether-saturated 1:1 $HCl:H_2O$ to the separatory funnel, stopper, chill, and extract again, adding the acid layer to the Erlenmeyer flask. Transfer the ether layer to the original 250-mL beaker. Using low heat on an electric hotplate, evaporate until the solution begins to darken. Remove from the heat and very cautiously add dropwise HNO_3 (*WARNING:* spattering is likely to occur).

Return the beaker to the low-heat electric hotplate and add additional dropwise HNO_3 until no further reaction occurs. Add 50 mL 1:1 $HCl:H_2O$ (*not* ether saturated) and evaporate to approximately 15 mL. Cool to room temperature, then in an ice bath, and repeat the double ether extraction, adding the acid layer in both cases to the Erlenmeyer flask. Discard the ether layer by flushing it down a sink with a very large volume of running water or by laboratory-approved disposal procedures. Evaporate the solution in the Erlenmeyer flask by heating first at a low temperature (on an electric hotplate) to drive off the dissolved ether, then at a higher temperature.

When the solution has been reduced to about 30 mL, remove from the heat, cool, add 10 mL HNO_3 and 25 mL $HClO_4$, and heat to fumes of $HClO_4$. While fuming, add HCl cautiously, dropwise, to evolve out the chromium as chromyl chloride. Continue fuming until dry salts form and fume evolution ceases. Cool, add 25 mL of HCl, and heat to dissolve the salts. Cool, add 20 mL of 1:1 $H_2SO_4:H_2O$, and heat to light fumes of SO_3. Cool to room temperature, rinse flask walls with water, and warm to dissolve the salts. Add 100 mL of 1F thioacetamide solution (37.5 g of thioacetamide dissolved in 500 mL of water, filtered, if necessary) if the test solution contains $<$100 mg Cu or 125 mL of 1F thioacetamide solution if the test solution contains 100 to 200 mg Cu.

Heat the Erlenmeyer flask in a boiling water bath (such as a 2-L beaker containing glass boiling beads) for 45 min and allow to settle for several hours. Gravity filter on Whatman No. 42 (or equivalent) with filter pulp. Wash four times with 5% (v/v) HCl. Transfer the paper and residue to the 500-mL Erlenmeyer flask, add 100 mL of HNO_3 and 20 mL of 1:1 $H_2SO_4:H_2O$, and heat immediately to fumes of SO_3. If the solution darkens, add HNO_3 cautiously dropwise until the solution is clear and fuming. Cool to room temperature.

Rinse down the walls of the flask with water and repeat the thioacetamide precipitation, filtration, and the destruction of the filter and residue with HNO_3 and H_2SO_4. Cool to room temperature. Rinse down the walls of the flask and transfer the solution to the electrolysis beaker (usually a 250-mL tall-form, lipless beaker). Add 2.0 mL of HNO_3 by pipet and dilute to approximately 150 mL. Connect and insert a platinum anode and a tared platinum cathode (wire gauze electrodes). Cover with a split watchglass and electrolyze at the current density and for the times recommended by the instrument manufacturer.

Some high-speed electrogravimetric analyzers operate at 2 A for 2 h; others may require much lower currents and overnight operation. At the end of the required period, raise the electrodes cautiously while directing a stream of water from a wash bottle over them. When they have cleared the surface of the solution, shut off the current. Disconnect the cathode and dip in two separate beakers of water, then in a beaker of low-residue methanol. Remove the methanol from the platinum gauze with a hot air dryer, then place the cathode on a clean surface in a drying oven at 110°C for 10 min. Cool in a desiccator and weigh.

Repeat the plating with a second tared platinum cathode. The completeness of the second plating can be tested by adding water to raise the liquid level in the electrolysis beaker or by carefully lowering the electrode ¼ in. (0.635 cm). If no plating occurs after several minutes on the portion of the electrode stem newly exposed to the solution, the electrolysis may be deemed complete. For work of the highest accuracy, the spent electrolyte is analyzed for copper by flame AA or ICP-OES. Calculate the copper result from the sum of the two electroplatings and the spent electrolyte copper values.

WEIGHING AS THE OXIDE

These methods fall into two categories: (1) those that produce precipitation residues that *may* be weighed as the oxide and (2) those that produce residues that *must* be weighed as the oxide. In the former category, there are only a few examples, aluminum 8-hydroxyquinolate being the most important. The reason for this paucity of options becomes obvious when one considers that such residues must wash free of excess reagent, must dry to a stoichiometric compound, then must ignite to a stoichiometric oxide without swelling or spattering.

Since there is a weight factor advantage in sensitivity and accuracy if one measures the analyte as part of a massive organic molecule, aluminum is most often weighed as the 8-hydroxyquinolate, rather than ignited to Al_2O_3. Such a luxury of choice is not possible with cupferron or alpha-benzoinoxime. Cupferrates liquify at a low temperature, and the molybdenum alpha-benzoinoxime compound is always contaminated with excess reagent. These metal-organic compounds are always ignited to the highest stable metal oxide, as are the oxalates and all precipitated hydroxides and hydrous oxides.

Special care is often required in igniting metal-organic precipitates. For example, cupferrates must be charred at a low temperature to avoid spattering when they are finally raised to an ignition temperature (usually 1000°C). Molybdenum and tungsten residues have ignition temperature limits of 525 and 725°C, respectively, due to the low sublimation temperatures of the oxides. Completely removing carbonaceous residues at these low temperatures sometimes requires lengthy ignition times. It helps to slowly open and close the muffle furnace door every 15 min after the first hour.

Determination of Titanium, Niobium, or Tantalum

(*WARNING:* Cupferron is a known carcinogen. Use protective equipment and work in an efficient hood.)

Prepare a solution that contains 25 to 100 mg of one of the listed elements in the absence of interferences in 10% (v/v) H_2SO_4 or 10% (v/v) HCl (in the case of titanium) or in borate-complexed chloride/fluoride anion exchange eluent (in the case of niobium or tantalum). [NOTE: 15g H_3BO_3 in 150 mL of boiling 1:1 HCl:H_2O will accomplish this for 300 mL of 4% (v/v) HF/14% (w/v) NH_4Cl in the case of niobium, while 8g H_3BO_3 in 150 mL of boiling 1:1 HCl:H_2O will serve for 350 mL of 4% (w/v) NH_4F/14% (w/v) NH_4Cl in the case of tantalum.] Chill in an ice bath. Prepare a 6% (w/v) cupferron solution by dissolving 30 g of the reagent in 400 mL of water with stirring, diluting to 500 mL, and filtering through Whatman No.4 filter paper (or equivalent).

Chill the reagent solution and also a wash bottle containing 5% (v/v) HCl. [NOTE: Unused cupferron solution may be stored for one week in a refrigerator.] Add 15 mL of the cupferron solution to the sample solution for each 5 mg of analyte expected (but not exceeding 100 mL) while stirring vigorously. Filter through Whatman No. 42 (15 cm) using a filter cone and filter pulp with suction. Rinse and police the beaker with cold 5% (v/v) HCl. Wash the residue five times with cold 5% (v/v) HCl. Transfer the paper and residue to a 600-mL glass beaker.

Add 100 mL HNO_3, 30 mL 1:1 H_2SO_4:H_2O, and 10 mL $HClO_4$. Macerate the paper with a glass stirring rod and immediately heat to boiling. Reduce to approximately 30 mL and cool for 1 min. Cautiously add two to three drops of HF and immediately heat to strong fumes of $HClO_4$. Cool to room temperature, dilute to 250 mL, and chill in an ice bath. Add 15 mL of cold 6% (w/v) cupferron solution for each 5 mg of analyte (but not exceeding 100 mL) while stirring vigorously. Filter through Whatman No. 42 (15 cm) (or equivalent) using a filter cone, pulp, and suction. Rinse and police the beaker with cold 5% (v/v) HCl. Wash the residue five times with cold 5% (v/v) HCl.

Transfer the paper and residue to an ignited, tared 100-mL porcelain crucible. Press a moistened 7-cm filter paper on top of the residue and heat under an infrared lamp in a hood for 2 h. Char in an open-door muffle set at 550°C in a hood. When the char is complete, place the crucible deep in the muffle and close the door. Ignite at 1000°C for 1 h. Cool in a desiccator for at least 2.5 h and weigh as the oxide [TiO_2: 59.951% Ti; Nb_2O_5: 69.905% Nb; Ta_2O_5: 81.897% Ta].

Determination of Tungsten

Prepare a solution that contains 50 to 80 mg of tungsten. Add 25 mL of HNO_3 and 25 mL of $HClO_4$ and heat to strong fumes of $HClO_4$. Cool to room temperature, add 10 mL of HCl, 200 mL of boiling water, 20 mL of 12.5% (w/v) cinchonine solution (25 g of reagent in 200 mL of 1:1 HCl:H_2O), and 1 g of cinchonine powder. Stir well and allow to stand overnight at room temperature. Gravity filter on Whatman No. 42 (or equivalent) with filter pulp. [NOTE: It may be necessary to warm the solution to dissolve crystallized excess cinchonine.]

Rinse and police the beaker with hot water. Wash the precipitate ten times with a wash solution (10 mL of 12.5% (w/v) cinchonine solution in 490 mL of water). Transfer the paper and residue to a platinum crucible and ignite at 725°C for 1 h (or longer, as required). Cool the crucible, add 20 drops of HNO_3 and 10 drops of HF, and heat to dryness on a sandbath. Ignite in a muffle at 760°C for 15 min. Cool in a desiccator and weigh as "impure WO_3."

Add eight pellets of NaOH and 10 mL of water and swirl carefully to dissolve. Warm on a low-heat hotplate on a transite sheet until the WO_3 has completely dissolved. Transfer to a 150-mL beaker. Add 15 mL of HCl to the crucible and set aside. Boil the solution in the 150-mL beaker for 1 min and then filter it through Whatman No. 42 (11 cm) (or equivalent). Rinse the beaker and wash the residue five times with water; discard the filtrate. Place the 150-mL beaker under the funnel and pour the HCl in the crucible through the filter. Rinse the crucible and wash the paper five times with hot water.

Remove the filtrate beaker and add a small piece of litmus paper to it. Add NH_4OH to blue litmus plus 10 mL excess. Boil for 1 min and filter through the same paper. Rinse the beaker and wash the paper five times with hot water. Transfer the paper to the original platinum crucible and ignite at 760°C for 1 h. Cool in a desiccator and weigh as the impurity correction [WO_3: 79.298% W].

WEIGHING AS OTHER IGNITED COMPOUNDS

Not all high-temperature ignitions lead to "naked" metal oxides. Thermally stable, stoichiometric sulfates, pyrophosphates, and molybdates are routinely weighed after igniting at red heat and beyond. Barium is the most important element that is weighed as the sulfate, although lead and strontium are sometimes determined by this means. Zirconium, hafnium, magnesium, manganese, and zinc can be precipitated with diammonium phosphate ($(NH_4)_2HPO_4$) and ignited to the respective pyrophosphates ($M_2P_2O_7$). Methods in which $AlPO_4$ and CdP_2O_7 are weighed after ignition are less accurate and seldom used. Ignited lead molybdate ($PbMoO_4$) has been used to quantify both lead and molybdenum; however, silver molybdate (Ag_2MoO_4) is used principally to quantify molybdenum.

Determination of Barium as the Sulfate

Prepare a 200-mL solution (free of calcium, strontium, and lead) containing 60 to 200 mg of barium in very dilute [approximately 1% (v/v)] HCl. If iron is present, reduce it by adding 1 g of hydroxylamine hydrochloride and boiling for 5 min. Otherwise, merely heat the solution to boiling. Remove it from the hotplate and immediately add 15 mL of a saturated solution of ammonium sulfate. Stir vigorously, return to the heat, and boil for 5 min, then allow to settle overnight at room temperature. Gravity filter through a double Whatman No. 42 paper (or equivalent) with pulp. Police and rinse the beaker and stirring rod, then wash the paper ten times with dilute ammonium sulfate wash solution [1 mL saturated $(NH_4)_2SO_4$ in 500 mL of water], then twice with plain water. Transfer the paper to a tared platinum or porcelain crucible and ignite for 1 h at 1000°C. Cool in a desiccator and weigh as $BaSO_4$ (58.840% Ba).

Determination of Zirconium as the Pyrophosphate

Prepare 100 mL of a 10% (v/v) H_2SO_4 solution that contains 50 to 100 mg of zirconium (niobium and tantalum must be absent). Add two drops of 30% H_2O_2 to check for the presence of titanium. If a yellow color develops at this point, add several drops additional 30% H_2O_2 and maintain an excess of this reagent throughout the precipitation by adding more as needed to maintain the yellow color. Add 10 mL of a fresh 10% (w/v) $(NH_4)_2HPO_4$ solution for each 10 mg of zirconium present. Stir well and warm at 50°C for 2 h. Cool to room temperature and let stand overnight. Gravity filter through Whatman No. 42 (or equivalent). Police and rinse the beaker and stirring rod. Wash the residue thoroughly with cold 5% (w/v) NH_4NO_3 solution. Use 200 to 300 mL of this wash solution for high levels of zirconium, less for smaller amounts.

Carefully dry and char the residue and paper at a low temperature in a tared platinum or porcelain crucible, then ignite at 1000°C for 1 h. Cool in a desiccator and weigh as ZrP_2O_7 (34.402% Zr). For the most accurate work, the ignition is performed in a platinum crucible and the ignited residue is fused with sodium carbonate, leached in water, filtered, ignited, and fused in potassium pyrosulfate. The cooled melt is leached in dilute H_2SO_4 and then the zirconium is precipitated with NH_4OH, filtered, and ignited. The residue is fused again with sodium carbonate, and all subsequent steps are repeated. After the second ammonia separation, the filtered residue is ignited, cooled in a desiccator, and weighed as ZrO_2 (74.032% Zr).

WEIGHING AS DRIED COMPOUNDS

If it is possible to dry and weigh a precipitate without any ignition step, that course is always preferable since the relative amount of material being weighed is always greater than for ignited residues. Another way of saying this is that the analyte element constitutes a smaller part of the weighed compound. By way of illustration, aluminum represents 52.925% of the ignited residue, Al_2O_3, but only 5.8727% of the dried 8-hydroxyquinolate, $Al(C_9H_6NO)_3$. The bulkier dried precipitates are more tolerant of weighing errors, leading to more accurate results in some cases. Dried residues are also often less hygroscopic than ignited residues.

A great many precipitates are weighed after drying, notably nickel and palladium dimethylglyoximates; aluminum and magnesium 8-hydroxyquinolates; the sulfides of arsenic (V), antimony (III), and mercury (II); silver and mercury chlorides; bismuth oxychloride; thallium (I) chromate; and the compound formed between rhenium and nitron. There are many others. Drying operations are conducted in an "air bath" or drying oven over the range 105 to 150°C, depending on the nature of the precipitate. The filtration device is generally also used to dry and weigh the precipitate. This may be a glass frit crucible, a porous bottomed porcelain crucible, or a platinum Munroe crucible.

Determination of Aluminum as the 8-Hydroxyquinolate

Prepare a solution that contains 20 to 60 mg of aluminum and 1 g of tartaric acid in 300 mL of 0.5% (v/v) HCl in a 600-mL beaker. Heat to 50° ± 2°C on a magnetic stirring hotplate, stirring slowly with a large Teflon-coated stirring bar and monitoring the temperature with a thermometer. Add 1 mL of 30% H_2O_2, then 15 mL of 2.5% (w/v) 8-hydroxyquinoline [12.5 g reagent + 25 mL glacial acetic acid + 475 mL hot water; then cool to room temperature]. Stir for 1 min, then add 15 mL of NH_4OH to precipitate the aluminum 8-hydroxyquinolate. Continue stirring for 10 min, maintaining the temperature at 50° ± 2°C.

Remove from the hotplate and allow the beaker to cool for 30 min. Gravity filter through Whatman No. 42 (or equivalent) with pulp and then rinse and police the beaker and the stir bar. Use a moistened piece of filter paper to remove stubborn traces from the stir bar. Wash the paper and residue five times with 1% (w/v) NH_4 OH. Transfer the paper and residue to the original beaker, setting the stir bar aside. Add 100 mL of HNO_3 and 10 mL of $HClO_4$ and macerate the filter paper with a stirring rod, then heat immediately to boiling and reduce to fumes of $HClO_4$.

Fume for 1 min after a clear solution forms. Cool to room temperature, dilute to 300 mL, add 1 g of tartaric acid, and stir. Add a small piece of litmus paper, then add NH_4OH to the first change to blue litmus; then add 5 mL of 1:1 $HCl:H_2O$. Remove the glass rod and insert the stir bar. Heat again to 50° ± 2°C with stirring. Add 1 mL of 30% H_2O_2, 15 mL 2.5% (w/v) 8-hydroxyquinoline solution; then after 1 min add 30 mL of NH_4OH. Continue to stir for 10 min at 50° ± 2°C, then cool for 30 min. Filter onto a tared fine-porosity fritted glass crucible with suction. Rinse and police the beaker and stir bar as before. Wash the residue five times with 1% (v/v) NH_4OH. Place the crucible in a drying oven at 135°C for 1.5 h. Cool in a desiccator and weigh as $Al(C_9H_6NO)_3$ (5.8727% Al).

Determination of Palladium as the Dimethylglyoximate

Prepare a solution containing 20 to 80 mg of palladium. [NOTE: This method is often applied to an HCl solution of the precipitated hydrous oxides (PdO_2 + RhO_2 + IrO_2) formed by a bromate /bicarbonate separation.] The HCl concentration should be 1% (v/v) or slightly less, and the solution volume should be about 400 mL. Add 5 mL of a 1% (w/v) solution of dimethylglyoxime in ethanol for each 10 mg of palladium expected to be present. Stir well, then let the solution stand at room temperature for at least an hour. Filter through a tared fine-porosity glass frit crucible using suction. Police the beaker and rinse it with 1% (v/v) HCl. Wash the residue five times with 1% (v/v) HCl and then five times with warm water. Place the crucible in a drying oven at 110°C for 1 h. Cool in a desiccator and weigh as $Pd(C_8H_{14}N_4O_4)$ (31.612% Pd).

OTHER GRAVIMETRIC DETERMINATIONS

The metals analyst is frequently called upon to use gravimetry to determine moisture, "loss-on-ignition," ash content, and other sample attributes with a more or less clearly defined (or definable) procedure. Such determinations consist of simply weighing a test portion before and after some thermal treatment, and the results undoubtedly reflect some independent reality. Loss-on-ignition of limestone samples, for example, represents moisture and CO_2 and possibly organic matter.

There are, however, a number of empirical tests based on gravimetric measurement wherein the physical meaning of the result begins to blur. Such tests go by names like "insoluble residue," "volatile matter," "filterable solids," "extractables," or, perhaps, "insoluble boron" or "insoluble aluminum." In all these cases, the procedures used and the quantities obtained are inextricably linked. The result is defined as what the procedure (properly executed) yields from a specific type of sample, and it is usually not possible to verify it with either standards or independent alternate test methods.

Even if a standard material is available, it usually can only serve to verify that the test procedure has been properly performed, but it cannot verify any value or assigned meaning of the test sample result. There is nothing inherently wrong with these test procedures (and, clearly, many of them are useful) so long as neither the analyst nor his clients lose sight of the empirical nature of these tests. It is always prudent to reference a written procedure for all reported data from testing of this kind.

CONCLUSION

Classical gravimetry is a demanding discipline with great technical rewards. In today's laboratory, it serves as a test case and bellwether for the survival of laboratory manipulative skills and the preservation of the knowledge of descriptive inorganic chemistry. More than for any other subcategory, separation science is an indispensable feature of gravimetric analysis. Here, more than anywhere else, the complexity of the task is linked to the complexity of the sample. Yet, it is in the arena of complex sample matrices where the temptation to abandon classical procedures in favor of sleek and swift comparative methodology must be resisted. For if we lose it here, we will lose it everywhere. If we do not make this point within the confines of the laboratory, we will never make it in the fiscal, "bottom-line" world outside.

REFERENCES

Erdy, L., *Gravimetric Analysis*, Parts I, II, and III, Pergamon Press, Oxford, 1965.

Gregory, E. and Stevenson, W. W., *Chemical Analysis of Metals and Alloys*, Blackie & Son, London, 1942.

Hillebrand, W. F., Lundell, G. E. F., Hoffman, J. I., and Bright, H. A., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953.

Standard Methods of Chemical Analysis , Vol. 1, 6th ed., N. H. Furman, Ed., Robert E. Krieger Publishing Co., Malabar, FL, 1975.

12

Titrimetry

WHEN AN ANALYTE IS QUANTIFIED by measuring the volume (or, on rare occasions, the weight) of a solution that reacts with it, we call the process volumetric analysis or titrimetry. Generally, the reaction in question proceeds to its equilibrium point or to some reproducibly measurable point near equilibrium, whereupon the addition of reactant solution (titrant) is halted and the amount consumed up to that point is recorded. The reactant endpoint may be indicated by the appearance or disappearance of a color or a precipitate or by a change in instrumentally measured potential or pH or some other property. The titrant may be added manually from a buret, or the whole process may be under closed-loop control with an automatic titrator.

Titrimetry is typically both faster and more versatile than gravimetry. It is usually faster because lengthy and complicated separation schemes are seldom necessary to prepare test solutions for titration. And it is more versatile because not only sample weight but also titrant concentration can be optimized to achieve the best accuracy at each range of analyte. That accuracy can be impressive at high analyte concentrations, but it sometimes falls short at levels below 5%, where gravimetric techniques are usually very strong.

Titrimetry also lacks the *independence* of gravimetry, relying as it does on standard materials—either pure substances or matrix-matched metal alloys—to quantify a result. Volumetric determinations are subject to a number of error sources, but, in general, the manipulative demands are less stringent than those imposed by gravimetry. The need for scrupulously clean volumetric labware to prevent "clingage" on buret walls is one concern. Another is the need for consistency in subjective apperceptions, such as in detecting a subtle color change or reading a meniscus level.

In the past (and to some very limited degree still today), volumetric techniques have been used to control metallurgical processes because they lend themselves to optimizing for speed. Today, the buret calibrated in analyte concentration has given way to microprocessor-controlled titrators that monitor and display a graph of reaction chemistry as they titrate samples without analyst intervention. Whether manual or automatic, a clear choice that remains is whether to base the work on normality or on a titer. If the titrant is a primary standard, the analyst can easily calculate the results both ways provided enough of the correct metal alloy standards accompany the unknowns in the sample set. If properly performed, the results should be identical, or nearly so. But if the titrant must, itself, be standardized, it may be expeditious to skip this extra step and place all faith in a titer. Sometimes, however, the best work is achieved by going the extra mile.

STANDARDIZATION OF TITRANTS

Some titrants are prepared from materials so pure and stable that they are regarded as primary standards. These are generally solids, which are sometimes first dried, then weighed, dissolved, and diluted to a fixed volume. Examples of compounds available as primary standard grades are: potassium dichromate, sodium oxalate, arsenious oxide, ceric ammonium nitrate, and potassium acid phthalate. A solution carefully prepared from these materials may be used directly in test sample titrations based on normality or to standardize other reagent solutions used for that purpose.

Examples of common titrants that are *not* primary standards are: ferrous ammonium sulfate, potassium permanganate, iodine, sodium thiosulfate, hydrochloric acid, and sodium hydroxide. These materials *cannot* be weighed or aliquotted and used without standardization if an approach based on normality is to be employed. In Chapter Three we described the preparation of standard reduction/oxidation titration solutions (see Table 3-5), including primary and "secondary" types. It will suffice here to review this briefly and to describe a typical process for acid/base titration solutions.

There are many approaches to the standardization of acids and bases, but let us confine our discussion to the procedure that is the simplest and most frequently employed. Solutions of 0.1 N sodium hydroxide (4.0 g dissolved in 1 L of water) are standardized by weighing to the nearest 0.1 mg 1 g of potassium acid phthalate (which has been dried at 120°C for 2 h) and then transferring it into a 250-mL Erlenmeyer flask. Then 50 mL of water that has been recently boiled and cooled is added, followed by three drops of a 1% (w/v) solution of phenolphthalein (in 4:1 ethanol:H_2O). The solution is then titrated with the (approx.) 0.1 N NaOH solution to the first permanent pink. Since 1 formula weight of potassium acid phthalate ($HKC_8H_4O_4$, 204.2236 g/f.w.) reacts with exactly 1 formula weight of sodium hydroxide (NaOH, 39.997108 g/f.w.), exactly 1.0000 g of $HKC_8H_4O_4$ is equivalent to 0.1958458 g of NaOH, or 48.965 mL of a 0.1000 N NaOH solution. For a "catch weight" (an exactly measured random amount) of $HKC_8H_4O_4$:

Normality of NaOH = (weight of $HKC_8H_4O_4$, in grams) × (4.8965)/(mL titration)

This is the same as dividing by the equivalent weight of $HKC_8H_4O_4$ and converting to liters:

Normality of NaOH =
(weight of $HKC_8H_4O_4$, in g)(1000)/(mL titration)(204.2236)

For the most accurate work, because of the possibility of CO_2 pickup, air should be excluded from the flask by passing a gentle stream of nitrogen through a multi-hole stopper, with one hole occupied by the buret tip, another for the gas inlet, and a third for the vent. The endpoint color should match that produced by a pH 8.6 buffer (25 mL of 0.2 *M* H_3BO_3/0.2 *M* KCl plus 6 mL of 0.2 *M* NaOH diluted to 100 mL with cooled, boiled water) containing three drops of 1% phenolphthalein.

Acids are most conveniently standardized by titration with standardized sodium hydroxide. Phenolphthalein and boiled, cooled water are required for the standardization of hydrochloric, nitric, and sulfuric acid solutions, which are the most commonly used acid titrants. Even though sulfuric acid is dibasic, the acid-base equilibrium constants are so large that the endpoint represents both hydrogen ions. This is, of course, an exception among polybasic acids. With phosphoric acid, for example, using a judicious selection of indicators and solution conditions, each of the three protons can be titrated. One must remember basic stoichiometry here: $N_A \times V_A = N_B \times V_B$, where N_A and N_B are the normalities of acid and base, respectively, and V_A and V_B are the respective volumes.

Perhaps the most frequently standardized redox titrants are ferrous ammonium sulfate and potassium permanganate. The former [39.2 g $(NH_4)_2SO_4{\cdot}FeSO_4{\cdot}6H_2O$ dissolved in 1 L of 1:100 $H_2SO_4{:}H_2O$ for a 0.1 *N* solution] is best standardized with a carefully prepared solution of primary standard potassium dichromate (0.1000 *N* : 4.9031 g/L) using a dilute sulfuric acid/phosphoric acid medium and either a sodium diphenylamine endpoint indicator for visual titration or a platinum-indicating electrode for potentiometric titration.

Potassium permanganate solution (3.2 g $KMnO_4$ dissolved in 1 L of 90°C water for a 0.1 *N* solution) should be aged in the dark for a week, then filtered before being standardized. Weigh 0.3 g of dried primary standard grade sodium oxalate to the nearest 0.1 mg and transfer it to a 600-mL beaker. Add 250 mL of boiled and cooled 5:95 $H_2SO_4{:}H_2O$ and stir to dissolve the salt. Add about 40 mL of (approximately) 0.1 *N* $KMnO_4$ solution by buret and stir until the color is discharged, then heat the solution to 60°C. Then carefully resume the titration to the first permanent pink. The net electron exchange is *2*:

$$MnO_4^- + 8H^+ + 4e^- \rightarrow Mn^{3+} + 4H_2O$$
$$2[C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-]$$

Thus the equivalent weight of $Na_2C_2O_4$ is 133.99913/2 = 66.999565 g/equivalent, and the normality of the $KMnO_4$ solution is given by: *N* $KMnO_4$ = (g $Na_2C_2O_4$) x (14.92547)/(mL titrated).

Iodine standard solutions are prepared by dissolving the element in water in the presence of about a four-fold excess of potassium iodide (12.7 g I_2 + 40 g KI, diluted to 1 L for a 0.1 *N* solution). Weigh 0.3 g of primary standard grade arsenious oxide (As_2O_3) to the nearest 0.1 mg and transfer it to a 250-mL Erlenmeyer flask. Dissolve it in 10 mL of 1 *M* NaOH. Add 15 mL of 1 N H_2SO_4 and stir to mix. Then add 50 mL of sodium bicarbonate solution (40 g $NaHCO_3$/L), followed by 5 mL of a 0.5% (w/v) soluble starch solution. Titrate with the (approx.) 0.1 *N* I_2 to the first permanent blue. Here four electrons are exchanged and the equivalent weight is 49.460345; thus:

$$N\ I_2 = (\text{g } As_2O_3) \text{ x } (20.21822)/(\text{mL titrated})$$

Sodium thiosulfate solutions (25 g of the $Na_2S_2O_3{\cdot}5H_2O$ salt + 0.1 g Na_2CO_3 dissolved in 1 L of boiled, cooled water for a 0.1 *N* solution) are standardized as follows. Add 10 g of KI to each of two 250-mL Erlenmeyer flasks, then add 100 mL of boiled, cooled water and 2 mL of HCl to each. To one flask add 40.00 mL of standardized 0.1 *N* $KMnO_4$ solution by buret. Stopper both flasks and let them stand for 10 min in the dark. Then add 2 mL of 0.5% (w/v) soluble starch solution to each and then titrate both with the (approx.) 0.1 *N* sodium thiosulfate solution to the first permanent blue. Subtract the blank reading from the permanganate-containing solution reading to obtain the corrected titration volume. Then calculate the normality of the thiosulfate from: *N* $Na_2S_2O_3$ = (*N* $KMnO_4$) × (40.00)/(corrected mL titrated.)

It must be emphasized that "secondary" standard titrants are so designated because they do not retain a standardized normality. It is essential, therefore, to restandardize them each time they are used. Many are deteriorated more rapidly by light, so it is prudent to store potassium permanganate, iodine, and sodium thiosulfate in the dark. In addition, sodium thiosulfate is acted upon by sulfur oxidizing bacteria (sometimes despite the presence of sodium carbonate or other added germicides). Sodium thiosulfate solutions that become turbid must be discarded, and the reagent bottle must be sterilized before reuse.

INDICATORS

Most visual titrations require an indicator that changes color at (or reproducibly near) the stoichiometric endpoint. Different mechanisms are involved in the color change reactions, but many involve the conversion of a colorless neutral organic molecule into a colored ion with conjugated double bonds. Most added indicators use up some finite amount of titrant, so, if it is feasible, for the most careful work some provision is made for an indicator blank.

Acid/Base Indicators

There is a long list of available acid/base indicators, but in most laboratories only a few are needed. They are all weak organic acids or weak organic bases that show different colors in their undissociated and dissociated forms. For the titration of strong acids or bases with strong acids or bases, almost any indicator will do since the pH break at the equivalence point is enormous (pH 4 to 10). *Phenolphthalein* [usually a 0.1% (w/v) solution in 4:1 ethanol:water] is a popular choice. It changes from colorless to red over the pH interval

TABLE 12-1—Selected acid/base indicators.

Common Name	Chemical Name	pH Range (Color)
Thymol Blue	Thymolsulfonephthalein	1.2 (red)–2.8 (yellow) [acid range]
Methyl Orange	Dimethylaminoazobenzene sodium sulfonate	3.1 (red)–4.4 (yellow)
Methyl Red	Ortho-Carboxybenzeneazodimethylaniline	4.4 (red)–6.2 (yellow)
Bromthymol Blue	Dibromothymolsulfonephthalein	6.2 (yellow)–7.6 (blue)
Thymol Blue	Thymolsulfonephthalein	8.0 (yellow)–9.6 (blue) [basic range]
Phenolphthalein	Phenolphthalein	8.0 (colorless)–10.0 (red)

8.3 to 10.0. Like all weak organic acid indicators, alcohol enhances its sensitivity to hydrogen ions by depressing its dissociation. *Methyl red* (pH 4.2—red to pH 6.2—yellow) and *bromthymol blue* (pH 6.0—yellow to pH 7.6—blue), prepared similarly, are sometimes recommended in place of phenolphthalein for strong acid and base titrations.

For the titration of weak acids and bases, it becomes very important to match the indicator to the (sometimes quite narrow) endpoint interval. Similarly, with polybasic molecules such as H_3PO_4, it is possible to match an indicator to the pH interval of each hydrogen ion's endpoint. In the case of phosphoric acid, the first hydrogen ion corresponds to the *methyl orange* interval (pH 3.1—red to pH 4.4—yellow); the second to the phenolphthalein interval (pH 8.3—colorless to pH 10.0—red) if the solution is saturated with NaCl; the third to the *thymol blue* interval (pH 8.0—yellow to pH 9.6—blue) if the solution is saturated with $CaCl_2$.

It should be noted that thymol blue is unique in having a second color change interval (pH 1.2—red to pH 2.8—yellow) and is, therefore, sometimes considered a valuable addition to the laboratory. The weak acid, acetic acid, is titrated with phenolphthalein since its endpoint is above pH 7. Sometimes acid/base indicators with undramatic color changes are mixed with a neutral dye that acts as an in situ visual filter to enhance the color transition. Thus, methyl orange is often modified by preparing a mixture with *xylene cyanole FF*. The combination appears green in basic solution, gray at the transition point (pH 3.8), and red in acid solution.

All known acid/base indicators have a transition range of about 2 pH units (see Table 12-1), but the precise point selected as the endpoint color change is not necessarily the middle of this range. One of the two colored forms may be visually recognizable at lower or higher concentrations than the other. Also, there are subjective factors involved that vary with the individual analyst. With all visual endpoint titrations, and especially when a titer approach is applied, the aim should be for consistency. For endpoints that do not fade, it is helpful to keep a vessel displaying the chosen endpoint close at hand as a series of samples is titrated.

Redox Indicators

These can be distinguished as "true" redox indicators—that is, substances that, themselves, undergo oxidation or reduction at the titration equivalence point—and "pseudo" redox indicators, which are other visual means of detecting the presence of an excess of titrant. The latter include: starch, which reacts with excess iodine to form a deep blue color (a surface reaction on the massive, polymeric starch molecule); thiocyanate, which reacts with excess ferric ion to form the red ferric thiocyanate complex; and in the case of potassium permanganate titrations, an excess of the strongly colored titrant itself.

True redox indicators are oxidized or reduced by excess titrant, producing a dramatic color change. The transition potential of the indicator must match the transition potential at the titration equivalence point. If it does not, it is sometimes possible to adjust titration conditions so that the two transitions correspond. This, for example, is the reason that sulfuric and phosphoric acids are added to the solution when reduced iron is titrated with potassium dichromate to a diphenylamine endpoint. Table 12-2 lists some redox indicators and the formal potentials at which their color changes occur under the conditions listed.

The color changes of many redox indicators are reversible, though sometimes other circumstances (e.g., the formation of a precipitate in the solution) prevent this feature from being utilized analytically. If the redox indicator is also a weak acid or base, the transition potential may depend in a sensitive way on the pH of the solution. It is always wise to maintain identical solution conditions in the titration of a series of samples.

Diphenylamine is an old indicator, still used, but now largely replaced by *sodium diphenylaminesulfonic acid* and the equivalent barium salt, both readily soluble in water, unlike the original compound, which has to be dissolved in concentrated sulfuric acid. With all three indicators the color change is sharp, going from colorless to deep purple at the first excess of oxidizing titrant.

TABLE 12-2—Selected redox indicators.

Indicator	Reduced Color	Oxidized Color	Conditions	Formal Potential, volts
Phenosafranine	Colorless	Red	1 M acid	+0.28
Methylene Blue	Colorless	Blue	1 M acid	+0.53
Diphenylamine	Colorless	Purple	1 M H_2SO_4	+0.76
Diphenylamine sulfonic acid	Colorless	Purple	Dilute acid	+0.85
Erioglaucin A	Yellow-green	Bluish-red	0.5 M H_2SO_4	+0.98
Ferroin	Red	Faint blue	1 M H_2SO_4	+1.11

Ferroin is the ferrous complex of *o*-phenanthroline, a dark red indicator that is oxidized to the light blue ferric complex at a potential of approximately +1.11 V in 1 *M* H_2SO_4. It is often used in titrations with cerium (IV) sulfate, using a small amount of a solution of osmium tetroxide as a catalyst. Like acid/base indicators, redox indicators require the consumption of a small amount of titrant beyond the analyte endpoint. In most cases this amount is very minute, however, and blanks are unnecessary except for certain umpire work. A notable exception is the "pseudo" self-indicator, potassium permanganate that requires a "practiced eye" to reproducibly stop the titration at the first minuscule trace of pink (often in a matrix-colored solution). For the less adept, a comparison blank is the best course. The rigorous-minded analyst will be frustrated in efforts to establish an iron titration blank in the case of the diphenylamine compounds since these indicators react very slowly with potassium dichromate in the absence of iron.

Indicators for Precipitation Titrations

There are two categories here as well: indicators that form colored precipitates or complexes in the presence of excess titrant and indicators that form a color as they adsorb on the surface of the analyte precipitate. Classic examples of the former case include the Mohr and the Volhard titrations. In the Mohr titration of chloride with silver nitrate, reddish silver chromate precipitates as soon as all the white AgCl has come down. The method requires the solution pH to fall in the range 6 to 10 since dichromate begins to form below pH 6 and silver precipitates as the hydrous oxide above pH 10. In the optimum pH range, the amount of added Na_2CrO_4 can be quite small (say, 0.15 g in a 100-mL test solution) and still lead to a good endpoint with a minimal indicator error. For most work, a blank is advisable, however, unless a titer has been established using identical conditions. The method can be used for silver determination by adding a known excess of standard chloride solution and applying the technique to the back titration.

The Volhard method is designed for the *direct* titration of silver in dilute nitric acid with standard thiocyanate solution. Added ferric ion forms the clear, red colored ion, $FeSCN^{2+}$, at the precipitation endpoint. Here, chloride can be determined indirectly by adding a known excess of standard silver solution, then back-titrating with the Volhard method. This is a less desirable approach, however, since the thiocyanate back-titrant tends to react slightly with the AgCl to form the even more stable precipitate AgSCN. As with the Mohr method, a blank or a titer is advised for both the direct and indirect approaches.

Adsorption indicators form a color when they adhere to the primary adsorption layer of excess titrant ion that forms on the analyte precipitate at the endpoint. If chloride is titrated with silver, before the equivalence point the colloidal AgCl particles are coated with chloride ions. The indicator, say fluorescein, being a weak organic acid is repelled from the negative surface layer by its own negative charge. At the endpoint the chloride ions on the AgCl particles are replaced with positive silver ions. The fluorecein anions then adhere and form the endpoint color. Since this class of indicators are weak acids and bases, they must be matched to the pH of the test solution (Table 12–3).

TABLE 12-3—Selected adsorption indicators.

Indicator	pH Range	Analyte	Titrant
Methyl Violet	<7	Ag^+	Cl^-
Fluorescein	7–10	Cl^-	Ag^+
Dichlorofluorescein	4–10	Cl^-	Ag^+
Thorin	1.5–3.5	SO_4^{2-}	Ba^{2+}

Metallochromic Indicators

The most effective way to detect the endpoint in an EDTA or other chelometric titration is generally by the use of a metallochromic indicator. This is, itself, a chelating compound that forms a stable, soluble, colored complex with the analyte and exhibits a significantly different color in the absence of the analyte. During a chelometric titration, the indicator holds its portion of the analyte, releasing it to the titrant only at the equivalence point, whereupon the color change occurs. Metallochromic indicators all also change color with pH, so their use is generally restricted to a narrow range of hydrogen ion concentration.

The highest resolution endpoint color changes usually occur at very low indicator concentrations, so it is important to select for indicators that show deep and significantly different colors in the free and metal-complexed forms. Among the better known metallochromic indicators are: Eriochrome Black T (employed in the EDTA titration of Mg, Ca, and total water hardness, among other uses), Calmagite, Murexide, and Pyrocatechol Violet. A unique use of these indicators is in conjunction with a specific ion electrode, which allows potentiometric endpoint detection for a chelometric titration. A copper complexed metallochromic indicator, say, is added to a pure cobalt solution, which is then titrated with some chelating titrant. At the endpoint, the copper is released by the indicator and immediately detected by a copper-specific ion electrode whose signal is used to indicate the endpoint and dead-stop an automatic buret.

TITRATION EQUIPMENT

Despite our coverage of lab equipment in Chapter Two, it is necessary here to say a few additional words about the tools of this particular subset of the metals analyst's trade. At one time titrations were performed in hand-stirred beakers and hand-swirled flasks against a back-lighted titration stand. Buret stopcocks were ground glass and had to be carefully cleaned and regreased on a regular basis. Today, a lighted magnetic stirrer and burets with Teflon stopcocks are the norm unless automatic titrators have replaced *all* manual operations. However, equipment maintenance remains an important key to success in volumetric analysis.

Burets, like all volumetric labware, must be scrupulously cleaned to eliminate chemical residues, which can contaminate solutions and produce liquid wall adherence. The exact cleaning regimen required will depend to an extent on what was last in them, but burets (and their stopcock barrels) can be adequately cleaned in most cases by rinsing several times with distilled water, then filling with concentrated sulfuric acid and allowing them to stand overnight. Several more rinses with water the next morning and they should be ready for use. Chromic acid (Cr (IV) + H_2SO_4) is not a good idea unless heavy organic residues must be removed since it leaves traces of chromium adsorbed on the glass that cannot be easily removed.

Stubborn permanganate stains will succumb to dilute hydrogen peroxide. Tin oxide residues from stannous chloride can be removed with concentrated hydrochloric acid. Motorized syringes and other piston-driven automatic burets present special cleaning problems since they must be drained and disassembled to change solutions or for routine maintenance. Caustic solutions—even very dilute sodium hydroxide titrants—will eventually cause the piston to begin to bind, producing a "stick-and slip" effect that will adversely affect their operation and the quality of the results. A regular program of rinsing such equipment with distilled water is usually all that is needed, but long-neglected maintenance may call for lengthy and laborious cleaning or costly replacement.

Reference electrodes for potentiometric titration are the cause of most erratic millivolt readings. These should be drained, flushed with distilled water, and refilled with fresh saturated potassium chloride solution if they have not been recently used. The electrical leads from the reference and indicating electrodes should be checked and their pin jack connector polished with a fine emery paper if corrosion is observed or suspected.

Useful additions to manual titration equipment are devices for improving the visibility of the meniscus. A plastic "snap-on" card with a horizontal black and white field will improve contrast, and a magnifying eyepiece will help the analyst to interpolate between buret divisions. A buret cap or an inverted 50-mL beaker should cover the top of the buret, even when in use. A buret should never be allowed to stand for more than a few minutes only partially filled with solution. And it should be drained and filled with distilled water before the analyst leaves for the day.

Over 90% of the volumetric analysis work of a metals lab can be accomplished with a 50-mL buret. Next in importance are 10-mL microburets, with only a small need for 25-mL, 5-mL, and 100-mL sizes. A collection of dropping bottles for indicators and other reagents is essential. Lighted magnetic stirrers and an array of Teflon-coated stir bars of various sizes and shapes are necessary. The stir bars are conveniently stored in compartmentalized plastic boxes.

TITRATION TECHNIQUE

Volumetric analysis is less demanding of special skills than gravimetry, but it still requires on-the-job training and practice. There was a time when analysts were schooled to hold the stopcock with their left hand (if they were right-handed) with their palm encircling the stopcock barrel so they could stir with their right. With magnetic stirrers this is no longer necessary, and the persistence of this technique now reveals the analyst's age. The character of a titration endpoint is unique to the chemistry, and each requires some adjustment until familiarity is achieved. The cleaned buret should be filled and emptied at least once with the titrant before it is filled and adjusted to the zero mark for the first test.

Titrations always begin with the rapid addition of titrant, then gradually slow as changes in the solution begin to occur. The magnetic stirrer should be set at the fastest speed at which splashing and excessive turbulence does not occur. The titrant stream should be directed into the vertical wall, not the central cavity of the solution vortex. Color change/visual endpoints are usually preceded by a small cloud of the endpoint color in the central vortex that gradually spreads. Potentiometric endpoints are preceded by a gradually increasing drift of the readout. The rate of titrant addition is "throttled-back" as the endpoint nears—first, from a stream to a rapid succession of drops. Finally, drops are added one at a time, allowing the system to reach complete equilibrium before the next drop is added. In certain work it is practical and desirable to add half and quarter drops by exuding titrant to form a hanging droplet on the buret tip, which is then washed into the solution with a stream of water.

Potentiometric methods conducted with digital read-out pH meters require some familiarization and practice with the specific endpoint in order to achieve manual titration results of an accuracy equivalent to that obtainable with the old-style mechanical panel meter or null-point galvanometer read-out displays. When one is looking for a rate of change of a digital display, the highest noise-free display sample rate is desirable, although it will probably never surpass the detection ease of the best analog displays. Digital devices, of course, excel in closed-loop automatic titration instruments.

Receding endpoints occur in many titration methods and are a source of error. A receding endpoint is an endpoint that fades in color or drifts in millivolt reading as soon as it is attained. Addition of another drop of titrant brings it back and it may stay a little longer, but it finally fades once again. The process continues, leaving the analyst in doubt as to which drop constitutes the true stoichiometric endpoint. That question may be difficult to answer, but it is usually not too difficult to extract reasonably good analytical data from such a method. The analyst merely establishes a titer based upon the persistence of the endpoint color for a short, exactly prescribed, but totally arbitrary time. The use of a titer (in essence, a one-point calibration of the method using a certified reference material that closely matches the matrix of the unknown sample) solves a host of other problems in volumetric analysis.

Among the problems that can be compensated for are: obscure endpoints due to matrix color; the effect of the matrix on the formal endpoint potential; weak color change at the endpoint; and even a limited degree of chemical interference from the matrix. With the use of a titer, some of the "purity" of the method is lost in the sense that the accuracy of the results becomes dependent upon the accuracy of the value certified on the reference material. Validation with additional reference materials is, of course, necessary, just as it is with titrations based on normality.

For the uninitiated, it is appropriate to pause here and formally define some titration terms:

Relation: An experimentally derived equivalence between two titrant solutions that react with each other (e.g., A mL of 0.1 N potassium permanganate = B mL of 0.1 N ferrous ammonium sulfate). This type of expression is generally used with a titer where exact solution normalities are not established and a back-titration is employed. It usually takes a form such as: (x mL ferrous ammonium sulfate/mL potassium permanganate).

Titer: An experimentally derived calibration factor relating the weight of analyte present in the sample portion to the primary titrant volume at the endpoint. It is generally determined by taking certified alloy reference materials that closely match the composition of the unknown material through the entire procedure. It usually takes a form such as: (*y* grams of chromium/mL of ferrous ammonium sulfate). For the best work, the titer should be an average of replicate portions of slightly differing certified reference materials.

Blank: If the true endpoint does not coincide with the most reproducibly detectable color change, it is best to establish a blank (if that course is possible). This merely takes the form of the volume of titrant required to see the experimental endpoint in the absence of analyte (e.g., C mL of 0.1 N potassium permanganate).

Using the examples given above, a titration of oxidized chromium with a measured excess of a 0.1 N ferrous ammonium sulfate solution followed by a back titration with a 0.1 N potassium permanganate solution would be calculated as follows:

$$\% \text{ Chromium} = [A - (B - C) \times D] \times E \times 100/F$$

where, A = mL 0.1 N ferrous ammonium sulfate; B = mL 0.1 N potassium permanganate; C = blank; D = relation; E = titer; and F = sample weight in grams.

There is, of course, one obvious advantage in working with normalities instead of a titer—the method in that case becomes independent of alloy reference materials and thus more "definitive." It does, however, remain a captive to the purity and preparation steps associated with the standard titrant. The normality approach is convenient when the titrant is prepared directly from a primary standard material, but may become cumbersome if a lengthy standardization process is required. Less than ideal endpoints or difficult matrices are best handled with a titer, which can be both fast and accurate if reliable and appropriate standard materials are available.

ACID/BASE TITRATIONS

The pH change at the endpoint of an acid/base titration bears directly upon the precision that can be expected from the analytical method. With strong acids and bases of 0.1 molar concentration or higher, we can expect about nine pH units of change with a drop or two of titrant. With 0.001 molar solutions, the same size increment of titrant will yield a break of only about two pH units (the minimum that can be detected with most visual indicators).

In addition to solution concentration, the pH break at the equivalence point is also affected by the dissociation constants. Thus, for example, when a weak acid is titrated with a strong base, the pH break at the endpoint is much smaller than when the same molar concentration of strong acid is similarly titrated. Clearly, a sizeable change in pH for a small increment in titrant is desirable for the best reproducibility whether a visual indicator or a pH meter is used. The pH break for a given chemical system can be expanded somewhat by increasing the analyte concentration (that is, increasing the aliquot volume or the test portion weight) or by increasing the titrant strength. While the former course tends to decrease error, the latter course tends to increase it.

For titrations that begin and/or end at pH values of 8 or higher and that utilize a pH meter, it is usually necessary to use a glass indicating electrode that has been designed to yield a low sodium error. One must also be aware that electrode readings (except in the case of the Ross electrode) are strongly affected by heat, including the heat of reaction, and a temperature compensator probe is often a good idea. Precipitates that form during the titration may coat the electrodes and degrade their performance and are also likely to adversely affect the analytical objective by consuming titrant.

The whole question of acid/base equilibria in the presence of diverse ions can be extremely complicated. For this reason, most of the titration systems used by the metals analyst are applied after isolation of the analyte. An exception is the titration determination of free acids in process solutions, which are often heavily laden with metals. The term "free acid" is somewhat empirical in the sense that it is meant to represent the hydrogen ion concentration of the solution solely in the presence of the metal ions. If one were to somehow remove these metal ions unobtrusively, the equilibrium would likely shift, producing an entirely different "free acid" concentration.

The problem of establishing a value for free hydrogen ion in such samples relates to the consumption of base titrant by the precipitation of metal hydroxides. The addition of a complexing agent, such as EDTA, although it prevents precipitation, is not a satisfactory solution since the hydrogen ion actively participates in the competition of metal ions for sites on the EDTA molecule. This process shifts the concentration of free acid in ways that are difficult to predict. Successful volumetric methods for free acidity are diverse and often quite clever. Thermometric and conductimetric endpoints have been used, as well as Gran plots (a graphical approach to extrapolating the true endpoint using only a few data points in a region where no precipitation occurs) and also titration to the first appearance of an iron precipitate in the presence of HF or NH_4F and iron (III) nitrate. There are several other approaches as well (see references to papers by A. Moskowitz et al., F. J. C. Rossotti et al., E. W. Bauman et al., W. E. McKee et al., F. J. Miller et al., and G. L. Booman et al.).

The majority of applications of acid/base titrations do not face such difficulties. Typically the analyte, isolated from its matrix, is made to undergo a reaction that liberates either hydrogen ions or hydroxyl ions in a concentration proportional to the analyte concentration. Titration of these with either standard base or standard acid, respectively, yields the analytical result. Below are examples of each type of determination.

Determination of High Levels of Boron

Weigh a steel sample (not larger than 0.7 g) containing 2 to 10 mg of boron into a Vycor, fused silica, or boron-free glass Erlenmeyer flask with a ground glass joint at the neck. Add by pipet 6.0 mL of 1:1 $HCl:H_2O$ and immediately connect to a vertically supported, water-cooled reflux condenser (use a Teflon sleeve on the ground glass joint and secure the joint with a plastic (Keck) clip). Heat the sample with an electric hotplate until the reaction ceases. Cool the flask to room temperature, then open the joint. Add by pipet 0.5 mL of HNO_3, reconnect the joint, and heat again under reflux for 15 min. Cool to room temperature, open the joint, and add by pipet 2.0 mL of 30% H_2O_2. Reconnect the joint and heat again for 15 min. Cool again to room temperature, open the joint slightly, then wash down the condenser into the flask.

Many iron, nickel, and cobalt alloys, including many high-temperature alloys, will yield a clear solution at this point. If significant residue remains, the solution must be filtered, ignited, fused with sodium carbonate, and the cooled melt leached in the filtrate. Transfer the solution to a mixed-bed ion exchange column (16 g CG-120, H^+ form, 100 to 200 mesh and 18 g CG-45, OH^- form, 200 to 400 mesh; mix dry then slurry with water and pack into a 1-cm glass column). Elute the sample solution and flask rinsings into a 600-mL Teflon beaker at <3 mL/min. Add water to the column until the total collected eluate is approximately 450 mL.

Place the Teflon beaker on a sandbath on a hotplate and boil for 5 min. Cool to room temperature, then chill slightly in an ice bath. Using a pH meter calibrated with pH 7.00 buffer and a magnetic stirrer, titrate the sample to exactly pH 7.00 ± 0.01 with 0.1 *M* NaOH, while sparging the solution with nitrogen gas. Record the buret reading. Add 50 g of mannitol and allow it to dissolve completely, then refill the buret and titrate again to pH 7.00 ± 0.01 with 0.1 *M* NaOH solution. Record the buret reading. The difference between the two volumes of 0.1 *M* NaOH is a measure of the boron in the sample.

The mixed bed resin removes both sample matrix interferences and anions from the dissolution medium. Boiling and sparging the solution with nitrogen removes the residual acidity of carbonic acid from absorbed atmospheric CO_2. Mannitol, like glucose and glycerol, forms a stable complex with borate, releasing a stoichiometric amount of hydrogen ion, which is then titrated. A titer based on weighed portions of primary standard grade boric acid is the best calibration approach. The procedure adapts readily to an automatic titrator.

High Aluminum Determination

Weigh a sample of iron, nickel, or cobalt alloy containing 60 to 80 mg of aluminum (not larger than 1.5 g) and dissolve it in HCl and HNO_3. Add 20 mL of 1:1 $H_2SO_4:H_2O$ and bring the solution to light fumes of SO_3 or salts, whichever occurs first. Cool, dilute to 100 mL, and boil to dissolve the salts. Cool and transfer to a mercury cathode cell. Electrolyze at 13 A for 4 h or until colorless. Filter through double Whatman No. 41 filter paper (or equivalent) and wash with water. Boil the filtrate down to 250 mL (if titanium precipitates, cool, add 4 mL of 1:1 $H_2SO_4:H_2O$, take to fumes of SO_3, cool and dilute to 250 mL). Add with stirring 25% (w/v) NaOH solution to a pH of 12.5 to 13.0 (use narrow range pH paper, such as that supplied by Merck).

Boil 1 min, cool to room temperature, and transfer to a 500-mL volumetric flask. Dilute to the mark and mix. Prepare dry funnels and dry Whatman No. 54 filter paper (or equivalent) (Whatman No. 540 or equivalent if the precipitate appears very fine). Place a dry 250-mL volumetric flask under the funnel. Fill the funnel with solution from the 500-mL volumetric flask and allow it to set the paper and drain, then discard this first portion of filtrate. Replace the 250-mL volumetric flask under the funnel and collect filtrate until the volume level is *above* the mark. With a long medicine dropper remove solution from the neck of the 250-mL flask until the meniscus is on the mark.

Carefully transfer the solution in the 250-mL flask to a clean 600-mL beaker. Rinse the 250-mL flask with three 25-mL portions of water and transfer the washings to the 600-mL beaker. Wash all caustic solution from the volumetric flasks at this point. If the sample must stand more than 2 h, add a small piece of litmus to the 600-mL beaker and adjust to just acid with HCl.

To determine the endpoint pH, add 325 mL of water in another 600-mL beaker and carefully adjust the pH to 10.20 ± 0.01 using a pH meter with a low-sodium-error indicating electrode calibrated at pH 10.00. Make the adjustment with various concentrations of NaOH and HCl, as required. With a plastic graduate add 30 mL of 28% (w/v) KF solution. Stir magnetically until the meter response stabilizes. The final reading should be in the pH 10 to 11 range. If it is not, add a few drops of HCl or NaOH to the KF solution, shake well, and repeat the test with a fresh portion of water. Average at least two close replicates as the specified endpoint pH.

Adjust the titer standard to pH 10.20 with either dilute HCl or dilute NaOH. Add 30 mL of 28% (w/v) KF solution and stir for 1 min. Then titrate the sample with either 0.2 *M* HCl (for 5 to 10% Al) or 0.1 *M* HCl (for 0.5 to 5% Al) to the empirically derived endpoint. Record the volume and calculate the titer. Treat unknowns and validation samples in the same manner. In strongly basic media, aluminum is present as a soluble aluminate that reacts with fluoride to release a stoichiometric amount of hydroxyl ions that are then titrated with standard acid.

REDOX TITRATIONS

Titrations based on reduction/oxidation reactions are the broadest category of volumetric determinations, being more frequently used in metals analysis than acid/base titrations or any other type. Unlike acid/base reactions, there is no solvent "leveling effect" in redox reactions. This refers to the fact that for acid/base titrations in an aqueous medium the interaction of water with the reactants is a normal part of the equilibria, but in redox work a titrant that reacts with water to any appreciable degree is usually unsuitable. Another way of saying this is that, concentrations aside, no acid or base is too "strong" to use as a titrant in aqueous solution. However, many oxidizing and reducing agents would be too reactive to use as a titrant. One consequence of this absence of a solvent leveling effect is that the potential change at the equivalence point of a redox titration is related only to the nature of the titrant used, not to its concentration.

Many reduction/oxidation reactions are readily adaptable to redox titrations, but some are not. As mentioned above, water must not play a significant role in the redox chemistry.

Also, the reaction rate between the analyte and the titrant must be reasonably rapid. Finally, the "feasibility" of the proposed titration is a measure of the degree of completeness of the analytical measurement reaction at the equivalence point. The quantity of unreacted analyte at the endpoint should be no more than 0.1% of the total amount present. The degree of completeness can be calculated from first principles using the Nerst equation: $E = E^\circ - (0.059/n)\log K$, where E is the formal half-cell potential of the system, E° is the potential of the half-cell reaction (table value), n is the number of electrons transferred, and K is the equilibrium constant. For the hypothetical reaction: $A + 3B \rightleftharpoons C + 3D$, composed of the reduction: $A + 3e^- \rightarrow C$ ($E^\circ_1 = +1.27$ mV) and the oxidation: $3B \rightarrow 3D + 3e^-$ ($E^\circ_2 = -0.85$ mV), we can write:

$$E = 1.27 - (0.059/3)\log [C]/[A]$$

Since we know $[C]$ and $[A]$ from the volume of known concentration titrant added, we can solve for E. And since the formal potential of the other half-cell must be the same, we can write:

$$E = 0.85 - (0.059)\log [B]/[D]$$

If we have started with a known amount of analyte, B, we can insert this value in $[D]$ and solve for $[B]$, the amount of unreacted B (in moles/liter) at the equivalence point.

The degree of drift in the titration curve before and after the equivalence point is a function of the number of electrons transferred in the half-cell reaction. These horizontal portions of the curve are flatter for systems in which several electrons are transferred and more steeply sloped for single and double electron transfer reactions. The net effect of both half-cell reactions is, of course, what determines the net shape of the curve, as well as the size of the potential break. As with all titrations, the shape of the curve and the size of the break play an important role in determining the precision of the method.

As with acid/base titrations, endpoint detection can be visual or instrumental. If millivolt measurements are made with a pH meter, platinum-indicating electrodes, especially those of wire or rod type, are popular, generally coupled with a saturated calomel reference electrode.

Determination of Iron

Weigh a sample that contains 100 to 300 mg of iron (do not exceed 3 g) into a 400-mL beaker. Dissolve the sample in HCl and HNO_3. If high chromium is present, it should be removed by dropwise addition of HCl while fuming with 15 mL of $HClO_4$. If high nickel is present, the sample should be fumed in H_2SO_4 instead, followed by treatment with ammonium persulfate if chromium is also high (see below). If vanadium is present, it will titrate as iron unless it is removed by a $NaOH/Na_2O_2$ separation (see below) or by other means.

For samples that have been fumed in $HClO_4$, but which do not contain vanadium, cool, dilute to 150 mL, and add NH_4OH to blue litmus plus 10 mL excess. Boil for 1 min, then filter through Whatman No. 41 (or equivalent) plus filter pulp. Wash with 1% (v/v) NH_4OH.

If the sample contains more than 10% nickel, it should be fumed in 15 mL of H_2SO_4, then cooled and diluted to 150 mL. Boil the solution to dissolve the salts and cool it somewhat. If chromium is less than 0.5%, the iron can be precipitated with ammonia as described above. Otherwise, add NH_4OH until the precipitate redissolves slowly, then add 2 g of ammonium persulfate and then 25 mL additional NH_4OH and boil for 2 min. Filter hot through Whatman No. 41 (or equivalent) plus pulp. Wash with 1% (v/v) NH_4OH.

If the sample contains vanadium and has been fumed in $HClO_4$, cool, dilute to 100 mL, add 1 g of Na_2O_2 and then 25% (w/v) NaOH solution to blue litmus plus 10 mL excess. Add another 1 g of Na_2O_2 and stir well. Boil for 3 min, cool to room temperature, and filter through Whatman No. 541 (or equivalent). Wash with water. Return the filter to the original beaker, add 50 mL HNO_3 and 15 mL $HClO_4$, and heat immediately to boiling. Continue heating to the evolution of fumes of $HClO_4$. Fume for 1 min, cool, dilute to 150 mL, and add NH_4OH to blue litmus plus 10 mL excess. Boil for 1 min, then filter through Whatman No. 41 (or equivalent) plus filter pulp. Wash with 1% (v/v) NH_4OH.

If the vanadium-bearing sample also contains high nickel, it can be treated similarly, but it is essential that the ammonia precipitate be filtered hot. In all cases, the ammonia precipitate is dissolved off the filter paper with alternate washings of 1:3 $HCl:H_2O$ and hot water, collecting the solution in the original beaker. The washings should continue until all traces of color have been removed from the filter paper.

Boil the solution until it is reduced to about 25 mL. If it is yellow at this point, no further separations are usually required. If it is green or blue, repeat the ammonia precipitation. Reduce the solution to <5 mL and, while hot, add 25% (w/v) $SnCl_2$ (25 g $SnCl_2 \cdot 2H_2O$ dissolved in 20 mL of hot HCl, then cooled and diluted to 100 mL with water) dropwise while swirling until the solution is free of yellow color, plus two drops excess.

Wash down the watchglass and beaker walls and dilute to 75 mL. Cool in an ice bath. Add 10 mL of a saturated solution of mercuric chloride. Stir and allow to stand for 3 min (use a timer or stopwatch). Then immediately add 45 mL of acid mix (add 300 mL of H_3PO_4 to 800 mL of water, stirring vigorously; cool in a water bath while cautiously adding 300 mL H_2SO_4 with vigorous stirring; dilute to 2 L, mix, and cool to room temperature). Add eight drops of 0.2% (w/v) sodium diphenylamine sulfonate (aqueous solution stored in a dark bottle). Then titrate with either 0.1 N or 0.2 N $K_2Cr_2O_7$ solution to the first permanent silky dark blue endpoint. If normality is used, %Fe = (mL $K_2Cr_2O_7$) × (N $K_2Cr_2O_7$) × 5.5847/(g Sample)

Determination of Chromium

Weigh a sample that contains 5 to 50 mg of chromium. Low-alloy steels are dissolved in 15 mL of 1:1 $H_2SO_4:H_2O$ and 10 mL of H_3PO_4; superalloys (0.1 to 0.2 g) are fused in 10 g of potassium pyrosulfate in a Vycor crucible with a lid. Stainless steels are dissolved in HCl and HNO_3 with a few drops of HF, as required. All samples are fumed in the H_2SO_4/H_3PO_4 mixture, cooled, and diluted to 350 mL. Add 30 mL of 25% (w/v) $AgNO_3$ and 60 mL of 10% (w/v) ammonium persulfate solution, stir, and boil for 10 min (any manganese will be oxidized). Add 5 mL of 1:3 $HCl:H_2O$ and boil for another 5 min (the MnO_4^- color will be discharged; if not add another 5 mL and continue boiling until it is; AgCl will precipitate).

Cool to room temperature, then in an ice bath. Insert platinum indicating and saturated calomel reference electrodes connected to an automatic titrator and titrate to a dead stop with 0.1 *N* ferrous ammonium sulfate. Multiply the vanadium content of the test portion by 0.339 and subtract this value from the apparent chromium concentration.

Determination of High Cobalt

Weigh a 0.2-g test portion if cobalt is <60% and a 0.1-g test portion if cobalt is >60%. Dissolve in any combination of HCl and HNO_3. Cool, add 10 mL of $HClO_4$, and heat to strong fumes of $HClO_4$. Continue fuming until 0.5 mL of liquid remains. If the nickel content exceeds 20% or the molybdenum content exceeds 5%, it will be necessary to isolate the cobalt by a chloride system anion exchange separation. Mark a series of 600-mL beakers to correspond to the samples and add a volume of potassium ferricyanide (22 g/2 L) according to the formula: $V = [[(E) \times (W) \times 10] + 30]/2$, where V = volume of potassium ferricyanide solution in mL, E = estimated %Co, and W = weight of sample in grams. Record the exact volume added.

Add 10.00 mL of potassium ferricyanide solution to each of two additional beakers for use in establishing a relation. To the relation samples, add 50 mL of ammonium citrate solution (200 g anhydrous citric acid + 200 mL water, add 270 mL NH_4OH cautiously with stirring, cool, dilute to 1 L, and mix), then 80 mL NH_4OH. Dilute to 450 mL and cool in an ice bath. Insert a platinum-indicating electrode and a saturated calomel electrode connected to an automatic titrator and titrate with cobalt nitrate solution (2.0 g cobalt metal dissolved in 50 mL of water and 20 mL of HNO_3, then diluted to 2 L and mixed) to the first potential break.

To the titer standards add 200 μL of disodium EDTA solution (90 g disodium EDTA dissolved in 600 mL of warm water and diluted to 1 L; store in a plastic bottle) and swirl to mix. To the corresponding 600-mL beaker, add 50 mL of ammonium citrate and 80 mL of NH_4OH, cool in an icebath. Then transfer the test portion to the 600-mL beaker, dilute to 450 mL, cool in an icebath and titrate with cobalt nitrate solution. Treat the samples identically and calculate as follows: Relation = (10.00)/(mL cobalt nitrate); Titer = $C/[V - (A \times B)]$, where C = wt. of cobalt taken, in g, V = volume of potassium ferricyanide, in mL, A = volume of cobalt nitrate solution used, in mL, and B = average relation. The % cobalt in the unknown sample is calculated as follows: $\%Co = [(V - A \times B) \times T \times 100/W] - Z$, where V = volume of potassium ferricyanide in mL, A = volume of cobalt nitrate in mL, B = average relation, T = average titer, W = sample weight in g, and Z = % manganese in the sample. If the cobalt has been isolated by ion exchange, the value of Z is zero.

PRECIPITATION TITRATIONS

This class of titrations is rarely used in metals analysis laboratories except, perhaps, for the classic titrations of halides with silver (and silver with halides). The reactions required for precipitation titration must be rapid, and supersaturation of the reaction product and coprecipitation of matrix species must *not* occur. Also, suitable endpoint indicators must be available. These requirements eliminate the use of many precipitation reactions in a titration scheme.

The titration of chloride, bromide, or iodide ion with silver nitrate solution can be monitored with specific ion electrodes for each of these analyte species. The change in pX (i.e., $-\log[X^-]$)at the equivalence point is greatest for iodide and smallest for chloride, reflecting the relative solubilities of the silver compounds (AgI being the least soluble and AgCl the most soluble). When silver is the analyte, it is best titrated with iodide for this reason, and a silver specific ion electrode can be used to detect the endpoint (see the section on Indicators for Precipitation Titration, above, for a discussion of visual endpoint work).

COMPLEXATION TITRATIONS

In order for a complex formation reaction to be "feasible" as a titration scheme, the analyte species must be completely "captured" by the ligand-former in one reaction step. For example, if an analyte can accommodate four coordination positions, it will not do to titrate it with unidentate, bidentate, or tridentate ligand formers since no clear break in the titration curve will occur. In these cases, competition between "naked" analyte ions and partially complexed species will smear out any dramatic concentration changes at the equivalence point. However, if such an analyte is titrated with a chelating agent that coordinates all four positions at once, a sharp and significant change in pM (i.e., $-\log[M]$) will occur at the endpoint. From this argument, it follows that cobalt (6-coordinate positions) cannot be titrated with ammonium hydroxide (unidentate), but *can* be titrated with EDTA (hexadentate).

That is not to say that no unidentate titrations are feasible. Until chemical waste disposal and workplace safety concerns eliminated its use, sodium cyanide solutions were used to titrate nickel. In this now-abandoned classic method, the nickel dimethylglyoximate precipitate is wet ashed with HCl, HNO_3, and H_2SO_4. Citric acid is added to the cooled solution, which is then made faintly ammoniacal and diluted to 200 mL. With a buret, a known volume of standard silver nitrate solution is added, then 1:10 HCl: H_2O until a precipitate forms.

Then 1:1 NH_4OH: H_2O is added until the precipitate just dissolves plus a small excess, followed by a portion of potassium iodide. The solution is then titrated with standard potassium cyanide solution until the precipitate just dissolves. When all the nickel has been complexed with cyanide, excess cyanide destroys the silver iodide cloud, clearing the solution. It is necessary to determine the relation between the silver nitrate solution and the potassium cyanide solution by titrating a reagent blank containing iodide. That correction is subtracted from the observed potassium cyanide volume.

Chelometric titrations are defined as those that involve polydentate ligands. EDTA is, by far, the most popular titrant. It must be understood that EDTA titrations always intimately involve pH conditions since hydrogen ions compete with the analyte for ligand sites on the molecule. The feasibility of an EDTA titration can be adjusted to some degree by reference to a table or graph of "alpha" values—a quantity that varies with pH. The quantity α depends upon the equilibrium constant for complex formation, the concentration of metal ion to be titrated, and an adjustable factor that relates to the means of endpoint detection and the required precision.

The relationship is: $\log \alpha = \log K - T + \log C$, where K is the equilibrium constant, T is the titration factor (with a typical value of 5 for visual endpoints, 4 for potentiometric endpoints, and 2 for the highest precision endpoints), and C is the analyte concentration. Looking up the calculated alpha value will tell the analyst the *lowest* pH at which the titration can be performed.

EDTA and other chelons are not noted for their selectivity, and, in fact, most metals can be titrated with these compounds. One important means of making such titrations practical, besides the use of separations and the selectivity that derives from operating in a buffered pH range, is the use of masking agents. For example, lead and nickel both react with EDTA, but in the presence of cyanide only lead will titrate.

Determination of Nickel

Weigh and dissolve (in HCl and HNO_3 and/or H_2O_2) a sample containing 30 to 70 mg of nickel (or use an aliquot scheme that produces a test solution in this range). Add 30 mL of 1:1 H_2SO_4: H_2O and bring to light fumes of SO_3 or salts. Cool, dilute to 200 mL, and heat to dissolve the salts. Add 30 mL of ammonium citrate solution (200 g citric acid + 200 mL of water, add cautiously while stirring 270 mL NH_4OH; cool, dilute to 1 L, and mix). With a pH meter (using dilute NH_4OH and HCl), adjust to pH 6.3 ± 0.1, add 30 mL of dimethylglyoxime solution (10 g reagent in 1 L of methanol) plus 1 mL for each milligram of cobalt, manganese, or zinc estimated to be present. Stir and (using dilute NH_4OH and HCl) adjust to pH 7.8 ± 0.1; remove and police the electrodes.

Heat the solution below boiling for 5 min, then let it stand at room temperature overnight. Filter on Whatman No. 40 (or equivalent) and wash with 1% (v/v) NH_4OH. Return the paper and precipitate to the original beaker; add 50 mL of HNO_3 and 15 mL of $HClO_4$. Heat immediately to boiling and boil down to strong fumes of $HClO_4$, then cool. If the solution is any color except light green, a second dimethylglyoxime precipitation is called for.

Establish a relation by adding 100 mL of water to a beaker. Add 0.5 g of ammonium nitrate and chill the beaker in an ice bath. Adjust to pH 2.0 ± 0.1 with HNO_3 and 1:1 NH_4OH: H_2O. Add 10.00 mL of bismuth nitrate solution [dissolve 19.7496 g $Bi(NO_3)_3$ in 500 mL of water, dilute to 1 L, and mix], then six drops of pyrocatechol violet indicator (0.1 g reagent in 100 mL of water). Titrate the blue solution to the first permanent yellow with 0.05 *M* disodium EDTA (37.22 g reagent dissolved in warm water and diluted to 2 L).

Dilute the titer standards and the unknown samples with 100 mL of water, add 0.5 g of ammonium nitrate, and chill in an ice bath. Adjust to pH 2.0 ± 0.1 using HNO_3 and 1:1 NH_4OH: H_2O. Add an amount (in milliliters) of 0.05 *M* disodium EDTA solution approximately equal to 0.4 times the estimated nickel level (in milligrams), recording the exact amount added. Readjust to pH 2.0 ± 0.1, if necessary. Chill in an ice bath. Add six drops of pyrocatechol violet indicator (the color of the solution should be green). Titrate with 0.05 *M* bismuth nitrate solution to the first permanent blue, then about 5 mL additional. Record the exact amount of bismuth nitrate solution added.

Back titrate with 0.05 *M* disodium EDTA solution to the first appearance of a green color. Record the total volume of 0.05 *M* disodium EDTA solution that has been added.

$$\begin{aligned}
\text{Relation} &= (\text{mL diNaEDTA})/10.00 \\
\text{Titer} &= (\text{g Ni taken})/[(\text{total mL diNaEDTA}) \\
&\quad - (\text{mL Bi(NO}_3)_3) \times \text{Relation}] \\
\%\text{Ni} &= \{[(\text{total mL diNaEDTA}) \\
&\quad - (\text{mL Bi(NO}_3)_3] \times \text{Relation}\} \times \text{Titer} \times 100/ \\
&\quad (\text{g sample})
\end{aligned}$$

AUTOMATIC TITRATORS

Before we close this discussion of volumetric analysis with some general remarks, it seems appropriate to devote a short space to the unique features and capabilities of the automatic equipment that is becoming common in certain metals analysis laboratories. Today's automatic titrators are a far cry from the cumbersome designs marketed in the 1950s and 1960s. Those early efforts were of two configurations—"dead stop" buret valves that terminated titrant delivery at a predetermined potentiometric or photometric signal level, and recording titrators that plotted classical step-function or first derivative peak shapes using a mechanical linkage to a piston-driven buret. Such devices were beset with maintenance problems, their time savings over manual techniques was minimal, and often the results obtained were poor compared to manual methods in trained hands.

Today microprocessor-controlled closed-loop feedback circuitry is utilized in automatic titrators, and their advantages have become real and significant. Usually a menu of titration protocols is provided. One useful example is an endpoint-seeking mode in which the system continuously calculates and monitors the value of dE/dV (i.e., the change in measured potential with the change in volume of titrant dispensed), while controlling the rate of titrant addition by reference to the time-based derivative, dE/dt (i.e., the change in measured potential per unit of time).

The value of dE/dt is an operator-selected parameter that the system attempts to meet but not exceed. The value of dE/dV, on the other hand, reflects only the reaction chemistry, and its maximum value occurs at the true endpoint. Some protocols utilize the second derivative of the potential to detect the endpoint (i.e., d^2E/dV^2). This quantity drops to zero at the equivalence point. Such physical parameters as the placement of the dispensing tip with respect to the electrodes and the speed and direction of the stirring motion can critically influence the accuracy of the results.

Automatic titrators can now prove their worth in metals labs with large volumetric analysis workloads provided that the methods developed for them are properly designed. They should prove to be faster that the corresponding manual determinations. They should be relatively free from the need for special skills and should be completely immune to "operator sensitive" factors. They should be applicable over a wide concentration range. And they should yield results with a routinely attainable precision and accuracy that is equal to or better than that afforded by the best routine manual titration methods in skilled hands. Table 12–4 summarizes some commonly employed titration measurements.

TABLE 12-4—Selected volumetric measurements.

Element	Titration Type	Key Reaction	Comments
Aluminum	Acid/base	$NaAlO_2 + 3HF \rightarrow AlF_3 + NaOH + H_2O$	Titrate released OH^-
Boron	Acid/base	$\text{Mannitol-}HBO_3 + NaOH \rightarrow \text{Mannitol-}NaBO_3 + H_2O$	Titrate released H^+
Chlorine	Precipitation	$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$	Dichlorofluorescein indicator
Chromium	Redox	$14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$	Correct for vanadium
Cobalt	Redox	$[Fe(CN)_6]^{3-} + Co^{2+} \rightarrow [Fe(CN)_6]^{4-} + Co^{3+}$	Back titrate excess $(Fe(CN)_6)^{3-}$
Copper	Redox	$2Cu^{2+} + 4I^- \rightarrow Cu_2I_2 + I_2$	Titrate released I_2 with $S_2O_3^{2-}$
Iron	Redox	$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$	First remove vanadium
Magnesium	Complexation	$H_2(EDTA)^{2-} + Mg(Ind)^- \rightarrow Mg(EDTA)^{2-} + H(Ind)^{2-} + H^+$	Eriochrome black T indicator
Manganese	Redox	$4Mn^{2+} + MnO_4^- + 8H^+ + 15H_2P_2O_7^{2-} \rightarrow 5Mn(H_2P_2O_7)_3^{2-} + 4H_2O$	pH control to avoid V interference
Phosphorus	Acid/base	$(NH_4)_3PO_4 \cdot 12MoO_3 + 23NaOH \rightarrow NaNH_4HPO_4 + (NH_4)_2MoO_4 + 11Na_2MoO_4 + 11H_2O$	Dissolve precipitate in standard base, then back titrate excess
Tin	Redox	$Sn^{2+} + I_2 \rightarrow Sn^{4+} + 2I^-$	Protect from air oxidation
Vanadium	Redox	$5VO^{2+} + MnO_4^- + 6H_2O \rightarrow 5VO_3^- + 2Mn^{2+} + 12H^+$	First oxidize in boiling dilute HNO_3

FINAL NOTES

Like so much of classical wet analytical chemistry, titrimetry carries with it a rich tradition of lore, terminology, and equipment, but the central core of this eclectic assortment remains of lasting value. Most analysts working today have never seen, much less used, a weight buret. And certain archaisms, such as the separate usage of the terms "iodimetry" and "iodometry" (for redox titrations directly with iodine, and with iodine produced in situ by the reaction of iodate with iodide), have faded into obscurity. No one any longer cares much how we grip a buret stopcock, or if we can stir a solution with a glass rod without hitting the beaker walls. These are shadows and reflections of an era when the art of titrimetry controlled the composition of tons of metal in Bessimer converters and open hearths and reverberatory furnaces. Let us look back upon them with respect, while we keep the useful core of this valuable technique alive and growing.

REFERENCES

Analytical Methods Guide, 6th ed., Orion Research,Cambridge, MA, 1973.

Baumann, E. W. and Torrey, B. H., *Analytical Chemistry*, Vol. 56, 1984, pp. 682–685.

Booman, G. L., Elliott, M. C., Kimball, R. B., Cartan, F. O., and Rein, J. E., *Analytical Chemistry*, Vol. 30, No. 2, 1958, pp. 284–287.

Day, R. A., Jr. and Underwood, A. L., *Quantitative Analysis*, 2nd ed., Prentice-Hall, Englewood Cliffs, NJ, 1967, pp. 74–220.

Encyclopedia of Industrial Chemical Analysis, Vol. I, F. D. Snell and C. L. Hilton, Eds., Interscience Publishers, New York, 1966, pp. 30–52.

Gregory, E. and Stevenson, W. W., *Chemical Analysis of Metals and Alloys*, 2nd ed., Blackie & Son, London, 1942.

Handbook of Analytical Chemistry, L. Meites, Ed., McGraw-Hill, New York, 1963.

Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953.

Kolthoff, I. M., Stenger, V. A., Belcher, R., and Matsuyama, G., *Volumetric Analysis*, Interscience, New York, 1957.

McKee, W. E. and Hamilton, W. F., *Industrial and Engineering Chemistry, Analytical Edition*, Vol. 17, No. 5, 1945, pp. 310–312.

Miller, F. J. and Thomason, P. F., *Analytical Chemistry*, Vol. 31, No. 9, 1959, pp. 1498–1500.

Moskowitz, A., Dasher, J., and Jamison, Jr., H. W., *Analytical Chemistry*, Vol. 32, No. 10, 1960, pp. 1362–1364.

Rossotti, F. J. C. and Rossotti, H. J., *Journal of Chemical Education*, Vol. 42, 1965, pp. 375–378.

Skoog, D. A. and West, D. M., *Fundamentals of Analytical Chemistry*, 4th ed., Saunder College Publishing, Philadelphia, 1982, pp. 422–424.

Standard Methods of Chemical Analysis, 6th ed., Vol. I, N. H. Furman, Ed., Robert E. Krieger Publishing, Malabar, FL, 1962.

Van Nostrand's Scientific Encyclopedia, 4th ed., D. Van Nostrand Company, Princeton, NJ, 1968.

Welcher, F. J., *The Analytical Uses of Ethylenediamine Tetraacetic Acid*, D. Van Nostrand Company, Princeton, NJ, 1958.

MNL25-EB/Mar. 1996

13

Absorption Spectrophotometry

ALTHOUGH THEY ARE SELDOM linked in people's minds, molecular and atomic absorption techniques show many common features. The basic optics of the instruments bear a certain resemblance. Both approaches excel at minor to trace level concentrations. And in their respective heydays, both techniques were promoted for their speed and selectivity. It seems natural to discuss them together in this brief survey of measurement techniques to compare and contrast them, as well as to illustrate the important roles that both continue to play in the metals laboratory.

UV/VISIBLE MOLECULAR ABSORPTION

Technically, molecular absorption spectrophotometry includes the important infrared region of the electromagnetic spectrum (0.78 to 1000 μm), where vibrational and rotational energy levels reveal so much about molecular structure. But the inorganic analytical chemist is generally much more involved with molecular absorption in the visible and near-ultraviolet (200 to 800 nm), where the incoming energy promotes changes in electron energy levels. Below 200 nm, air components begin to absorb significant amounts of radiation so that work there requires evacuated or helium-purged optical paths.

However, in the standard UV/visible region much can be accomplished. The quantitative relationship between path length through an absorbing medium and the absorbance of radiation was first defined by Bouguer in 1729; however, it is usually attributed to Lambert (1768). The connection with the concentration of an absorbing species was defined by Beer in 1859. The combination of these concepts takes different forms in the world literature, but in the United States the conventions derive from the Joint Committee on Nomenclature in Applied Spectroscopy (Society for Applied Spectroscopy and American Society for Testing and Materials), whose report was published in 1952 (Hughes, H. K., *Analytical Chemistry*, Vol. 24, 1952, p. 1349). It takes the form

$$A = \log(I_0/I) = abc_1 = \epsilon bc_2$$

where

A = absorbance,
I_0 = intensity (or power) of the incident light beam,
I = intensity (or power) of the transmitted light beam,
a = the absorptivity constant,
b = the light path in centimeters,
c_1 = concentration of the analyte species in grams/liter,
ϵ = the molar absorptivity constant, and
c_2 = concentration of the analyte species in moles/liter.

The quantity $\log(I_0/I)$, commonly called the absorbance, is also sometimes known as the "extinction" or the "optical density" of the solution. Analyte concentration is thus linearly proportional to absorbance for a constant light path length. Transmittance, today, is a less frequently used concept than absorbance even though the detector signal of most spectrophotometers is linearly proportional to it. It is related to absorbance by $A = \log(1/T)$, where T is the transmittance. The readout of some old filter photometers is in units of T, so calibration curves from these instruments are best plotted on log-linear graph paper.

Filter photometers are a comparatively primitive form of measuring device by today's standards, but they represented in their day a significant advance from color comparators, such as the Duboscq, which provided a standardized means of visually estimating color matches between unknown and standards. The Klett-Sommerson filter photometer was at one time the most widely used instrument of this type. It utilized a projection lamp, a photoresistor, a collection of narrow bandpass filters, and large-capacity, long path-length glass sample cells. The "Klett" was such a workhorse that its use persisted well into the modern spectrophotometer era, and it would not be surprising if some units were still in use today.

Spectrophotometers differ from filter photometers in that wavelength selectivity is achieved by means of a monochromator—comprised of either a prism or a diffraction grating and a network of mirrors and slits to direct the light. The bandpass of radiation reaching the sample chamber is typically much narrower with these instruments. Light throughput, however, may not be improved over a filter photometer. The detector may be a *phototube*, which is a vacuum tube with electrodes maintained at some potential between which a current flows if photons fall on the negative terminal. A more sensitive detector is a *photomultiplier*, which uses a cascade effect between a series of electrodes, each successive one at a higher potential than the last, to vastly amplify the sensitivity to impinging photons. A *photodiode array* is a solid state device that can be used to measure an entire wavelength region simultaneously.

Single-beam spectrophotometers have traditionally fallen into two classes: "workhorse" instruments (such as the Bausch & Lomb Spectronic 20™) and research-type instruments (such as the Beckman DU™). In their day, both of these devices were widely used. The Spectronic 20 was a grating instrument with a single test tube sample holder. The Beckman DU was a prism instrument with a four-cuvette sample holder. Today, computer-controlled photodiode array instruments represent the state of the art in both categories.

Another classification for spectrophotometers refers to their optical bench design. Single-beam instruments simply pass the monochromator-selected light through the sample cell and then into a detector. Dual-beam instruments split the monochromator-selected light into two beams. This is usually accomplished with a mechanical chopper, which is a rotating device that alternately presents a free path and a mirrored surface to the light beam. When the free path is present, the beam passes through the sample cell. When the mirror is present, the beam is diverted at a right angle to a series of other mirrors that direct it through the reference cell.

Both beams are then recombined at a half-silvered mirror that directs them to the detector. The detector then measures a "chopped" signal that alternates between the absorbance of the sample solution and the absorbance of the reference solution. The detector output is enhanced by an amplifier that is precisely tuned to the "chopped" frequency, extracting the two absorbances. In some configurations, this demodulated output drives a variable density filter in the reference light path to increase its absorbance and balance the two halves of the detector output. This version of a double-beam instrument is called an optical null design. There are other, quite distinct, designs as well. Some modern instruments using solid-state detectors simulate a dual beam instrument with a single-beam design by alternately scanning the reference and the sample and subtracting the complete spectra from each other, all under computer control.

The light source is usually a tungsten filament lamp for all measurements down to about 350 nm. Near-UV measurements between 350 and 200 nm usually employ a deuterium discharge tube with a quartz window. Light from the source enters the monochromator through an entrance slit and is then collimated by a lens system into a parallel beam that impinges on a prism or a grating. The dispersed light then falls on an adjustable exit slit. By turning the prism or grating, light of the appropriate wavelength can be made to pass through the slit. And by narrowing the slit width, a certain limited additional wavelength selectivity can be achieved.

Prisms do not disperse light as uniformly as diffraction gratings. Prism instruments tend to disperse light more broadly at the UV end of the spectrum and less broadly at the red end of the spectrum. Thus, with prism instruments, opening the slit when operating in the UV region allows more light energy to pass without diminishing wavelength selectivity.

A diffraction grating acts as a dispersing element by reflecting light from the spaces between its ruled parallel grooves. These thousands of reflections form an interference pattern that produces an orderly series of uniformly dispersed spectral lines (or slit images). With grating instruments, a given exit slit setting produces the same degree of selectivity (or bandwidth) across the entire wavelength region in which the spectrophotometer was designed to operate.

The sample chambers of commercial instruments take a number of forms. Perhaps the most common is designed to accommodate a cassette of four or more 1-cm square-sided glass cuvettes, which may have lids to slow the evaporative loss of volatile solvents. Other designs include cylindrical cells with flat optical faces at each end and path lengths of 2, 4, or 6 cm. Micro-cuvettes with extremely small internal volumes and "sipper" or flow-through cells are also available.

Other features of commercial instruments include external wavelength and slit controls and insertable filters for use in certain wavelength regions. In some designs, the phototube detector assembly is readily interchangeable to accommodate tubes sensitive to certain spectral regions. A light-proof shutter is generally the means of introducing the light beam to the sample chamber. With cassette designs, some means is provided for moving the individual cuvettes into the light path.

Spectrophotometric Measurements

UV/visible instruments are utilized in a number of different ways. First, there is the role as a qualitative identification tool, primarily of interest in organic analysis. Absorbance versus wavelength scans can be laboriously obtained with a conventional single-beam instrument (rezeroing the reference and measuring the sample absorbance at regular wavelength increments, then plotting the results), but they are best obtained on one of the recording designs (either double-beam or simulated double-beam). Many materials have a characteristic UV/visible spectrum that allows them to be "fingerprinted" by this means in a process analogous to qualitative infrared analysis.

Also, in developing a new spectrophotometric quantitative method, it is usually a good idea to record the spectrum of the colored species being measured in order to make the best decision on exactly where on the absorbance curve the readings should be taken. It should be noted that the best spot is not always on an absorbance maximum. If the maxima are sharp peaks, utilizing them may require an unrealistic degree of instrumental stability. Sometimes it is appropriate to also record the spectrum of the unreacted dye or the spectrum of the sample background in order to avoid regions of interference.

In the simplest quantitative measurements, a series of calibration standards is measured along with appropriate cell, sample, and reagent blanks, as needed. With the light-proof shutter closed, the instrument is first adjusted to infinite absorbance (or zero percent transmittance) with a potentiometer. This compensates for the "dark current" caused by thermal electron emission in the phototube or photomultiplier. Readings are then generally taken versus water or some simple solvent as a reference. Occasionally sulfuric acid is used as the reference.

After subtracting the appropriate blanks, the corrected absorbance is plotted on rectilinear coordinate graph paper versus concentration (or versus weight of analyte with an explicitly stated volume). Convention places absorbance on the ordinate. If the curve obeys Beer's law, the relationship is linear (ideally over the entire concentration range of interest), and its equation can be calculated by a simple least squares linear regression. Such an equation can be used to convert the corrected absorbances of unknown test solutions to concentrations of analyte.

If the curve is not linear over any portion of interest, it is usually best to read the values from the graph. If the only error associated with spectrophotometric measurement was that associated with reading an instrument scale, such as with a dial analog readout, it would be possible to define an absorbance region of maximum precision, and it could be recommended that test conditions be adjusted so that all readings be taken in that region. In fact, with modern instruments the error limits of the measurement are defined by "shot noise" in the photomultiplier (a statistically distributed background emission of photoelectrons superimposed upon the "dark current").

Such a situation complicates the delineation of a region of maximum precision. It has been suggested, however, that such a region is defined by an inflection in the plot of log(concentration) versus the square root of the observed transmittance [see *Annual Book of ASTM Standards*, Vol. 03.05, American Society for Testing and Materials, Philadelphia, 1993, Practice for Photometric and Spectrophotometric Methods for Composition (E 60)].

Differential spectrophotometry provides a means of extending the usefulness of UV/visible molecular absorption techniques outside the low and trace concentration realm. In this variant, the reference solution is replaced by a synthetic standard accurately prepared at some concentration below that expected to be present in the unknown. The standard and the unknown are prepared identically. With the standard in the light path, the absorbance reading is adjusted to zero by opening the slit or increasing the gain on the detector amplifier.

Reading the absorbance of the unknown under these conditions of virtual scale expansion will often yield improved precision at high analyte concentrations. Even greater precision can be achieved by "pinning down" the infinite absorbance (0% transmittance) end of the scale with a synthetic standard prepared above the level of the unknown and adjusted to zero transmittance with the dark current control. While such techniques can improve precision significantly at high absorbance readings, they have limitations and should not be considered a substitute for good gravimetric or volumetric procedures, which excel at high analyte concentrations.

Multiple-component measurement is often feasible by reading absorbances at different areas of a test solution's spectrum. The technique is more frequently applied in quantitative organic analysis by infrared spectrophotometry, but it has also been usefully applied to metal analysis by UV/visible spectrophotometry (see example below). It is usually the case that the absorbance peaks of the components are not fully resolved from each other. That is, for a two-component system, A and B, A contributes some absorbance to B's absorbance peak at wavelength, λ_B, and B contributes some absorbance to A's absorbance peak at λ_A. With this situation, we prepare four calibration curves: A at λ_A, A at λ_B, B at λ_A, and B at λ_B; then we measure the unknown at λ_A and at λ_B. Let us here assume that all four calibration curves pass through the origin. In this case we can write

$$A_A = C_A S_{AA} + C_B S_{BA}$$

$$A_B = C_A S_{AB} + C_B S_{BB}$$

where

A_A = the unknown's absorbance at λ_A,
A_B = the unknown's absorbance at λ_B,
C_A = the concentration of A in the unknown,
C_B = the concentration of B in the unknown,
S_{AA} = the slope of A's calibration curve at λ_A,
S_{BA} = the slope of B's calibration curve at λ_A,
S_{AB} = the slope of A's calibration curve at λ_B, and
S_{BB} = the slope of B's calibration curve at λ_B.

All the quantities are known values except C_A and C_B. Their values can be found by solving these two simultaneous equations in two unknowns.

The process can sometimes be extended to a three-component system; however, beyond that, manual data manipulation becomes impractical. With computer-controlled diode array instruments that store the entire spectrum in memory, it is possible to calculate good approximations for many components by using software that applies iterative approximation techniques to a great many wavelengths.

Chemistry for Spectrophotometric Determinations

Up to this point we have confined the discussion to the measurement step itself. But before listing some illustrations, we should include a few remarks about the how and why of what we are measuring. There are thousands of compounds and complexes that are strongly colored or strongly UV-absorbing, but only a small percentage find utility in spectrophotometric methods. Still, this leaves quite a large number of specific and nonspecific reagents to sort through in selecting a suitable chromophore. Three texts can be unreservedly recommended in this regard: *Colorimetric Determination of Traces of Metals* by E. B. Sandell, 3rd ed., Interscience Publishers, New York, 1959, which is a classic and in its day an exhaustive treatment of its subject; *Colorimetric Determination of Nonmetals*, D. F. Boltz, Ed., Interscience Publishers, New York, 1958; and *The CRC Handbook of Organic Analytical Reagents* by K. L. Cheng, K. Ueno, and T. Imamura, CRC Press, Boca Raton, FL, 1982. Most questions concerning the spectrophotometric determination of the components of metals and alloys can be answered by consulting one or more of these books.

Table 13-1 lists some frequently utilized spectrophotometric reagents, the analytes they are often used for, and the recommended wavelength where measurements are made. In selecting a spectrophotometric approach, the analyst must keep a careful eye to a number of important parameters. If these are not fully described in the literature associated with a new method, he must do the experiments required to define them. Many of these hinge upon the *specificity* of the reagent. How many elements besides the analyte form colored species with it? How likely are these elements to occur in the intended sample matrix? Also, does the sample matrix contain elements that are likely to form turbidity in the measured solution? Are there simple chemical separation schemes for isolating the analyte that will not interfere with the color reaction?

Masking techniques are another alternative for dealing with interferences. These consist of the addition of one or more complexing agents to bind with problem matrix elements so that they do not react with the color reagent or precipitate in the solution. Compounds of cyanide, citrate, tartrate, oxalate, pyrophosphate, or chelating agents like EDTA are common masking agents used in many methods. The specific ones cho-

TABLE 13-1—Selected spectrophotometric methods.

Element	Reagent	Wavelength, nm	Reference	Remarks
Aluminum	8-Hydroxyquinoline	390	Chloroform	Extract after isolation
Antimony	Brilliant Green	645	Toluene	Extract after masking (pyrophosphate)
Arsenic	Molybdate	850	Water	Distill with HCl/HBr first
Boron	1,1-Dianthrimide	620	Sulfuric acid	Incubate at 100°C to develop color
Chromium	Diphenylcarbazide	540	Water	Good for tramp levels
Cobalt	Nitroso-R-salt	520	Water	ZnO separation common
Copper	Neocuproine	455	Chloroform	Extract after evolving Cr
Iron	1,10-Phenanthroline	510	Water	Reduce Fe; remove Cu
Lead	Dithizone	520	Chloroform	Extract after masking (cyanide)
Manganese	*meta*-Periodate	545	Water	Background: destroy color with NO_2^-
Molybdenum	Thiocyanate	475	Butyl acetate	Reduce Fe and Mo with $SnCl_2$
Nickel	Dimethylglyoxime	465	Water	Oxidizing conditions; extract with $CHCl_3$, then back extract
Niobium	Hydrogen peroxide	362	Sulfuric acid	High Ti interferes
Phosphorus	Molybdate	830 (650)	Water	Reduce with hydrazine sulfate
Silicon	Molybdate	815	Water	Extract with $CHCl_3$, reduce, then back extract
Tantalum	Pyrogallol	415	Water	Stabilize with tartrate
Titanium	Diantipyrylmethane	390	Water	Filter insolubles, ignite, fuse, and recombine
Tungsten	Dithiol	635	Butyl acetate	Extract after removing Mo

sen must, of course, be compatible with the intended chemistry.

Another important method parameter is the *blanking* approach required. All spectrophotometric methods have a cell blank if the cuvettes used for the reference and the test solution are not perfectly matched. This often-neglected step is simply accomplished by filling all the cells with the reference solution, adjusting the reference to zero absorbance, and reading the other cells against it. Much more important are the sample blank, that is, the test solution minus the color reagent; and the reagent blank, the reagents minus the sample. One or both of these may represent a significant part of the total absorbance, and it behooves the analyst to be aware of the relative importance of these blanks in each method.

If a blank reading is very significant, it is wise to average multiple blanks for the best accuracy. In a few methods, it is possible to easily and accurately measure the combined sample and reagent blank by destroying the colored complex after its absorbance is measured. Another important method parameter is color development time. Some reagents form a stable colored complex instantly, while others may require an hour (or incubation at a fixed temperature for a fixed time). And yet another parameter is the color stability once formed. Some colored species must be measured within a short window of time, while others can be measured one day and rechecked the next morning.

Important Details

It is important that the laboratory maintain a regular program of wavelength and absorbance checks on spectrophotometric equipment. This can consist of a wavelength scan (manual or automatic) using a standard holmium oxide glass cell (or other absorbance wavelength standard) to confirm that the maxima occur at the correct wavelength readings. Also, measurement of a graded series of standard filters will confirm measured absorbance response. Routine measurements in nonpolar solvents after a solvent extraction usually require some means of screening out errant water droplets from the light path. Separatory funnel stems are often stuffed with cotton or a rolled piece of filter paper. These are better for this purpose than Pyrex wool, which tends to contaminate cuvettes with tenaciously adhering fibers. Collection vessels—often a volumetric flask—may contain a pinch of anhydrous sodium sulfate to react with and hold any water that makes it that far.

Methods that utilize a sulfuric acid medium are a special problem. The analyst is confronted with filling a cuvette with a small opening and wiping the optical surfaces free of any drips without getting burned. The best approach is to keep a cloth or a paper towel thoroughly soaked with water, as well as a supply of dry lint-free wipers, close at hand. The optical surfaces are first wiped with the wet towel, then dried with the wipers.

Below 400 nm, quartz cells (with a much lower UV cut-off absorbance than borosilicate glass) should be used. All cuvettes should be thoroughly cleaned immediately after use. The cleaning must be tailored to the solutions used, of course, but heavily contaminated cells often yield to a 1:1:1 HCl:ethanol:water mixture.

Determination of Manganese (up to 1.6% Mn)

Weigh a 0.1-g sample of steel into a 250-mL Erlenmeyer flask . Dissolve in any combination of HCl and HNO_3. Add 5 mL of $HClO_4$ and heat to fumes of $HClO_4$. Cautiously, add HCl, dropwise, while fuming to evolve chromium. Cool, add 20 mL of water, and then 25 mL of H_2SO_4/H_3PO_4 mixture

(500 mL water + 500 mL H_3PO_4, cool, add cautiously, with stirring and cooling, 1000 mL H_2SO_4), then 25 mL of potassium *meta*-periodate solution (16 g KIO_4, 10 mL HNO_3, dilute to 2 L with water). Boil for 3 min and cool to room temperature. Transfer to a 100-mL volumetric flask, dilute to the mark, and mix well. Measure the absorbance versus water at 545 nm.

Add three drops of 10% (w/v) sodium nitrite solution to the cuvette. Mix by inverting, using a plastic finger cot, and then measure the absorbance of this blank at the same wavelength. Subtract the second reading from the first and calculate the manganese concentration from the calibration curve. [Note: For the most accurate work, it is best to use an aliquotting scheme with larger sample weights and to take separate sample aliquots for the sample reading and the blank.]

Determination of Copper

Weigh a steel sample containing 0.05 to 1.5 mg of copper into a 250-mL Erlenmeyer flask. Dissolve in any combination of HCl and HNO_3. Add HF dropwise to volatilize silicon. Cool, add 15 mL $HClO_4$, and heat to fumes of $HClO_4$. Cautiously, add HCl dropwise to the fuming solution to volatilize chromium. Fume until the volume has been reduced to approximately 10 mL. Cool, add 7 mL of water, and swirl to dissolve the salts. Add 1 mL of HCl and transfer the solution to a 100 or a 250-mL volumetric flask (depending on the copper level). Dilute to volume and mix.

Dry filter some of the solution into a 100-mL beaker and remove an aliquot of the filtrate containing 0.01 to 0.30 mg of copper, transferring it to a 150-mL beaker. To the aliquot add 5 mL of hydroxylamine hydrochloride solution (100 g/L) and 10 mL of citric acid solution (300 g/L). Stir well and adjust to pH 5.0 ± 0.1 with 1:1 NH_4OH: H_2O. Add 10 mL of neocuproine solution (0.1 g in 100 mL of absolute ethanol). Transfer the mixture to a 125-mL separatory funnel and add 15 mL of chloroform. Extract for 30 s and drain the (lower) organic layer through cotton into a 50-mL volumetric flask containing 7 mL of absolute ethanol. Add 10 mL of chloroform to the separatory funnel and extract again for 30 s. Drain the organic layer into the same flask. Discard the aqueous layer through the top and wash the separatory funnel and funnel stem with absolute ethanol into the volumetric flask. Dilute the flask to the mark with ethanol and mix. Read the absorbance at 455 nm versus chloroform. Subtract a reagent blank from the readings and calculate the percent copper by reference to a calibration curve.

Simultaneous Determination of Niobium and Titanium

Weigh a 0.2-g steel sample into a 250-mL beaker. Add (in this order) 25 mL of HCl, 5 mL of HNO_3, 25 mL of water, and 25 mL of solvent mix (400 mL H_3PO_4 + 300 mL water, stir well and cool, then cautiously, with stirring and cooling add 120 mL H_2SO_4; dilute to 1 L, cool, and mix). Heat slowly to dissolve the sample, then bring to light fumes. Fume for 1 min (no longer), cool for 1 min, then cautiously add 25 mL of dilution mix (cautiously with cooling and stirring, add 350 mL of H_2SO_4 to 600 mL of water; dilute to 1 L, cool, and mix). Transfer to a 50-mL volumetric flask using 3.0 mL of HCl and 10.0 mL of stannous chloride tartaric acid solution (dissolve 88 g $SnCl_2 \cdot 2H_2O$ in 60 mL of HCl with warming; dissolve 50 g tartaric acid in 100 mL of water with warming; combine the two solutions and dilute to 250 mL with water) and enough dilution mix to dilute to the mark when cool. Mix well and transfer a 1.0-mL aliquot to each of two dry 50-mL beakers. To one beaker add 25.0 mL of H_2SO_4 and to the other add 25.0 mL of hydroquinone solution (15.0 g of hydroquinone + 450 mL H_2SO_4 in a dry 500-mL volumetric flask; add a stirring bar and close with a glass stopper; cover with a light shield, and stir magnetically until dissolved; remove the stir bar, dilute to the mark with H_2SO_4, mix well, and store in the dark. Prepare 24 ± 1 h before use in all cases).

Swirl to dissolve the white precipitate that forms and allow the solutions to stand for 10 min. Read the absorbance at both 400 and 500 nm versus H_2SO_4. Subtract the cell blank, the sample blank, and the reagent blank (prepared by substituting 1 mL of water for the sample aliquot) from the test solution reading at each wavelength. Assuming no intercepts, if S_A is the slope of the niobium calibration curve at 400 nm, S_B is the slope of the niobium calibration curve at 500 nm, S_C is the slope of the titanium calibration curve at 400 nm, and S_D is the slope of the titanium calibration curve at 500 nm, then

$$S_A W_{\mathrm{Nb}} + S_C W_{\mathrm{Ti}} = A_{400}$$

$$S_B W_{\mathrm{Nb}} + S_D W_{\mathrm{Ti}} = A_{500}$$

where

W_{Nb} = the weight of niobium in the final sample aliquot,
W_{Ti} = the weight of titanium in the final sample aliquot,
A_{400} = the corrected absorbance reading for the test solution at 400 nm, and
A_{500} = the corrected absorbance reading for the test solution at 500 nm.

It is a simple matter to solve these simultaneous equations for W_{Nb} and W_{Ti}. If tungsten is present, the approach fails because it absorbs at both wavelengths. However, if titanium is absent, niobium and tungsten can be determined in an identical manner. All three components can be analyzed by an elaborate scheme that involves separation of the tungsten by coprecipitation with molybdenum using alpha-benzoinoxime.

ATOMIC ABSORPTION

Ground state atoms absorb light just as molecules do. However, while molecules can be studied in solution, for analytical purposes the absorption of light by atoms must be studied in flames, vapors, and plasmas. Some of these are high-energy phenomena, where atoms tend toward excited and ionized states that *emit* light. To the extent possible, instruments and analytical schemes are designed to suppress such phenomena while maintaining an abundant population of ground state atoms. The seminal work in this field was published in 1955 (Walsh, A., *Spectrochimica Acta*, Vol. 7, 1955, p. 108); however, commercial instruments did not appear until the 1960s.

By now the basic principles of atomic absorption are familiar to most analysts. A high-intensity light source comprised of the emission spectrum of the element of interest is produced by either a hollow cathode or an electrodeless discharge lamp. Such lamps are designed to emit sharp spectra with narrow lines and a low background. The electrodeless discharge lamp (EDL) is a more intense light source than the hollow cathode lamp (HCL)— this usually results in better sensitivity since the detector amplifier can be operated at lower gain. However, EDLs are only available for a small number of elements (notably As, Bi, Ge, Hg, Pb, Sb, Se, Sn, Te, Tl, Cd, Zn, Ti, P, and certain alkali metals). HCLs, on the other hand, are available for most elements.

Some combinations of elements are also available in a single HCL, saving cost and lamp warm-up time. But these multi-element lamps occasionally generate difficulties due to spectral overlaps, and their intensities tend to be lower than that of single-element lamps. Whatever source is used, the light beam generally first passes into a mechanical chopper, such as that described above for a dual-beam UV/visible spectrophotometer. One portion of the light passes through the atomizer region (a flame, a graphite furnace, or perhaps a mercury cold vapor cell) where ground state atoms of the analyte absorb the characteristic energy.

The other portion of the light avoids this region. Another chopper alternately passes the reference and sample beams into a monochromator, where the analytical wavelength is selected and passed to a photomultiplier tube and its associated demodulating amplifier. Such an arrangement compensates for noisy, fluctuating source lamps (but not for noise from the flame or from furnace wall emission). The demodulator circuit generates an output signal proportional to the difference between the sample and reference beams, which is in turn proportional to the analyte concentration. There are, of course, numerous other instrument configurations.

Calibration Modes

Atomic absorption has a limited linear dynamic range when compared to some other techniques, like ICP-OES, but with careful multi-point calibration the nonlinear portion of the response curve can be utilized. Calibration curve quantification, either manual or by means of an "on-board" computer, is probably the most commonly used approach. However, if the analyst is willing to confine his work to the linear response concentration region, some additional options are open to him.

The *method of additions* is an extremely useful approach, especially in the presence of a heavy matrix or for trace level work with the graphite furnace atomizer. Two conditions are critical to this tactic: (1) the analyst must know the extent of the linear range so that the sample solutions all remain within it; and (2) a representative analyte-free blank must be available. In practice, one spikes several identical portions of the sample solution with exactly measured increments of pure analyte and measures these along with a representative blank.

The blank-corrected values are plotted versus concentration on linear graph paper divided into a positive and negative quadrant with corrected absorbance on the ordinate and the concentration of analyte running positive and negative from the centered origin on the x -axis. The added concentrations of analyte are plotted in the right quadrant, and the line is extended to $y = 0$ in the left quadrant of negative x-values. The negative x-value at $y = 0$ represents the unspiked analyte concentration in the test solution.

It is a relatively simple matter to automate this calculation using a computer or a statistical pocket calculator. Just perform a least-squares fit of the line and solve the resulting equation for $y = 0$. A very powerful simplified version of the same approach (sometimes referred to as the *spiking technique*) is simply a one-point method of additions. One merely splits the dissolved test portion into two equal volumes (or begins with two identical test portion weights), spikes one (often at about one half of the expected level of analyte concentration), and dilutes both to the same volume. This approach works well for both flame and graphite furnace work, although, of course, it is not as rigorous as the true multipoint method of additions.

The rationale behind both of these approaches is to compensate for matrix effects, which can be significant in certain complex alloy systems. If the analyst wishes to test for matrix effect, he can perform the following experiment: Add a series of increments of analyte to pure water, measure the absorbances, and draw the curve. Then add the same series of increments of analyte to the sample solution, measure the absorbances, and draw the curve on the same graph paper sheet. If the two curves are parallel, the sample shows no matrix effect. But if the curves are not parallel, a matrix effect exists with the sample solution. Some workers have also advocated determining the blank by a method of additions, but this approach can sometimes lead to seriously erroneous blank values. It is usually best to determine the blank directly from a synthetic matrix, using the average of several replicates.

The *bracketting* technique is a useful calibration approach at analyte concentrations above 1%, where a higher level of precision is always required. Prepare two standards, one at about 5% (of the amount present) *below* the level of analyte expected and one about 5% (of the amount present) *above* the level of analyte expected. The solutions are all diluted to the same final volume, which is selected to yield readings within the linear range and generally between 0.2 and 0.5 absorbance units. The solutions are measured in order of increasing concentration to effectively negate any memory effects. The blank-corrected absorbances can then be quantified graphically or by means of a simple algebraic expression (see Fig. 13-1).

Element Sensitivities

It is probably safe to say that a completely satisfactory theoretical explanation of the characteristic AA sensitivity of each element has not yet been formulated. There *is* considerable insight in this area, however, and trends can be delineated. Elements of lower atomic weight tend toward greater sensitivity than high atomic weight elements because under identical conditions there tends to be a higher population of light elements in the analytical light path. There are certain elements for which good ground state resonance lines do not exist except in a region obscured by molecular bands. Other elements have an abundance of low-lying energy states just above the ground state. Under any practical analytical condition, a significant portion of the analyte is distributed among these states and thus does not absorb at the ground

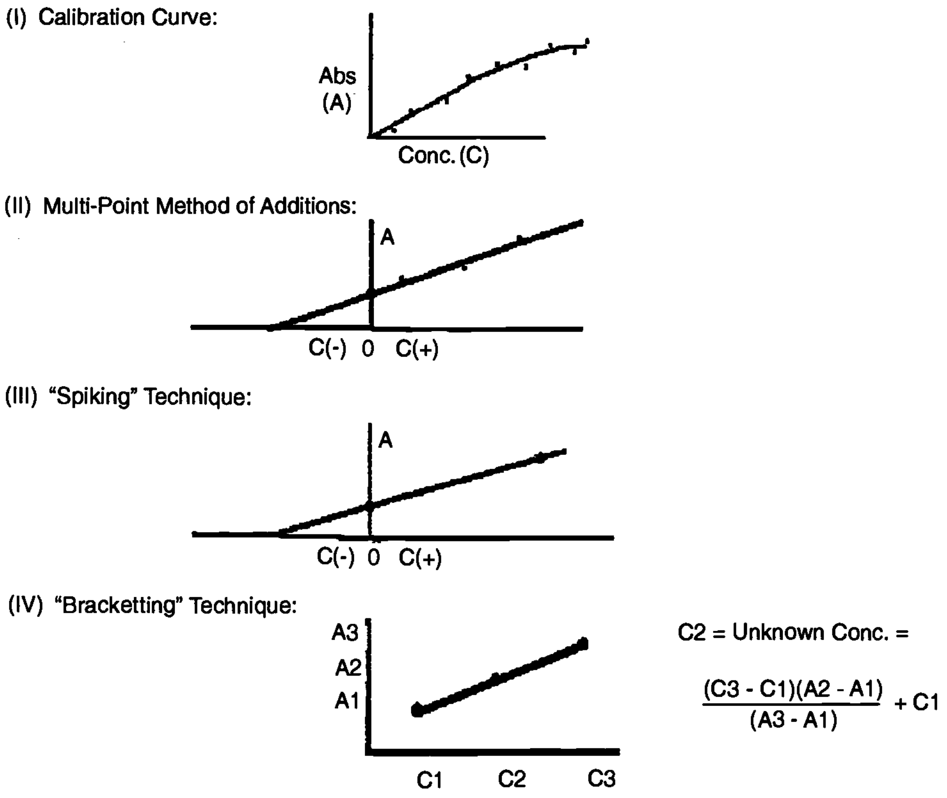


FIG. 13-1—Atomic absorption calibration options.

state resonance line. Many of the rare earth elements, for example, are very insensitive for this reason.

Also, there are a number of elements that tend to form thermally resistant oxides, nitrides, or carbides in either a flame or a graphite furnace atomizer. Examples of this effect are the poor sensitivities for niobium, tantalum, hafnium, zirconium, tungsten, and boron. It is interesting to note that atomic absorption becomes practical for many of these elements with an atomic absorption instrument fitted with a gas-jet-assisted plasma discharge lamp. In this device, a solid sample is sputtered by argon ions in the absence of any oxygen, nitrogen, or carbon.

Table 13-2 lists the relative sensitivities of the elements by atomic absorption of the more conventional flame and graphite furnace configurations. A more conventional means of expressing sensitivity is the concentration (in ppm), which produces 1% absorbance (0.0044 absorbance units). Such values vary between instruments and can be found in the manufacturer's literature.

Interferences

Like so many emerging methodologies, atomic absorption went through a period when it was touted as interference free. In fact, to this day it remains as one of the better instrumental techniques in this regard. But it is *not* interference free. Actually, several different classes of interferences can be delineated. *Physical effects* are one common source of error that leads to erroneous results. If the density, viscosity, and surface tension of the sample solution and the calibration solutions are not approximately the same, the transport rate into the flame or the deposition and subsequent atomization in the graphite furnace will differ, leading to error. Matching the sample matrix with synthetic standards is one solution to this problem, the method of additions is another. The simplest course is to dilute the sample until the physical effect becomes negligible, but this is only feasible where sufficient analyte sensitivity can be retained.

Chemical effects are interferences that result in a decrease in analyte signal. They are caused by the formation of compounds or complexes in the sample solution that reduce the population of ground state analyte atoms produced by the atomizer. A classic example is the reduction of calcium absorbance in an air/acetylene flame caused by the presence of phosphate in the sample solution. There are several different ways of dealing with interferences in this category. The simplest, which sometimes works, is to raise the atomization temperature. For example, phosphate has no effect on calcium in the hotter nitrous oxide/acetylene flame. Another approach is to add to both the sample and the calibration standards a reagent that forms a soluble complex with the analyte which is more stable than the interfering complex or compound but that releases the analyte thermally as a ground state atom. Similarly, a reagent could be added which reacts with the interferent, releasing the analyte. *Matrix modifiers* in graphite furnace AA are a group of reagents that are used to overcome chemical effects from undesirable side reactions, sometimes by forming a volatile species with the interferent that is removed during the "char" cycle before atomization occurs.

Ionization effects occur when analyte atoms are excited past the ground state to the free ion form. The formation of analyte

TABLE 13-2—Relative sensitivity of the elements by atomic absorption (*Note*: 0 = worst sensitivity; 4 = highest sensitivity).

Element	Wavelength, nm	Relative Sensitivity	Recommended Flame Oxidizer
Aluminum	309.3	3	Nitrous oxide
Antimony	217.6	2	Air
Arsenic	193.7	3	Air
Barium	553.6	3	Nitrous oxide
Beryllium	234.9	4	Nitrous oxide
Bismuth	223.1	2	Air
Boron	249.7	0	Nitrous oxide
Cadmium	228.8	4	Air
Calcium	422.7	4	Air
Cerium	[a]...	0	[a]...
Cesium	852.1	3	Air
Chromium	357.9	3	Nitrous oxide
Cobalt	240.7 (242.5)	3	Air
Copper	324.8	3	Air
Dysprosium	421.2	2	Nitrous oxide
Erbium	400.8	2	Nitrous oxide
Europium	459.4	2	Nitrous oxide
Gadolinium	407.9	0	Nitrous oxide
Gallium	287.4	2	Nitrous oxide
Germanium	265.1	2	Nitrous oxide
Gold	242.8	3	Air
Hafnium	286.6	0	Nitrous oxide
Holmium	410.4	0	Nitrous oxide
Indium	303.9 (325.6)	3	Air
Iridium	264.0	1	Nitrous oxide
Iron	248.3	3	Air
Lanthanum	550.1	0	Nitrous oxide
Lead	283.3	3	Air
Lithium	670.8	4	Air
Lutetium	336.0	0	Nitrous oxide
Magnesium	285.2	4	Air
Manganese	279.5	3	Air
Mercury	253.7	2	Air
Molybdenum	313.3	3	Nitrous oxide
Neodymium	463.4	0	Nitrous oxide
Nickel	232.0	3	Air
Niobium	334.4	0	Nitrous oxide
Osmium	290.9	0	Nitrous oxide
Palladium	247.6	2	Air
Phosphorus	213.6	0	Nitrous oxide
Platinum	265.9	2	Nitrous oxide
Potassium	766.5	4	Air
Praseodymium	495.1	0	Nitrous oxide
Rhenium	346.0	0	Nitrous oxide
Rhodium	343.5	3	Air
Rubidium	780.0	3	Air
Ruthenium	349.9	2	Air
Samarium	429.7	1	Nitrous oxide
Scandium	391.2	0	Nitrous oxide
Selenium	196.0	2	Air
Silicon	251.6	2	Nitrous oxide
Silver	328.1	4	Air
Sodium	589.0 (589.6)	4	Air
Strontium	460.7	4	Air
Tantalum	271.5	0	Nitrous oxide
Tellurium	214.3	3	Air
Terbium	432.6	0	Nitrous oxide
Thallium	276.8	3	Air
Thullium	371.8	3	Nitrous oxide
Tin	286.3	2	Nitrous oxide[b]
Titanium	365.3 (364.3)	2	Nitrous oxide
Tungsten	255.1	0	Nitrous oxide
Uranium	358.5 (351.5)	0	Nitrous oxide
Vanadium	318.3 (318.4, 318.5)	2	Nitrous oxide
Ytterbium	398.8	3	Nitrous oxide
Yttrium	410.2	0	Nitrous oxide
Zinc	213.9	4	Air
Zirconium	360.1	0	Nitrous oxide

[a] No absorbance has been measured.

[b] H_2/air shows better response but more interferences.

ions means that less analyte is available to absorb the ground state resonance line, and the analytical response is diminished. The best solution to this problem is to add to both sample and standards a fixed amount of an ionization suppressor reagent. This consists of an easily ionized element (sodium, strontium, or lanthanum solutions are often employed), which is, to some degree, ionized in place of the analyte.

Spectral effects consist of two types: atomic line interferences due to nonanalyte absorbance lines from the sample matrix components (or nonanalyte emission lines from the other elements in a multi-element lamp) and molecular band interferences and other forms of nonspecific absorbance (smoke, light scatter) that contribute to the spectral background. In the case of atomic line interferences, narrowing the slit or using an alternate resonance line usually solves the problem, although these remedies may decrease sensitivity. Of course, if the problem is a multi-element lamp, one can always substitute the single-element version.

If the problem is with the sample matrix, one can usually chemically separate the analyte from the offending element. Line interferences are comparatively rare in atomic absorption work. Nonspecific and molecular absorbance are much more common, but they can be corrected for using a number of different techniques, including the continuum-source, Zeeman, and Smith-Hieftje approaches.

In the *continuum-source background correction* system, a tungsten iodide lamp (for the visible region) or a low-pressure deuterium or hydrogen lamp (for the UV region) is used to produce a noncharacteristic (line-broadened and overlapped) light beam that a chopper sends through the atomizer in pulses. These pulses alternate with pulses of a line source (the HCL or EDL). Smoke, salt particles, and molecular vapors absorb both beams equally (provided that the beams have been initially balanced in intensity), so that the difference in the two sets of signals is the background-corrected analyte absorbance.

It should be noted that some atomic absorption *does* occur in the continuum beam since it does include the resonance wavelength, but it is a negligibly small fraction of the total absorption and has no influence on the correction process. Continuum-source background correction, unlike the other commonly employed schemes, results in no sensitivity loss for any analyte provided that the continuum beam and the line source beam are precisely aligned. Achieving such an exact alignment, however, is not always easy with the design of most commercial instruments. Continuum source correction presumes that the background is uniform across the bandpass of the slit width setting. If "structured" background occurs within the spectral bandpass (say, emission lines from a matrix element), then another correction system may be a better choice.

The *Zeeman background correction* system is not one, but several, instrumental schemes for compensating for background. The Zeeman effect, which describes the influence of a magnetic field on a beam of light, was sought in vain by Michael Faraday in 1862, but discovered in 1896 by Pieter Zeeman using more sensitive equipment. In the normal Zeeman effect, spectral lines are split into three components: the *pi line*, which remains at the original wavelength and is linearly polarized parallel to the magnetic field direction, and two *sigma lines*, which are displaced to the right and left an amount proportional to the magnetic field intensity (e.g., about 0.1 A for 8 kG) and which are polarized perpendicular to the magnetic field direction. However, with many elements (e.g., Fe, Ni, Cu, Cr, and Hg) an anomalous Zeeman effect occurs in which, instead of two, an entire array of proportionately displaced sigma lines is generated.

The Zeeman effect is utilized in AA background correction schemes in a number of quite distinct designs. In one configuration, the atomizer is subjected to the magnetic field, which is cycled on and off at 60 times per second. The line source beam exiting the atomizer passes through a stationary linear polarizer, which passes the sigma components and rejects the pi component. When the magnet is on, the sigma components are shifted away from the resonant wavelength, where atomic absorption occurs and only the background is measured. When the magnet is off, both atomic absorption and background absorption are measured. Electronic subtraction of the two signals yields a background corrected output at the analytical wavelength.

Other configurations place the magnet around the line source rather than around the atomizer (these are termed "source-shifted" systems). Here, the pi components of the source are absorbed by both analyte and background, while the sigma components are absorbed only by the background. Some designs use a rotating polarizer to detect first one, then the other signal. Other arrangements use a Wollaston prism to direct the pi and sigma components to separate photomultipliers.

The Zeeman correction approach suffers some loss of sensitivity, and calibration curves tend to have a reduced linear region. Curves also "roll over" at high concentrations so that the same absorbance is obtained from two distinct analyte concentrations—one high and one low. The advantages tend to outweigh these problems, however. The signal-to-noise ratio is superior to most other systems, resulting in better precision and lower detection limits. The correction is generally very accurate, and structured background presents no special problem.

A third background correction system in commercial use is the *Smith-Hieftje* design. Here, a hollow cathode lamp is momentarily pulsed at a high input current level so that it produces a burst of line-broadened, self-absorbed continuum radiation. A cold atom cloud accumulates in front of the cathode, absorbing the intense line spectra emitted from the back of the cathode. Such continuum radiation is absorbed by the background, while the low current, narrow-line spectrum is absorbed by both the analyte and the background. Electronically subtracting the two signals yields the corrected absorbance. This approach is simple and requires less exact alignments than conventional continuum-source correction. Not all elemental line sources broaden effectively when their hollow cathode lamp is pulsed, however. For these cases, there is a significant loss of sensitivity.

Flame Atomic Absorption

Flame atomization atomic absorption was the first commercial form that this technique took, and it remains important as a comparatively inexpensive supplement and alternative to ICP-OES. The fuel is usually acetylene; the oxidizer is air or nitrous oxide. Occasionally, a hydrogen/air or an argon-sheathed hydrogen flame is used for special applications. The pre-mix burner, in which the gases are mixed before reaching the burner head, has become standard for most instruments. There are a number of different types of nebulizers These all utilize gas flow to aspirate the sample through a capillary and a cross-flow or impact bead to nebulize the solution, and they all incorporate a "spoiler" or other arrangement for rejecting all but the finest droplets.

The need for fine droplets is explained by the fact that within a relatively brief time over a short trajectory the droplets must be dried to minute salt crystals, which must then be vaporized into dissociated ground state atoms. Large droplets that did not completely vaporize would lead to burner clogging with the attendant danger of a flashback explosion as well as to erroneous measurements. Throwing away such a significant portion of the sample reduces the sensitivity, but increases the accuracy of the measurements, especially in the presence of a heavy matrix such as a dissolved metal alloy.

With a flame AA aspirating liquid, one is measuring a rate. Such signals can be conveniently filtered of a-c noise, making the readings more reproducible than is usually the case with discrete peak measurements, such as those measured in electrothermal AA. Each gas mixture utilizes a specially designed burner. The air/acetylene flame operates at about 2500°K and is suitable for all of the easily vaporized elements. The nitrous oxide/acetylene flame is about 500°K hotter and is usually reserved for refractory oxide-forming elements. Because of the greater tendency of this mixture to flashback, the flame is lit with air and switched over to nitrous oxide. When work is complete, the flame is switched back to air before it is extinguished.

Electrothermal Atomic Absorption

When one considers how little of the sample actually reaches the analytical measurement region in flame AA, it is no surprise that atomic absorption is in principle an exquisitely sensitive technique. When an instrument is configured to take full advantage of that inherent sensitivity, some truly remarkable detection limits can be achieved. Of the many designs developed, commercial electrothermal instruments have largely settled on the Massmann furnace used with the L'vov platform.

A hollow graphite tube (often manufactured of the thermally resistant pyrolytic graphite) is held in graphite cones connected to water-cooled copper contacts. The L'vov platform is a shallow boat (manufactured from the same material) that rests in the bottom center of the tube. The entire assembly is enclosed in a sealed chamber with optical quartz end windows to allow passage of the line source beam. Argon gas enters at the sides and exits through an aperture in the center of the tube where the sample (generally 5 to 40 μL) is injected by an auto-sampler.

In analyte-shifted Zeeman systems, the furnace is partially encircled by a magnet assembly. The furnace is programmed through a heating cycle consisting of a drying step to desolvate the sample, a "char" step to remove interfering volatiles and to place the analyte in a form suitable for atomization, and finally an atomization step wherein the ground state atom cloud is created and atomic absorption occurs. This thermal program may have a number of additional features:

precise rate-of-rise ramping between steps, gas flow interrupts (commonly, during the "char" step), and injections of reactive gases (e.g., oxygen or air to facilitate char or hydrogen to reduce oxides to metals).

The purpose of the L'vov platform is to delay the atomization of the analyte until the furnace atmosphere has achieved a high and stable temperature. For many elements, this discourages "memory" effects due to condensed analyte at the tube ends and leads to improved peak shape, sensitivity, and precision. With the graphite furnace atomizer, what is being measured is a discrete event—the atomization and atomic absorption of a large part of the total sample aliquot. The best results with the L'vov platform are usually from peak area, while atomization directly from the furnace wall with its faster atomization yields better results from peak height.

As mentioned above, there are numerous *matrix modifiers* that have been applied in furnace work. Chloride in the sample aliquot is a particular problem due to the formation of volatile analyte chlorides that are partially lost during the char cycle unless ammonium nitrate or diammonium EDTA is added. In both cases, with these additions volatile ammonium chloride is evolved away during the char step, leaving the analyte in the furnace in a form more amenable to atomization.

Nickel (generally in the form of nickel nitrate) is a valuable addition in many determinations and is particularly useful in tramp work with iron-base alloys. Compounds such as nickel selenide have favorable atomization characteristics. Magnesium nitrate and combinations of palladium and magnesium nitrate are highly advocated for numerous determinations. The choice of matrix modifier and the exact conditions, rates, plateau times, and temperatures of the program, including the choice of platform or wall atomization, are all highly empirical functions. The lore associated with electrothermal atomic absorption has begun to rival that associated with gas chromatography. However, instrument manufacturers provide a great deal of guidance to ease the burden of methods development.

Since the emergence of this technology in the 1970s, there have been various attempts to directly determine solids (particularly metal alloy chips), some of which have met with reasonable success. However, it must be remembered that the use of such minute samples as those required by a solids GFAA approach requires an extremely homogenous sample material if the results are to be truly representative.

Other Forms of Atomic Absorption

In 1939, atomic absorption was first described as an analytical technique for the detection of mercury vapor (Woodson, T. T. in *Revue of Scientific Instruments*, Vol. 10, 1939, p. 308), and to this day the cold vapor technique remains a highly sensitive and useful approach for that element. The chemically generated elemental mercury vapor is passed into a quartz cell in the instrument light path.

Hydride techniques came much later and have yet to be fully accepted due to precision problems. In hydride generation, a solution of sodium borohydride is used to generate selenium, arsenic, antimony, germanium, bismuth, lead, and tin hydride gases, which are passed by a flow of inert carrier gas to a flame-heated quartz tube in the light path or in other configurations directly into the burner flame itself. In some schemes, the hydrides are frozen out in a cold trap, which is subsequently heated rapidly to create an analytical signal pulse. Such systems produce extremely sensitive responses, but, unfortunately, often lack good reproducibility.

The use of a glow discharge sputtered source with solid samples is a recent advance since it allows sensitive determinations of boron, zirconium, and other elements that have been closed to AA determination. Since the argon-sustained plasma jet is free of oxygen, nitrogen, and carbon, refractory compound-forming elements have been opened to the advantages of AA determination. The disadvantage of a solids approach remains, however— the sample must be homogenous since only the solid surface will be sampled.

Chemistry for Atomic Absorption Determinations

There are those who believe that the only chemical manipulations involved in atomic absorption analysis are those reactions involved in the dissolution of the sample material. That perspective is unfortunate since the measurement technique can be enhanced substantially by the use of isolation and preconcentration steps, which will greatly extend its usefulness. A simple mercury cathode electrolysis can extend flame AA sensitivities so that 0.001% aluminum or titanium are easily quantified. Similarly, the determination of tin can be extended to 0.001% and below by aspirating MIBK/TOPO extracts into a flame AA.

Similar approaches are possible with electrothermal techniques, extending what are already high sensitivities into new realms. One important note that the analyst must remain aware of is that the new highly sensitive techniques do not usually preclude the application of old enhancement protocols. Thus, the potential remains to extend new approaches even beyond their instrumental promise. It is not always wise to think first in these terms, but the rapidly evolving requirements of material specifications mandate such contingency plans.

REFERENCES

Annual Book of ASTM Standards, Vol. 03.05, American Society for Testing and Materials, Philadelphia, 1993.

Annual Book of ASTM Standards, Vol. 03.06, American Society for Testing and Materials, Philadelphia, 1993.

Brown, S. D., *Analytical Chemistry*, Vol. 49, No. 14, 1977, pp. 1269A–1281A.

Colorimetric Determination of Nonmetals, D. F. Boltz, Ed., Interscience Publishers, New York, 1958.

Day, Jr., R. A. and Underwood, A. L., *Quantitative Analysis*, 2nd ed., Prentice-Hall, Englewood Cliffs, NJ, 1967, pp. 290–335.

Dulski, T. R. and Bixler, R. R., *Analytica Chimica Acta*, Vol. 91, 1977, pp. 199–209.

Flame Emission and Atomic Absorption, Vols. 1–3, J. A. Dean and T. C. Rains, Eds., Marcel Dekker, New York, 1975.

Fuller, C. W., *Electrothermal Atomization for Atomic Absorption Spectrometry*, The Chemical Society, London, 1977.

Manning, D. C. and Slavin, W., *Analytical Chemistry*, Vol. 50, No. 9, 1978, pp. 1234–1238.

Marks, J. Y.,Welcher, G. G., and Spellman, R. J., *Applied Spectroscopy*, Vol. 31, No. 1, 1977, pp. 9–11.

McKaveney, J. P., *Analytical Chemistry*, Vol. 33, No. 6, 1961, pp. 744–747.

Mile, B., Rowlands, C. C., and Jones, A. V., *Journal of Analytical Atomic Spectroscopy*, Vol. 7, 1972, pp. 1069–1073.

Reichardt, M. S., *Atomic Spectroscopy*, Vol. 13, No. 5, 1992, pp. 178–184.

Sandell, E. B., *Colorimetric Determination of Traces of Metals*, 3rd ed., Interscience Publishers, New York, 1959.

Segre, E., *From Falling Bodies to Radio Waves*, W. H. Freeman & Co., New York, 1984, pp. 153, 183.

Siemer, D. D., "Atomic Absorption Spectrometry," *Metals Handbook*, 9th ed., Vol. 10: *Materials Characterization*, American Society for Metals, Metals Park, OH, 1986, pp. 43–59.

Smith, S. and Hieftje, G., *Applied Spectroscopy*, Vol. 37, 1983, p. 552.

Thompson, K. C. and Thomerson, D. R., *Analyst*, Vol. 99, 1974, pp. 595–601.

Van Nostrand's Scientific Encyclopedia, 4th ed., D. Van Nostrand Company, Princeton, NJ, 1968.

Walsh, A., *Spectrochimica Acta*, Vol. 7, 1955, p. 108.

Walsh, A., *Analytical Chemistry*, Vol. 46, No. 8, 1974, pp. 698A–708A.

Also, instrument manuals, 1976 and 1985 from Perkin-Elmer Corp., Norwalk, CT, and product literature from Analyte Corp., Medford, OR.

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Emission Spectroscopy

IF THE READER FELT THAT the last chapter gave short shrift to an important subject, he may be outraged by the treatment presented here. The reason for such abbreviated coverage is that both absorption and emission spectroscopic techniques have an extensive and current literature authored by individuals far more knowledgeable and experienced in these areas. Our purpose with these chapters is to introduce these techniques and to illustrate how chemistry plays a role in their use. The reader is referred to the Bibliography and to the references that accompany these chapters for necessary details of both theory and application.

Here we have chosen another unconventional grouping, combining in one chapter all the common measurement techniques that involve the emission of electromagnetic radiation. By *optical emission* we mean any analytical technique in which emitted visible (or UV) radiation is measured. Thus, this category includes: flame emission; arc and spark electrical discharge excitation; and d-c, microwave, inductively coupled, and glow discharge plasmas. By *X-ray fluorescence,* we mean any technique in which emitted X-rays are measured. However, a few special approaches have been reserved for the next chapter. The special category of atomic fluorescence will be discussed in the next chapter as well.

OPTICAL EMISSION

As with all emission phenomena, optical emission involves the expulsion of photons as electrons in excited states drop back to lower states. In the case of optical emission, the process involves the excitation or ejection of outer shell (or valence) electrons. The line spectra produced by these electron transitions are characteristic of the element involved, but also depend in a sensitive way on the character and intensity of the excitation source.

Optical emission spectrometers are designed to produce, disperse, and collect this light to accurately quantify the elemental composition of the sample. A sequential monochromator is configured for measuring the intensity of one wavelength at a time, while polychromator designs can allow 60 or more wavelengths to be measured simultaneously. Sequential units are more flexible, allowing ready access to alternate wavelengths when interferences are a problem. Simultaneous instruments offer incredible throughput for well-characterized sample systems.

Until recently, optical emission for metals analysis was primarily a solids-based technique, but the advent of the stable, hot ICP source has opened the realm of solutions-based work with its attendant potential freedom from sample inhomogeneity errors. The solids-based approach, however, remains the workhorse of the metals industry, and it is unlikely to be supplanted by slower techniques that require sample dissolution. However, the solutions-based ICP approach provides some extremely valuable support to an industry that has become increasingly dependent upon certified alloy reference materials.

It is possible with a solutions-based ICP instrument to operate relatively independently of such materials by preparing synthetic solution standards from pure materials. This is a poor, but arguably passable substitute for wet chemically certified alloy reference materials in some instances. Of course, validation of the work with one or more appropriate primary standard alloys elevates the reliability significantly. The purity of the "pure" materials is one area of concern since suppliers rarely list contaminants such as surface and matrix oxygen among the certified trace elements. The preparation technique is another concern. And it is seldom that a sample matrix is duplicated exactly synthetically—the ignored elements may prove to be an important source of error. These reservations aside, the solutions-based ICP approach with or without adequate dissolved alloy standards can provide valuable support for the metals analysis laboratory.

Optical Designs

Since the nineteenth century, when optical spectroscopy emerged as a discipline, hundreds of spectrometer designs have been devised. Today, just about three basic designs dominate in commercial instruments. *Scanning monochromators*, which view one analytical wavelength at a time, are generally based on the *Czerny-Turner* configuration. Here, light from the source passes through an entrance slit to a concave collimating mirror that directs it to a flat diffraction grating. The grating is rotated with a stepper motor under computer control to direct the selected wavelength to a concave focusing mirror, which directs it to the exit slit. The diffracted entrance slit image passes through the exit slit and is measured, usually with a photomultiplier tube.

In modern instruments, the grating is rapidly slewed to the approximate region of the desired line; then the instrument takes a series of measurements at small wavelength increments in a peak-seeking subroutine that searches for a match to a stored model of the line profile and a maximum within that profile. This process is reasonably rapid, but, when combined with the actual measurement integration, it tends to accumulate significant analytical time, especially if a large number of analytes must be measured per sample. Sometimes sample volume is exhausted before the analysis is complete.

Polychromators, or "direct-readers," which simultaneously measure 10 to 60 wavelengths, are based mostly on the *Paschen-Runge* design. Here, light from the source is focused with a lens onto the entrance slit, then passes to a concave diffraction grating whose arc defines the *Rowland circle*. The dispersed wavelengths exit through a series of secondary slits along the circle and are each measured by an individual photomultiplier tube. The photomultiplier current is accumulated as charge on a capacitor in each element channel.

In one type of system, at the conclusion of the exposure, each channel is interrogated and its charge converted to a digital value. In another system, the interrogation of all channels proceeds throughout the exposure with running digital totals being accumulated.

A special type of polychromator is based on the *echelle design*. *"Echelle"* is French for "ladder" and suggests the rungs of spectral orders that this optical design generates, as well as the coarse rulings of the echelle grating itself. Light from the source enters the entrance slit, then passes to a concave collimating mirror. It is then directed to the echelle grating at a high angle of incidence. The dispersed light then passes into a prism that cross-disperses the spectrum. A concave focusing mirror then forms a square at the focal plane with spectral orders stacked in one direction and wavelengths within each order arrayed in the other direction. Such a square or rectangular spectral image is ideal for the use of solid state detector chips such as photodiode arrays (PDAs), charge-coupled devices (CCDs), or charge injection devices (CIDs) with or without specially designed masks (to eliminate all but selected lines). Such optical systems are part of several commercial spectrometers, including designs that allow the analyst to take a pixel-based "snapshot" of a sample spectrum. Such "snapshots" can be stored on tape or floppy disk and reexamined later, much as a photographic plate spectrum could be extracted from the archives and measured for a new element on a densitometer.

It is appropriate at this place to say a word about the gratings themselves since they are the key to the success of any optical design plan for a spectrometer. A diffraction grating differs from most prisms in that the slit image is resolved and dispersed in a highly regular manner. The diffraction gratings used in spectrometers are all reflection gratings in that they consist of a series of very narrow parallel grooves in a reflecting surface. Incident in-phase polychromatic light that strikes the grating at an exact angle is dispersed into a spectrum because each exiting reflecting wavelength has traversed a slightly different path. The extent of the dispersion of a grating is related to how fine and close together the grooves are, while the sharpness of the spectral lines is generally related to groove width and to how many total grooves there are.

The echelle grating is unusual; it is composed of very fine grooves ruled much further apart than is common with other gratings. Such a grating has high resolution but low angular dispersion. When crossed with a prism or a low-resolution grating, the characteristic stacked spectral orders or "echellogram" is produced.

Master gratings are painstakingly produced on a vibration-isolated ruling engine. Replicas of these master gratings are then produced by contact processes. One option of this duplication approach is that the groove angle of the replicas can be "blazed" for extra efficiency at certain high order wavelength regions where particular line interferences may be less of a problem. A cheaper approach to the manufacture of gratings is the use of a photographic/holographic process. Such gratings have fewer imperfections and thus fewer spectral "ghosts" than replica gratings. They can also be made larger for higher resolution spectra.

Emission Sources

An optical emission source has two basic functions: (1) to create a plume of atoms and ions that accurately represents the concentration of the analytes in the test portion; and (2) to excite that plume in such a manner that the emitted photons can be used to accurately quantify the analytes: in other words, sampling and excitation. Sources can sometimes be tailored to a specific application. In time-resolved spectroscopy, for example, the exposure is electronically gated to view only that portion of a cyclic discharge that yields the most analytically useful emission. Such stratagems can increase sensitivity dramatically. While no source is used exclusively for a single type of sample, it *is* possible to loosely categorize "solids" sources and "solution" sources.

The *d-c arc* is utilized primarily for solids, sometimes in the form of powders. It is a very sensitive source, suitable for trace level components, but it is not very precise. The electrodes are often made of amorphous carbon or graphite with "crater" and other designs used to contain powder samples and various additives. These additives include: "carriers" to promote vaporization of the analyte; "buffers," which are readily ionizable substances to help stabilize the discharge current and voltage; and graphite powder to additionally facilitate the "burn." The d-c arc is also sometimes used with liquids using special electrode designs. Since nitrogen from the air produces cyanogen molecular bands, usually the arc chamber is purged with argon.

A significant "pre-burn" time is often used (i.e., the interval in which the discharge operates before light is allowed to enter through the entrance slit of the spectrometer). This allows sufficient time for the plume to become stable and representative of the analytes. But even under ideal conditions the d-c arc tends to wander. It is considered only a moderately hot source as electrical discharges go (5000 to 7000 K), and the spectra produced are largely characterized by neutral atomic lines. The primary use of this source today is in the rapid screening of pure substances for impurities. With a direct-reading polychromator, the d-c arc probably accomplishes that specific task more rapidly than any other commonly employed technique. At concentrations above about 0.1%, its usefulness as a quantitative technique diminishes. There are other more reproducible forms of arc discharge, including capacitive and various kinds of noncapacitive intermittent d-c arcs, as well as a-c arcs.

Spark sources are high-voltage intermittent discharges usually triggered by a thyratron tube or a solid state rectifier. They are used almost exclusively with a conductive solid sample as the cathode (although a rotating carbon disk electrode and other configurations for solution work sometimes find use). The anode is often tungsten or thoriated tungsten. The burn mark is large unless the discharge is stabilized by a flowing sheath of argon. The spark is a hot source, generating many singly charged ionic species. Long pre-burns are common before exposure is initiated. The use of intensity ratio calibrations with a series of standards that closely match the unknown sample can lead to accurate and precise results. With most alloys, the intensities of major and minor components are ratioed to the intensity of the base metal (e.g., stainless steel components are ratioed to iron).

Glow discharge sources are fundamentally different from arcs and sparks in that the sampling and excitation processes are uniquely separated from each other, albeit by only a small distance. The glow discharge source samples the conductive solid sample by sputtering with low-temperature ionized argon; thus, no elements are selectively volatilized, as with thermal sources. Sputtered sample atoms diffuse to a region where they are excited by high-energy electrons. It is from this hot "negative glow" region that the intense sample emission is generated. Unlike arcs and sparks, the glow discharge source can excite high-excitation potential elements without line broadening because the high-energy region remains diffuse.

One difficulty is that the sputtering rate is matrix dependent, but the use of normalized intensities (if all sample components are known) or closely matching standards can circumvent difficulties for gross composition analysis. The glow discharge source with its gentle "ion milling" etch rate seems a natural approach for depth profile surface studies. But the quantification of analyte concentration as a function of sputter depth appeared intractable until empirical expressions were derived by Bengtson and Lundholm (Bengtson, A. and Lundholm, M. in *Journal of Analytical Atomic Spectroscopy*, Vol. 3, 1988, p. 879).

There are several glow discharge configurations for pin or disk samples, including the Grimm lamp, first described in 1968 (Grimm, W. in *Spectrochimica Acta*, Vol. 23B, 1968, p. 443). In the Grimm lamp, the flat sample disk is in electrical contact with a water-cooled cathode. The end of the anode is a cylinder nearly touching the sample surface. Argon enters near a quartz window at the far end of the anode and is pumped out near the anode/cathode gap. Some time is required to finely polish the sample, pump down the sample chamber, and pre-burn the sample surface.

The *inductively coupled plasma* (ICP) has found its greatest use as a "solution" source utilizing liquid aerosol samples. However, there are configurations in which solid samples can be used. Commercial solution-based instruments were first marketed in the 1970s (along with the closely related d-c plasma instruments). The ICP was at first, perhaps, viewed as a more versatile (albeit more expensive) alternative to flame atomic absorption, but it is now generally recognized that plasma emission and atomic absorption are complementary techniques.

The ICP source is an atmospheric pressure argon plasma (ionized gas and free electrons) sustained by a radio frequency field of either 27.12 or 40.68 MHz. The power output is somewhere between 1 and 5 kW, depending on the design. The plasma torch takes different forms but usually consists of three nested quartz cylinders. The innermost tube tapers to near capillary dimensions at its tip. It is used to transport the sample aerosol into the plasma by means of an argon flow of usually about 1 L/min. An auxiliary or "plasma" argon flow (1 to 5 L/min) is sometimes used between the middle and innermost tubes to help light and sustain the plasma. Cooling argon (about 15 L/min in many designs) flows between the outer and middle tube. There are also smaller "mini-torch" designs that utilize much less argon.

Three or four turns of a water-cooled copper induction coil encircle the entire torch at a point just above the termini of the two inner tubes. To light the plasma, a small Tesla coil is used to inject electrons as high-frequency current flows in the copper coil. The plasma that forms is in the shape of an elongated toroid, like a surrealistic donut. An impedance-matching circuit is necessary to balance and optimize power transfer to the coil.

The normal analytical observation area is 10 to 20 mm above the highest loop of the induction coil. The temperature in that region is 6000 to 8000 K, and light emission there is largely due to sample ions rather than excited sample atoms. The spectrum shows many lines that are not prominent in other forms of excitation. There are, of course, many argon lines as well. The exact viewing height of the plasma is always a compromise for multi-element work since analytes vary in the vertical location of their maximum line intensities.

The rapid growth and current widespread use of the ICP is largely attributable to the fact that the source is both hot and stable. Calibration curves are linear over three to six orders of magnitude, sometimes allowing major, minor, and trace components to be determined from a single sample dilution. Solutions are the dominant sample introduction form allowing freedom from solid sample inhomogeneity effects by applying a rational sampling and dissolution plan. The sample nebulizer and associated spray chamber are the key to an accurate and precise analysis in many cases.

Most sample inlets are fed by peristaltic tubing pumps to minimize effects from differences in viscosity between solutions. For the most accurate work, mass transfer differences are corrected by the use of an internal standard (an element not present in the sample matrix, which is added in the same amount to all solutions measured).

There are several types of nebulizer. The *concentric glass nebulizer*, which is sensitive to blockage of its fine capillary, is best suited for work with very dilute solutions. The *cross-flow nebulizer* is available in fixed and adjustable versions. It shows somewhat less tendency to blockage but is still not tolerant of high levels of dissolved solids. For such solutions, a *Babington-type nebulizer* is required, which offers freedom from blockage but at the price of degraded sensitivity and precision. Poor precision is also associated with the use of most HF-resistant nebulizers and spray chambers.

Other nebulizer designs include frit or grid systems and ultrasonic systems (which require heating and cooling of the aerosol to remove excess solvent). For most types of nebulizer, a spray chamber removes large droplets from the aerosol. This can take several forms. In some, the untreated aerosol is made to traverse a circuitous path; in others, an impact surface or "spoiler" is placed in the aerosol stream. Large droplets either break up into smaller ones or fall out and are drained away.

Solid sampling for the ICP is nearly a separate field with many alternate approaches. While none of these has emerged as clearly dominant, spark ablation to generate a solid-gas aerosol, which is then transferred to the plasma through plastic tubing, has proven useful for alloy sorting. Other techniques include laser ablation (useful as a microprobe of small areas) and direct sample insertion (the sample is raised into the plasma with a graphite rod). The graphite furnace has been employed as a vaporization device with the ICP, and hydride generation systems can operate in a "pulse" mode, but are more typically set up as a continuously pumped flow injection system to generate a rate-type signal.

Other types of sources for optical emission spectroscopy include the d-c plasma and chemical flames. The *d-c plasma* or "plasmajet" source produces an inverted "Y"-shaped plasma between a tungsten cathode and two carbon anodes. Each electrode is also an argon source (2 L/min at the cathode and 1 L/min at each of the anodes). The liquid sample aerosol enters from under the crook of the plasma "arms" in an argon flow of 4 L/min. Measurement with this source is similar in most respects to measurement with the ICP source except that three orders of calibration linearity are usually all that can be expected, and long-term drift becomes a problem as the electrodes erode away.

The *microwave plasma* source typically uses helium rather than argon. It has found its widest use to date as an elemental detector for gas chromatography. *Flame sources* have become somewhat *passé* for emission work. They are still sometimes used with solutions to determine the alkali metals—an area where they remain a match for the most modern techniques. Traditionally, flame emission sources utilize either premix burners similar to those used in AA work or total consumption burners in which fuel and oxidant are mixed at the burner tip. Acetylene and oxygen—a mixture that is never used in AA work—was a common flame emission combination.

Detectors and Readout

The classic approach to detection and readout in optical emission instruments is the use of a *photographic plate*. Such plates can be stepped to record multiple sample exposures and in their day represented an important advance over film techniques that were difficult to align with a master. Like film, the plates had to be developed and dried in a darkroom, then painstakingly measured by finding and recording the density of the analytical lines using a microdensitometer (essentially a photometer that could be positioned and scanned across any small region of the photographic plate). The technique is still in use in many labs today, although, like classical wet chemistry, the expertise involved is rapidly becoming a lost art.

Photographic plate work had some important advantages that, until recently, had been missing from the electronic readout systems that came to replace it. Plate spectra could be rapidly scanned by an expert spectroscopist to detect the tell-tale lines of impurity traces when high-purity materials needed to be certified for the absence of harmful elements. Plates were easily stored for future reference and in some cases could be retrieved from storage and examined for previously unanticipated analytical needs. They could even serve as evidence in litigation cases. But the entire process was much too slow for the day-to-day analytical needs of most metals industries.

The photomultiplier detector in scanning monochromators and in direct-reading polychromators developed rapidly from an expensive luxury to a *sine qua non*. The advent of these instruments led to a series of design innovations that improved their performance. Vacuum tanks for the optics gave access to ultraviolet lines, and thermostated systems provided good optical stability. Background correction was provided by means of a moveable refractor plate or entrance slit. Computer control replaced counter tubes and clock dials with teletypes and thermal printers.

Today, most spectrometers are controlled by a dedicated personal computer. Graphics software can display the scanned region near an analytical line to check for line overlaps and to optimize the mode of background correction. Analytical programs can be used to compensate for line interferences with interelement corrections and for viscosity effects with internal standard corrections.

Photodiode arrays are solid state devices that can measure a portion of the spectrum simultaneously. They can be used in one of several modes, but have been popularly applied to echelle grating systems to take advantage of the added resolution. Such systems are sometimes used with spectral masks, forming a type of direct-reading spectrometer.

Unfortunately, photodiode arrays are approximately ten times less sensitive than a photomultiplier tube under the same conditions. They also contain a limited number of diodes in the array, which somewhat restricts resolution. *Charge-coupled devices* (CCDs) and *charge injection devices* (CIDs) are high-resolution solid state devices that have been incorporated in some spectrometers. They consist of large arrays of minute pixels.

CCDs are read destructively by transporting packets of charge across the chip. They have an excellent signal-to-noise ratio and are ideal for low-light applications. CIDs are read nondestructively by addressing individual pixels . By selectively integrating the signals on individual pixels, it is possible to expand the dynamic range until it is equal to that of a photomultiplier. A wavelength conversion phosphor coating has extended wavelength coverage into the UV. Both CCDs and CIDs show virtually no dark current if cooled to liquid nitrogen temperatures, and both types of chip make it possible to operate with real-time background correction.

Some of the spectrometers based on this technology in essence have completed the circle begun years ago with the photographic plate since it is now possible to take an "electronic snapshot" of an echelle spectrum. Analytes can be easily quantified using dozens of different lines, and the data can be quickly screened for the line that yields the best results. The data can also be stored on disk or tape and retrieved for further analysis at a later time.

X-RAY EMISSION

X-ray emission, better known, perhaps, as X-ray fluorescence, owes its origin to fundamental studies by H. G. J. Moseley just before his tragic death at the age of 27 in World War I. X-ray emission spectroscopy, unlike optical emission, derives from the ejection of *inner* shell electrons from the analyte atom. While electron beams and particle beams can accomplish this type of event, for our purposes here we will limit the discussion to initiation by an impinging X-ray beam of appropriate energy. The ejected inner shell electron (termed the photoelectron and, incidentally, studied in the separate field of X-ray photoelectron spectroscopy or ESCA) has a profound effect on the atom it has just vacated.

A series of quantum-permitted relaxations occur as higher orbital electrons drop down to lower energy levels in a cascade effect to fill the void and stabilize the electron shell structure. Most of these transitions are accompanied by the release of photons in the X-ray energy range. These secondary X-rays are characteristic of the analyte atom. The spectra are much simpler than optical emission spectra, where outer shell electrons are involved. The reason is that there are only a small number of permitted transitions among the inner shell electrons.

The X-ray emission lines are termed K, L, or M lines depending upon whether the electron was ejected from the K, L, or M shell. These are further designated as alpha or beta, depending upon the subshell of the transition and by a subscript number for their relative intensity (1 is higher intensity than 2). The K lines require the highest primary X-ray energy since electrons in that innermost shell are the most tightly bound. L lines require less energy input and are used extensively with low-energy sources, such as those employed in energy dispersive instruments. M lines find application only with a few high-atomic-number elements.

It is important to understand that the emission of secondary X-rays is not the only possible effect of the photoejection of an inner shell electron. Sometimes a secondary electron is ejected. When these Auger ("o-zhay") electrons are ejected from an atom, no secondary X-rays are emitted, and the so-called "fluorescent yield" diminishes. This phenomenon is a frequent occurrence with low-atomic-number elements and thus erodes the usefulness of X-ray emission for "low Z" elements.

Secondary X-rays from Element A never have sufficient energy to photoeject electrons from Element A, but secondary X-rays from Element B *may* have enough energy to photoeject electrons from Element A. This is the origin of X-ray enhancement effects. There are even rarely observed third element effects in which B promotes A, which then promotes C. Thus, X-ray fluorescence must deal in an effective manner with interelement correction. Two other important concerns are sample size and the effect of the sample's metallurgical history.

Hardware

Wavelength-dispersive instruments were introduced commercially in the early 1950s and are still the workhorse of nearly all metals industries. In these instruments, a high-power *X-ray tube* is used to generate the primary X-ray beam. This is a modern, water-cooled version of the Coolidge tube (developed in 1913), in which an electrically heated filament emits thermal electrons that flow in a vacuum across a potential gap of somewhere between 15 and 100 kV and strike a metal-coated copper anode. The metal coating may be rhodium, chromium, tungsten, or any of several other metals chosen for the beam spectrum produced.

This primary beam spectrum contains lines characteristic of the target coating and a continuum generated by the deceleration (*bremsstrahlung* or "braking" radiation) of the thermal electrons as they interact with the electron clouds of the target atoms. The beam passes through a beryllium window and strikes the sample surface. Both the characteristic and continuum X-rays in the primary beam contribute to the generation of secondary X-rays from the sample. The characteristic lines of the primary beam are more efficient at exciting the sample, but to be effective they must be just above the absorption edge wavelength for the analyte line.

The energy, E, contained in the absorption edge wavelength, λ, derives from the Planck relationship, $E = hc/\lambda$, where h = Planck's constant (6.62620×10^{-34} J·s), and c = the speed of light in a vacuum (3×10^{10} cm/s). In this case, E is the exact energy that will photoeject an inner shell electron. As a practical matter, it is not possible to tailor the target material of the X-ray tube to the analysis, so usually the sample excitation is provided by the primary beam continuum. The secondary X-rays from the sample pass through a collimator and strike an analyzer crystal.

The collimator (sometimes termed a Soller slit) is an array of adjacent parallel metal strips that acts to produce a beam of reasonably parallel X-ray wavelengths. The *analyzer crystal* performs exactly the same function for the secondary X-rays that a prism or diffraction grating performs with visible light—it disperses them in space so that individual lines can be measured. In this case, the X-ray wavelengths are so short that only the lattice spacing in a crystal is a suitable diffraction medium. The crystal compound is composed of low-atomic-number elements to control background from secondary X-ray emission in the crystal itself.

Crystals are selected for their dispersion characteristics as defined by Bragg's Law: $n\lambda = 2d\sin\Theta$, where n = the spectral order (1,2,3, . . . etc.), λ = the X-ray wavelength, d = the crystal lattice spacing, and Θ = the angle at which λ will be dispersed. Some common analyzer crystal materials are lithium fluoride, germanium, and PET (pentaerthritol). Crystals may be flat (nonfocusing) or curved (focusing). In most modern instruments, several interchangeable crystals are provided to optimize dispersion for different analytical requirements.

In a sequential instrument, the angle formed by the sample, the crystal, and the detector (Θ, but commonly measured as 2Θ) may be varied mechanically by a device known as a goniometer. In a simultaneous instrument, there are many crystals and detectors, sometimes a separate crystal/detector for each element channel. In such instruments, there may be 30 or more channels. Needless to say, such massive analytical capabilities come with a breathtaking price tag.

X-ray detectors for wavelength dispersive instruments are generally of the flow proportional and scintillation designs. *Geiger tubes* may be associated with very old equipment. They lack any ability to distinguish the X-ray photon energy and suffer severe counting losses even at moderate intensities due to excessive recovery time between counts.

Scintillation detectors use a thallium-doped sodium iodide crystal in front of a photomultiplier. When struck by an X-ray photon, such crystals emit a burst of 410-nm light of an intensity proportional to the energy of the X-ray photon. *Flow proportional detectors*, like Geiger tubes, contain a wire at a high electrical potential with respect to the housing. However, these devices also have thin polymer windows and a flow of P-10 counter gas (90% Ar/10% CH_4). When an X-ray enters the window, argon atoms become ionized in proportion to the X-ray energy. The cathode housing neutralizes Ar^+ ions, while the wire anode collects the free electrons. The result is an electrical pulse proportional to the X-ray energy. The flow proportional detector can discriminate X-ray energy two to three times better than a scintillation detector, but both are more than adequate for a spatially dispersed simple spectrum such as those encountered with wavelength dispersive instruments. Both detectors can recover in about 1 μs. Such low "dead times" allow count rates of more than 30,000 counts/s using appropriate software on a modern spectrometer.

Energy dispersive instruments are quite different in design than the wavelength dispersive devices we have been discussing. They emerged as a practical, low-cost alternative in the 1970s. Planck's relationship tells us that the wavelength and energy are proportional quantities, but the energy "dispersion" here is mathematical rather than physical. An X-ray beam—now more commonly produced by a low-power tube, but sometimes by a radioactive material—strikes the sample surface, generating secondary X-rays. These then strike a semi-conductor detector (or a sealed proportional detector) a short distance away. The energy-discriminated signal produced by the detector is processed by a multi-channel analyzer, which, in effect, sorts through the pulses and arranges them in order of increasing energy. One important feature of the pulse processing is a so-called "pile-up rejector" circuit, which helps to minimize data artifacts due to a pulse being received before the previous pulse has been fully processed.

The X-ray source for sample excitation takes different forms in energy dispersive units. Sometimes the primary beam comes from a 10 to 500-W Coolidge-type tube, usually air cooled. Sometimes the beam from such a tube first strikes a secondary target emitter to generate characteristic X-rays from the target element. If the characteristic line is just above the analyte's absorption edge, the analyte in the sample will be excited very efficiently, and its spectrum on the low-energy side of the analyte peak will have a low background.

As with wavelength dispersive instruments, thin element filters are used to remove continuum or interfering target lines from the primary beam. Radioactive sources are advantageous only for portable field applications since practical radioisotopes produce a comparatively low flux of X-rays. In devices that employ such sources, the sample often sits just a short distance above a ring-shaped emitter. The emitter sits on a lead ring with a detector in the annular space just a short distance below.

One of the strengths of energy dispersive spectrometers in the laboratory derives from the *semiconductor detector* that is often incorporated in the instrument. The lithium-drifted silicon (Si(Li)) detector consists of a gold-coated p-type silicon layer and an n-type silicon layer separated by a lithium-doped region. The two sides of the device are under a reversed bias of 600 V. An X-ray that enters the p-type silicon side creates an electron hole-pair for each 3.8 eV of input energy.

Such devices produce a signal proportional to the energy of the detected X-ray photon with an energy resolution ten times better than that of a scintillation detector and three times better than that of a flow proportional detector. Such resolution begins to compare with the wavelength resolution of dispersing crystals in wavelength dispersive spectrometers and is actually superior at high energies (low wavelengths) where suitable crystals are generally not available. The detector and its associated preamplifier must be cooled in liquid nitrogen to reduce electronic noise.

The pulse-processing circuitry is fairly complex, even before analog to digital conversion, and the system must be energy calibrated to correct for drift. Otherwise, pulses will be assigned an incorrect energy, and both qualitative and quantitative work will be compromised. At the present time, quantitative work with an energy dispersive spectrometer, even under ideal conditions, is not up to the standards of precision and accuracy achievable with a properly used wavelength dispersive instrument. For the qualitative identification or "semi-quantitative" analysis of a totally unfamiliar substance, however, probably no other technique is more suitable.

Software

Obtaining a reliable quantitative analysis of a complex alloy matrix using X-ray fluorescence was not as easy as it might have appeared to early workers. The instruments have always been noted for the reproducibility of the sample line intensities they produced, but attributing concentrations to those intensities has proven to be a puzzle that it has taken nearly a half-century to unravel. The problem was (and is) the sample matrix, which enhances and diminishes analyte intensity in a bewilderingly complex manner even in relatively simple samples.

The first response to the problem was the use of closely matching comparison standards. This approach is simple and straightforward and is still in use in some places where the sample mix is small and well-characterized. The standards must closely match the unknowns in all components, and they must be very homogenous so that the solid surface represents the whole standard. The problem with this approach, which vexed early X-ray spectroscopists, was that any slight deviation from the ordinary run of samples would usually throw a monkey wrench into the system.

It was soon found that, if you had a sample that could somehow be diluted or spread out into a thin film, you could calibrate with one matrix and then tolerate a great deal of variation in the unknown sample matrix and still get the correct results. Thin films work for particulate samples on membrane filters and metal cations on ion exchange paper. Dilution works for solutions and molten salt fusions (where La_2O_3 is sometimes added as an X-ray absorber to effectively increase the apparent dilution).

The use of an added internal standard is applicable to some types of samples. It should be an element affected by the matrix in a similar manner to the analyte [this often means ($Z_{analyte} \pm 1$)]. In fact, this approach is seldom used since a complex analysis may require many different internal standards and each may produce matrix problems of its own. If applicable to the sample form, the method of additions is a straightforward approach to dealing with matrix problems.

The intensity response for the analyte must vary in a linear way with concentration over the whole range of additions, however.

In order to explain the next approach, we must take a moment to consider another phenomenon of X-rays: scatter. When an X-ray beam interacts with the sample surface in addition to the inner shell photoejection of an electron, some of the primary beam X-ray photons interact with outer shell electrons and are scattered. If the collision is *elastic* (i.e., the angle of incidence equals the angle of reflection), no energy is lost and the radiation that results is termed *coherent* or *Rayleigh scattered*.

If the collision is *inelastic*, energy is lost and the X-ray photon's path is deflected—this is called *incoherent* or *Compton scattered* radiation. Such scatter results in emission lines in the sample spectrum. These lines are affected by the sample matrix in a manner similar to the way the analyte line is affected and can, in principle, be used to correct for the matrix effect. Usually the Compton scatter line is used. This approach is effective but only infrequently used. Theorists have not exhaustively characterized this correction scheme, so it must still be regarded as empirical.

Finally, there are the mathematical correction models designed to account and correct for matrix element effects on the observed analyte intensity. In order to follow the course of this work, it is necessary to briefly consider the kinds of effects that contribute to the matrix effect. First, the matrix elements can absorb some of the analyte fluorescence. Second, the analyte, itself, can absorb some of its own fluorescence. Third, the matrix elements can enhance the analyte fluorescence. All of these effects are in turn influenced by the physical parameters of the instrument, which are held constant, presumably, throughout the calibration and the analysis of unknown samples.

In 1955, Sherman published the first system of equations that attempted to describe a relationship between sample composition and X-ray intensities. This was followed by a succession of other mathematical models, including Lucas-Tooth/Pyne (1964), Traill-Lachance (1966), and Rasberry-Heinrich (1974). Each of these required the analysis of a large set of chemically analyzed standards in order to derive a reliable set of constants. It came to be recognized that deviations from a linear response curve of analyte concentration versus observed analyte intensity produced portions of a hyperbola for absorption by the matrix and absorption by the analyte, itself, but that enhancement effects by the matrix produced curvature that was not hyperbolic.

This work was initially impractical for the average laboratory due to the computer power required. But, in the 1970s computers of adequate capability began to be associated with commercial instruments. The approach is iterative. Intensities are measured and used to calculate a first approximation of the analyte concentrations using the simple slope and intercept of each calibration curve: $C_a = mI_a + B$, where C_a = the concentration of Element a, m = the slope, I_a = the intensity of Element a, and B = the intercept.

Next, the first correction is applied to the data. This takes some form similar to: $C_a = (mI_a + B)(1 + \alpha_{ab}C_b + \alpha_{ac}C_c + \ldots + \alpha_{an}C_n)$, where the α terms are constants derived from the solution of a complex set of equations based on data from a large and select set of standards. The C terms represent the concentrations of the other elemental components of the sample. The computer compares the first correction to the uncorrected data. If the data have changed, it inputs the first correction data into the same equation and compares the results of the second correction to the results of the first correction. It repeats this process until no changes occur and then outputs the data. Some version of this process is at work in most X-ray spectrometer software packages today. It has been very successful where a suitable array of standard materials is available for the initial calibration. At least a hundred standards are usually required to calibrate for a range of alloys (such as stainless steels or brasses). And the spectroscopist must apply judgement in selecting materials to include in the calibration. Excellent work can be performed in this manner, but it is not the state of the art.

In 1968, Criss and Birks published the first practical fundamental parameters scheme that began to remove X-ray fluorescence from the empirical realm. The goal has always been to establish a relationship between sample matrix and measurement system that is direct and unequivocal, but the connection had always been clouded by undefined parameters. The equation that emerged has nearly 30 variables, including such terms as fluorescent yields and mass absorption coefficients for all the sample elements and an entire sequence of terms related to the geometry of the spectrometer.

Given the computer power available today, such a theoretical construct is directly applicable to laboratory needs. With such a system in place, the spectroscopist measures the sample analyte intensities to generate a first approximation of the true analyte concentration. This is then used to calculate new theoretical intensities using the fundamental parameters equation. The first estimate of analyte concentration is then multiplied by the ratio of the first estimate of theoretical intensity to the second estimate of theoretical intensity to generate a new estimate of concentration.

This process is repeated until successive iterations show no change.

In many cases, such software systems require minimal numbers of standards for a sound calibration. And the ranges of the calibrations are typically much wider than those required by empirical approaches. There are no specific cautions here except that validation standards are the final word on work of this kind. Weaknesses in the model stem from assumptions about the spectral distribution of the X-ray tube, which may vary as the tube ages with use.

CHEMISTRY FOR EMISSION SPECTROSCOPY

We cannot leave this subject without a word about chemistry, since we have been talking about physical phenomena in this chapter almost exclusively. It is unfortunate that the spectroscopist usually feels himself cut off from the world of beakers and flasks because they can make his life much easier. Most modern X-ray spectrometers are designed with what is termed inverted optics so that solution cells can be accommodated. There is no reason why the solution placed in these cells cannot be separated chemically if that is what is required for an accurate analysis. The mercury cathode, for example, is an excellent means for removing interferences. Membrane filters mounted on plastic disks and covered with Mylar film secured by a close-fitting ring or a rubber band are another convenient way to apply chemical separation techniques to X-ray work. Such deposits as elemental selenium and tellurium, zirconium and hafnium para-bromomandelates, rare earth fluorides, or even the hydrolyzed "earth acid" oxides can all be analyzed as matrix-free thin films, usually with excellent detection limits.

In Part III we discussed numerous schemes for applying chemical separations to the elimination of line interferences in optical emission spectroscopy. There are many more problems with line interferences and many more chemical separations that can be used to deal with them. The best preparation for a new problem is a detailed understanding of what can be done with wet chemistry. In Part V, we will suggest some guidelines for laboratory practices and recommend quality assurance measures that relate directly to ICP-OES calibration with pure solutions. Work with this analytical technique has now become quite commonplace, but without some chemical background it can be fraught with errors.

REFERENCES

Annual Book of ASTM Standards, Vol. 03.05, American Society for Testing and Materials, Philadelphia, 1993, Designation E 172 and others.

Annual Book of ASTM Standards, Vol. 03.06, American Society for Testing and Materials, Philadelphia, 1993, Designations E 356, E 416, E 1097, E 1172, E 1361, E 1479, E 1507, and others.

Bertin, E. P., *Principles and Practice of X-ray Spectrometric Analysis*, 2nd ed., Plenum, New York, 1975.

Birks, L. S., *X-ray Spectrochemical Analysis*, Interscience Publishers, New York, 1969.

Boumans, P. W. J. M., *Line Coincidence Tables for Inductively Coupled Plasma Emission Spectrometry*, Vols. I and II, Pergamon, New York, 1980.

Dawson, J. B., Snook, R. D., and Price, W. J., *Journal of Analytical Atomic Spectrometry*, Vol. 8, 1993, pp. 517–537.

Faires, L. M., "Inductively Coupled Plasma Atomic Emission Spectroscopy," *Metals Handbook*, Vol. 10, 9th ed., American Society for Metals, Metals Park, OH, 1986.

Farnsworth, P. B., "Optical Emission Spectroscopy," *Metals Handbook*, Vol. 10, 9th ed., American Society for Metals, Metals Park, OH, 1986.

Fields, R. E., Baker, M. E., Radspinner, D. A., Pomeroy, R. S., and Denton, M. B., *Spectroscopy*, Vol. 7, No. 9, November/December 1992, pp. 28–35.

Harvey, C. E., *Spectrochemical Procedures*, Applied Research Laboratories, Glendale, CA, 1950.

Inductively Coupled Plasma Emission Spectroscopy, Parts I and II, P. W. J. M. Boumans, Ed., John Wiley & Sons, New York, 1987.

Inductively Coupled Plasmas in Analytical Atomic Spectrometry, 2nd ed., A. Montaser and D. W. Golightly, Eds., VCH Publishers, New York, 1992.

Jarrell, R., *American Laboratory*, October 1993, pp. 28–34.

Jenkins, R., *Analytical Chemistry*, Vol. 56, No. 3, 1984, pp. 1099A–1106A.

Jenkins, R., *X-ray Fluorescence Spectrometry*, John Wiley & Sons, New York, 1988.

Jenkins, R., Gould, R. W., and Gedcke, D., *Quantitative X-ray Spectrometry*, Marcel Dekker, New York, 1981.

Lachance, G. R., *Spectrochimica Acta*, Vol. 48B, No. 3, 1993, pp. 343–357.

Leyden, D. E., "X-ray Spectrometry," *Metals Handbook*, Vol. 10, 9th ed., American Society for Metals, Metals Park, OH, 1986.

Massachusetts Institute of Technology Wavelength Tables, The MIT Press, Cambridge, MA, 1969.

Parsons, M. L., Forster, A., and Anderson, D., *An Atlas of Spectral Interferences in ICP Spectroscopy*, Plenum, New York, 1980.

Pella, P. A., "X-ray Spectrometry," *Instrumental Analysis*, 2nd ed., G. D. Christian and J. E. O'Reilly, Allyn and Bacon, Boston, 1986.

Pilon, M. J., Denton, M. B., Schleicher, R. G., Moran, P. M., and Smith Jr., S. B., *Applied Spectroscopy*, Vol. 44, No. 10, 1990, pp. 1613–1620.

Slickers, K., *Automatic Emission Spectroscopy*, Bruhlsche Universitatsdruckerei, Geissen, Germany, 1980.

Van Nostrand's Scientific Encyclopedia, 4th ed., D. Van Nostrand Company, Princeton, NJ, 1968.

Winge, R. K., Fassel, V. A., Peterson, V. J. and Floyd, A., *Inductively Coupled Plasma Emission Spectroscopy*, Elsevier, New York, 1985.

Also, Thermo Jarrell-Ash and Rigaku instruction manuals.

Other Measurement Techniques

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THIS CHAPTER HAS BEEN RESERVED for the remaining measurement techniques likely to find use in a metals analysis laboratory. To be concise and to keep our focus, we will not discuss instruments or procedures for the measurement of physical properties if there is not a direct tie-in with compositional results. Thus, while measurements of refractive index, surface tension, flash point, viscosity, or coating weight may be a part of the analytical laboratory's assignment, the reader will have to look elsewhere for guidance in these areas. Similarly, the specialized fields of surface analysis and thermal analysis, as well as physical metallurgy tools such as X-ray diffraction and microprobe techniques, will not be included.

For enlightenment, the reader is referred to many fine texts in these disciplines and to the publications of the American Society for Testing and Materials and the American Society for Metals. What *does* remain to be covered are: the thermal evolution methods for the determination of carbon, sulfur, nitrogen, oxygen, and hydrogen; mass spectrometry in several of its most useful forms; several types of chromatography; and a miscellany of techniques that turn up from time to time in certain metals industries. A final coda will touch upon a few developments that may become important in the future.

THERMAL EVOLUTION

It is common but erroneous to lump these methods under the heading, "Combustion Methods," an appellation that some may question even for carbon and sulfur methods. It is just as misleading to refer to the oxygen, nitrogen, and hydrogen methods as "Inert Fusions" since, for example, in the case of oxygen determination, high-temperature reaction chemistry is taking place. Terminology aside, thermal evolution methods can be divided into those that employ a reactive gas (carbon and sulfur determination, using oxygen) and those that employ an inert gas (oxygen, nitrogen, and hydrogen, using helium, argon, or, rarely, nitrogen).

Carbon and Sulfur Determination

Commercial instruments for carbon and sulfur determination are based on either infrared absorbance or thermal conductivity detection. The sample is weighed into a ceramic (usually zirconia-based) crucible, one or more accelerator materials are added, and the crucible is inserted into a sealed, vertically mounted quartz combustion tube surrounded by several turns of a copper induction coil. A flow of oxygen enters from the top of the combustion tube, impinges on the sample—which is being melted by inductive coupling with the work coil—and carries reaction products out of the bottom of the assembly.

Accelerators are substances that oxidize readily and exothermally and that couple readily with the radio-frequency field of the induction coil. They are used to ensure that a sufficient temperature is achieved to melt the sample and react all of its carbon and sulfur with oxygen. Common accelerators are copper, tin, iron, and tungsten; the first two are often used in the form of granules or chips and the latter two often in the form of fine powders.

Carbon reacts to form both carbon monoxide and carbon dioxide, and sulfur forms sulfur dioxide. In addition, any hydrogen in the sample will form water vapor, and many metal oxides will be generated in the form of fine dust. The dust is removed from the combustion tube effluent by means of a porous filter dust trap, while the water is absorbed by anhydrous magnesium perchlorate. Carbon monoxide is converted to carbon dioxide by means of a rare earth/copper oxide catalyst maintained at 400°C.

Infrared detection of both carbon and sulfur is now common, although new thermal conductivity designs have also been developed. Infrared cells utilize a number of different designs, but typically consist of a mechanically chopped emitter source at one end of a measuring chamber that is being swept by the effluent oxygen stream. A bandpass filter and solid state detector at the opposite end of the chamber produce a diminution in the pulsed output signal as the analyte molecule (CO_2 or SO_2) enters the chamber. The discriminated absorbance signal is integrated and the area under the curve converted to %C or %S, based on calibration with metal alloy certified standards.

In dual element systems, SO_2 is measured first, then CO is converted to CO_2, then CO_2 is measured. The reason for this is because the rare earth/copper oxide catalyst converts some SO_2 to SO_3, which must be scrubbed out with a cellulose trap or it will contaminate the system. An important advantage of infrared absorbance detection is that it is very selective. Thermal conductivity detection, in contrast, responds almost identically to CO_2 and SO_2, so in these systems SO_2 is either trapped out with MnO_2 or is reversibly adsorbed on an inert substrate, then later released by heating.

Some designs allow the determination of trace levels of sulfur using this latter approach. Modern instruments for carbon and sulfur determination are fully automated and computer driven. Samples are weighed on an integrated self-calibrating balance, and results appear in percent. Calibration, blanking, and a considerable amount of diagnostic trouble-shooting are incorporated in the software.

Oxygen, Nitrogen, and Hydrogen Determination

Commercial instruments for the determination of these gases in metals are also based on infrared and thermal conductivity detection. Oxygen is converted to CO_2 and measured by either form of detector; nitrogen and hydrogen must be measured with a thermal conductivity detector. For oxygen and nitrogen, the sample is weighed into a graphite crucible that has been out-gassed in a heated cleaning cycle. The crucible is then connected between two water-cooled copper electrodes so that it completes a d-c circuit. Current is applied as a pulse of 600 to 1300 A, rapidly heating the crucible to 3000°C.

For oxygen and nitrogen determination, the most common carrier gas is helium, which sweeps out the carbon monoxide (formed by reaction of the crucible with oxygen in the sample) and molecular hydrogen and nitrogen. The effluent carrier passes through a dust trap that removes graphite dust. In a few designs, carbon monoxide is measured directly with an infrared detector, using a cell designed to detect the CO wavelength. More typically, CO is converted to CO_2 by a heated rare earth/copper oxide catalyst.

This is followed by a magnesium perchlorate trap to remove the water vapor that forms from any hydrogen present in the sample. If nitrogen and oxygen are to be determined by the same instrument, the gas then passes into a silica gel column that is held at an isothermal temperature. The CO_2 and the N_2 are separated chromatographically, and each is measured by thermal conductivity detection. In another design, CO_2 is measured by an infrared cell, then the effluent gas is scrubbed of CO_2 in a sodium hydroxide/clay ("Ascarite II") trap, and nitrogen is then measured by thermal conductivity.

For hydrogen determination, argon is sometimes used as the carrier gas. Here CO is converted to CO_2 with iodine pentoxide (I_2O_5) at room temperature, so that hydrogen is *not* converted to H_2O. The CO_2 is scrubbed out with sodium hydroxide/clay, and then N_2 and H_2 are separated chromatographically. The early eluting H_2 is measured by thermal conductivity. Some hydrogen determinators are designed to measure so-called "diffusible" and "nondiffusible" hydrogen in steel using special molten metal samplers. With these devices, the cooled sampler is inserted directly into the apparatus before it is opened.

Sampling and sample preparation for gas analysis has been discussed at some length in Part II of this book. Special instruments have been developed for programmed heating effluent gas analysis. With these devices, certain oxide and nitride forms can be distinguished in alloys. Such instruments are similar to conventional oxygen and nitrogen determinators except that the sample is heated very slowly. A series of discrete oxygen and nitrogen peaks corresponds to the concentrations of many metal oxide and nitride inclusions. An instrument for the determination of oxygen, nitrogen, and argon in metal alloys has also been marketed.

Miscellaneous Techniques

It should be briefly noted that there are other thermal evolution schemes and commercial devices. The now-dated approach of *vacuum fusion* was for many years the principal technique for the analysis of oxygen, nitrogen, and hydrogen in metals. It consisted of a rather large and complicated glass apparatus under high vacuum. Sample gases were evolved in a platinum or nickel bath, which was inductively heated. Gases were manipulated by columns of mercury controlled by stopcocks, their pressures measured on a Macleod gauge.

Hot extraction used temperatures below the melting point of an alloy. *Vacuum hot extraction* was used for hydrogen determination; *hydrogen hot extraction* was sometimes used for interstitial nitrogen and surface oxides. The former technique was merely a simplified form of the vacuum fusion apparatus that took advantage of the comparative ease of hydrogen extraction by employing a lower temperature. Hydrogen hot extraction is a reactive technique in which noncombined nitrogen in the sample forms ammonia gas and transition metal oxides form water vapor by reaction with hydrogen gas, both at around 550°C. It is, of course, imperative that the system be thoroughly purged with argon before and after hydrogen is introduced.

MASS SPECTROMETRY

Inorganic mass spectrometry has flirted with the metals industry for decades but has never really captured its heart. Perhaps that is now changing as some of the technique's shortcomings are being resolved by new technologies. Thermal ionization techniques have always been a mainstay of the nuclear industry, where the ability to distinguish isotopic concentrations easily justified its considerable cost. Spark source instruments found favor among scattered specialized, "high-tech" industries that needed to screen materials for trace and ultra-trace levels of contaminants. Again, the price tag was very high for the needed resolution. The technique was lengthy and error-prone, and instrument "down-time" was a major headache. There is little wonder that few chose to walk in this heady realm. Today, the glow discharge and inductively coupled plasma ion sources, as well as the quadrupole mass analyzer, have changed the technical and economic picture considerably. It is just possible that love has finally begun to bloom.

Ion Optics

Resolution requirements aside, the high-vacuum analyzer and detector systems of mass spectrometers are identical for organic and inorganic applications. The resolution issue cannot be dismissed, however, since it directly affects performance with complex alloys. In addition, high-energy ion sources produce ions with a wide range of kinetic energies. This situation ordinarily calls for a so-called double-focusing design, such as the Mattauch-Herzog, which uses a preliminary electrostatic sector to refocus ions of the same kinetic energy before they enter the magnetic sector.

In the magnetic sector, the ions travel a curved path whose radius of curvature, r (in cm), is given by $r = (2Vm/qB^2)^{1/2}$, where V = the accelerating voltage (in volts), m = the ion mass (in atomic mass units), q = the ion charge (in coulombs), and B = the magnetic field strength (in gauss). Older designs employ a photographic plate at the focal plane, which records the entire spectrum, integrating each line and providing a permanent record. Later versions generally employ a dynode electron multiplier, which is analogous in design to a photomultiplier.

This device is located at one place on the focal plane, and ion beams are brought to it by varying either the electrostatic or the magnetic field. Another double-focusing design, the Nier-Johnson, has been also used for inorganic work. Unlike the Mattauch-Herzog design, it cannot be used with a photographic plate. The time-of-flight mass spectrometer, in which a pulse of ions is allowed to travel down a neutral drift tube toward a detector at a rate inversely proportional to the square root of each ion's mass, is, as yet, seldom employed in inorganic work.

Likewise, the ion trap, ion cyclotron, and other designs remain to be exploited in inorganic analysis. The quadrupole mass filter, however, is having a large impact on this subfield. This device is designed to allow only one mass-to-charge ratio ion to travel a stable path to the detector. It can be tuned to monitor one such peak or to sweep across a range of peaks to generate a spectrum. The quadrupole consists of four precisely machined (or cast) rods (often of hyperbolic cross section) aligned in parallel, equally spaced. Opposite rods are electrically connected, and a d-c potential is imposed on the opposed pairs.

Also, a radio-frequency a-c potential (variable in magnitude and frequency) is applied to the rod pairs. The combined effect of the d-c and a-c fields on ions injected down the center of the assembly is to produce oscillations in their trajectory. At any given setting, only one type of ion can traverse the rods to the detector; all others will collide with one of the rods. The applied a-c and d-c potentials can be scanned very rapidly with little residual hysteresis effect.

The quadrupole is a comparatively inexpensive, but low-resolution device. Until recently, its most common use has been in GC-MS applications where the gas chromatograph supplies the component separation, while the quadrupole's rapid scanning can be used to monitor the effluent GC peaks. A new and growing application of the quadrupole is in the glow discharge and ICP source instruments built for inorganic analysis. The quadrupole's high-ion transmission efficiency couples well with these sources, and its simple design holds down the total cost. The low-mass resolution is a significant drawback, however.

Ion sources

For several decades, *spark source mass spectroscopy* was the only viable means for compositional survey work with metals at the ultra-trace (<0.1 ppm) level. It was and is a cumbersome technique of exquisite sensitivity and poor precision. In most schemes, the sample must be machined into the two opposing electrode pieces, across which a 1-MHz, 20 to 100-kV a-c potential is applied under high-vacuum conditions. A plasma cloud forms with the breach of the vacuum gap and expands toward an accelerating slit.

Collisional recombination transforms most of the ions back into neutral atoms, so that only about 0.1% of them enter the spectrometer. Those that do have a range of dissimilar energies and must be refocused by the electrostatic sector of a double-focusing design before they enter the magnetic sector and are deflected onto the focal plane. An out-gassed, ion-sensitive photographic emulsion at that location can be used to record the slit images and has the advantage of integrating the response so that source variations are smoothed out. Such plates are developed and measured on a microdensitometer just like optical emission plates.

The spectra, however, are considerably simpler. Usually less than 300 isotopic forms must be dealt with, and most of these are present as singly charged cations. Of course, there are some multiply-charged ions (especially from major sample components) and a miscellany of artifacts from charge-exchange, polyatomic, residual gas, and even diffusion pump oil ions. The emulsion, itself, can generate ions that are reflected back by the magnetic sector and contribute to plate fogging. Graded exposures are typical because of the limited dynamic range of the emulsion. Calibration is based on comparison to a standard.

In place of a photoplate, an electron multiplier can be placed at one location on the focal plane and the fields varied to scan the spectrum. Since the total ion beam current is monitored before the second focus, it is possible to obtain a rough quantification by comparing it to the magnetically separated analyte current. Accurate results, however, are only possible with the use of relative sensitivity factors (RSFs). These are derived from work with standards. The RSF is the number by which the raw data must be divided to obtain the correct result.

Unlike the spark source, the *glow discharge source*, as we saw in the previous chapter, is a low-energy, highly stable excitation source. Its advantages for optical emission carry over for mass spectrometry applications. Its low-pressure argon chamber is reasonably compatible with the high-vacuum inlet of a mass spectrometer. Its ion yield is very uniform, resulting in stable and generally similar relative sensitivity factors (the range is approximately 0.2 to 3.0).

The precision of the technique is significantly better than that of spark source mass spectrometry and is usually sufficient for the determination of major components. As described in Chapter Fourteen, low-temperature argon ions created by electrons thermally expelled from the cathode are accelerated toward the sample surface through a region known as the "dark space." They collide with the sample surface, sputtering away a variety of ions and atoms.

The positive sample ions are returned to the sample cathode, but the neutral species diffuse to a region known as the "negative glow," where they become ionized by collision with electrons (and also by mechanisms involving collisions with excited argon atoms). The sample ions are then extracted into the mass analyzer through a differentially pumped inlet that removes most of the argon.

The GDMS spectrum consists principally of singly charged atomic cations (M^+), but molecular species such as argides (MAr^+), dimers (M_2^+), and even oxide ions (MO^+) may complicate the scene. Isobaric interferences are overlapping mass-to-charge ratio effects. These occur in spark source and ICP source mass spectrometry as well. Some troublesome effects in glow discharge work are $^{56}Fe^{40}Ar^+$ on $^{96}Mo^+$, $^{52}Cr^{40}Ar^+$ on $^{92}Mo^+$, and $^{58}Ni^{40}Ar^+$ on $^{98}Mo^+$, which affect molybdenum determination in stainless steels.

Such problems are not prevalent, however. The GDMS spectrum tends to be comparatively clean compared to those from other techniques. Calibration curves can be linear over several orders of magnitude, but questions about the degree of representativeness of the sampling are sometimes raised. As described in the last chapter, the sputtering rate of this source is somewhat matrix dependent, and thus calibration with reliable solid standards becomes imperative.

This technique is slow by comparison to ICP-MS and also somewhat inflexible. Lengthy pump downs and sample preburns are necessary to exclude background species from air and water vapor and to achieve stable ion signals. A new a-c source has been developed for nonconductive samples, but there remains no practical way to synthesize standards or to apply the powerful tool of isotope dilution to GDMS. Certain determinations, such as oxygen and nitrogen in steel, which are impossible by ICP-MS, can be achieved by GDMS, however, and the simplicity of working with solids has some practical appeal.

The technique that has generated the most interest in recent years is ICP-MS based on the *inductively coupled plasma source*. This is currently the only source that allows the continuous introduction of inorganic solution samples into a mass spectrometer (although the thermospray LC-MS interface used in organic work has undeveloped potential in this area). The key to ICP-MS is the mass analyzer inlet, which is a water-cooled, two-stage differential pumping system.

The ICP torch is a quartz design similar to that used in ICP-OES work except that it is mounted horizontally directly opposite a 1-mm orifice. The ions generated by the plasma enter a region pumped to a working pressure of about 1 torr (133 Pa) through a platinum, tantalum, or nickel sampler cone. Then they pass though a similar skimmer cone into a region pumped to 10^{-4} torr (0.013 Pa), which is the working pressure of the mass analyzer.

The advantages of a solution approach to metal analysis have been discussed at length earlier in this volume, but these come at a price here since the solution matrix contributes significantly to spectral interference problems. Isobaric interferences when acid-dissolved metals are introduced into the system include $^{14}N_2^+$ on $^{28}Si^+$, $^{40}Ar^{16}O^+$ on $^{56}Fe^+$, $^{35}Cl^{16}O^+$ on $^{51}V^+$, and $^{40}Ar^{35}Cl^+$ on $^{75}As^+$.

Such problems are compounded by the production of molecular ions from the sample matrix itself. $^{46}Ti^{16}O^+$ on $^{62}Ni^+$, $^{48}Ti^{16}O^+$ on $^{64}Zn^+$, $^{62}Ni^{16}O^+$ on $^{78}Se^+$ are examples. The abundance of oxide (and hydroxide) ions in the spectrum can be controlled to some extent by varying instrumental parameters. However, the sample matrix can often suppress (and sometimes enhance) the sensitivity of the analyte ion signal. On average, matrix effects are mass-related, light elements being most strongly affected and heavy matrix elements having the greatest effect. The effect is believed to be related to a defocusing of the ion optics by large concentrations of the matrix element ions. Sometimes an internal standard correction is effective in reducing this influence on the results.

ICP-MS has a distinct advantage over other forms of mass spectrometry in that the instrument can be calibrated using synthetic standards prepared from pure substances. Thus, in a sense, appropriate standards are always available. Although here, as elsewhere when such an approach is relied upon, the final authority for the validation of the work should rest with appropriate alloy standards. ICP-MS also adapts readily to *isotope dilution*, a standardless definitive technique in which a stable enriched isotope of the analyte element is added as a spike to the sample solution.

To understand the process, let us assume we are attempting to analyze boron by a definitive procedure. The natural abundance of boron's two isotopes is known to be 19.7% ^{10}B and 80.3% ^{11}B. We spike a 1.00-g dissolved sample of some metal alloy containing boron with 1.00 mg of boron from a solution that is enriched in ^{10}B, say 85.0% ^{10}B and 15.0% ^{11}B. Then we allow the mixture to equilibrate, and then we measure the $^{10}B^+$ and $^{11}B^+$ ion peaks to obtain a ratio, R, of the two isotopes in the spiked sample. We know that R must be given by the following:

$$R = (\text{g } ^{10}\text{B})/(\text{g } ^{11}\text{B}) = [(0.197)(1.00)X + (0.850)(0.001)]/[(0.803)(1.00)X + (0.150)(0.001)]$$

where X is the weight fraction of boron in the unknown sample. Since we have measured R, we can solve for X

$$X = (0.0015R - 0.00085)/(0.197 - 0.803R)$$

and obtain an unambiguous, noncomparative measure of the boron concentration in the sample. In practice, however, the procedure is seldom straightforward. Because of mass spectral interferences, often the analyte species must first be chemically separated.

Equilibration sometimes requires changing the analyte's oxidation state. And the ionization/transport/detection process in the spectrometer can perturb the true ratios. There are procedures for compensating for most problems, but they fall far outside of anything that should be attempted outside of a research facility. Isotope dilution has, until recently, been strictly in the province of thermal ionization mass spectrometry, in which the sample solution is dried onto a filament that is subsequently resistively heated in the vacuum chamber of the spectrometer inlet.

The ICP-MS potentially allows great flexibility in the application of this technique, but it remains to be seen how widespread its use will become. Enriched isotopes are available for about 60 elements. A unique feature of isotope dilution is that any needed chemical separations are not required to be quantitative once spike equilibration has been achieved since only the *ratio* of the isotopes is important.

Since there are two emerging technologies—GDMS and ICP-MS—discussed here, it is appropriate to briefly highlight their differences and relative strengths. While both techniques are quantified using a simple spectrum of monatomic, singly charged ions, GDMS has fewer background lines and thus fewer potential line interferences. GDMS is almost exclusively a solids technique and so is plagued with the same calibration problems as spark source mass spectrometry. Despite consistent relative sensitivity factors, if standards are not available, results are suspect.

ICP-MS, being primarily a solution-based technique, can be easily calibrated by preparing synthetic solution standards. Any number of compensating internal standards are also easily added to both samples and standards. The ultimate detection limits of GDMS are somewhat superior to that of ICP-MS. GDMS can also be used to determine gaseous elements, which are impossible by ICP-MS. But for all its stability, GDMS may not be sampling standards and unknown samples in an identical manner since the sputtering of a metal surface is matrix related. It may thus be sometimes necessary for calibration standards to be very close to the composition of the unknown samples. ICP-MS, on the other hand, possesses all the sampling advantages of a solution-based technique.

Isotope dilution is an important option with ICP-MS, allowing definitive work for standards production and to umpire discrepant data from other techniques. Isotope dilution is basically impractical with GDMS. ICP-MS is also a much faster technique than GDMS, but sample solutions must be prepared, adding to the analysis time. Several manufacturers are marketing or developing solid sampling accessories for ICP-MS instruments. These include a laser ablation device and a spark ablation device. A convertible source GD-ICP-MS instrument is also available.

CHROMATOGRAPHY

There are many forms of chromatography—column, paper, thin-layer, high-performance liquid, gas-liquid, gas-solid, ion, and others. Only a small fraction of these may find application in a metals analysis lab, so the following discussion will be directed toward techniques that relate to the metals industry. In the most general description, all forms of chromatography involve a mobile and a stationary phase. The mobile phase carries the sample through the stationary phase. Since the components of the sample have varying affinities for the stationary phase, they vary in the speed with which they move and are thus separated in time and space from each other.

It could be argued that chromatography as an important separation technique belongs more properly in Part III of this volume. However, the most important applications of chromatography in the metals business involve instruments in which the separation process is intrinsically bound to the measurement process, so this brief survey finds a place here.

Gas Chromatography

In gas chromatography, the mobile phase is a gas that passes through a packed (or wall-coated) column of the stationary phase. Carrier gas passes through a heated injection port or sampling valve, where a measured quantity of gaseous or liquid organic sample is introduced. In the case of a liquid sample, in particular, the injection port must be heated at a temperature sufficient to vaporize all components of the sample. The carrier stream (which can be helium, hydrogen, nitrogen, argon, or another gas, depending on the analytical requirements) transports the sample to a tubular column containing the stationary phase.

The column is in a temperature-controlled chamber (or "oven"), where it can be maintained at an isothermal temperature or programmed at precise rates through a range of temperatures. Cryogenic cooling, utilizing a spray of liquid nitrogen or (less often) liquid carbon dioxide, is a useful option. Thus, the working range of the column oven can be extended from −70 to +400°C.

The column materials are the essence of this technique, which contains much lore and art. If the active substrate of the stationary phase is a solid, the technique is known as gas-solid chromatography. If the active substrate is a liquid (either supported on an inert material or coating the tube walls), the technique is known as gas-liquid chromatography.

The stationary phase employed in a given separation is selected from among hundreds of possible choices by an expedient blend of hard science and empirical skill. Simple gas mixtures are typically separated on a solid stationary phase—molecular sieves, silica gel, activated alumina, activated charcoal, or a porous polymer. These last-mentioned materials have proven to be extremely versatile. Porous polymers are useful for polar liquids and even sulfur gases. They are unique materials that produce chromatograms in which water elutes early and generally as a symmetrical peak. They are marketed under trademarks like Chromosorb (Johns-Manville Corp.) and Porapak (Waters Associates).

Complex liquid mixtures are usually separated on a stationary liquid phase coated at some selected loading on a solid support such as diatomaceous earth (sometimes known as *kieselguhr*). Tables of McReynold's constants or Rohrschneider constants are sometimes used to help select an appropriate liquid phase. These constants were obtained by measuring the relative retention times of a small number of "test probe" compounds on hundreds of different liquid phases.

So-called "low selectivity" phases like methyl silicones (e.g., OV101 and SE30) tend to elute compounds in order of increasing boiling point and are used extensively for hydrocarbons and for many other types of compounds. Methyl/phenyl silicones (e.g., OV17) are widely used for sugars and amino acid derivatives. Polyethylene glycol (e.g., Carbowax 20M), especially as the terephthalic acid terminated form, is used for phenols.

Other widely used liquid phases include the adipate and succinate forms of polyethylene glycol and polydiethylene glycol (EGA, EGS, and DEGS) for fatty acid methyl esters, and carborane derivatives of silicone oil (the DEXSILs), which show minimal column bleed (baseline shift due to movement of the liquid phase into the detector) even at 400°C and thus are suitable for separations of high-boiling compounds such as steroids, triglycerides, and certain aromatic compounds.

Alternatives to the packed wide-bore column are the wall-coated, wide-bore column and the coated or uncoated capillary column. The capillary column, in particular, represents a distinct leap in resolution, but its use requires some special skills and the patience to wait hours for the elution of peaks. Capillary columns are often associated with gas chromatography/mass spectrometry (GCMS) work.

The detectors used in gas chromatography are numerous and have evolved considerably over the 40 years or so that these instruments have been available. *Thermal conductivity detectors*, which compare heat transfer to that in the reference carrier flow, have been a mainstay of gas chromatography over all of that time. The more versatile hot-wire filament design has largely replaced the microthermistor, which is more sensitive but limited to work with gases.

About three orders of magnitude more sensitive is the *flame ionization detector*. Here, a hydrogen/air flame ionizes the effluent components, causing them to accelerate across a voltage drop. Like the thermal conductivity detector, it responds to most compounds. The *electron capture detector* is much more sensitive than the flame ionization detector, but only for halogen-bearing compounds. In this device, a ^{63}Ni beta-emitting source excites the carrier gas, which then ionizes the effluent components.

Flame photometric detectors use a hydrogen/air flame, an optical filter, and a photomultiplier tube to monitor effluents bearing a specific element. The device has been widely used for sulfur compounds, which tend to be insensitive by other methods of detection. A recent update of this concept involves a dedicated ICP-OES system to monitor various elemental lines; microwave plasma systems are used as well.

The *photoionization detector* uses an ultraviolet light source to ionize effluent compounds. It is selective based on the wavelength of the light source employed. An *electrolytic conductivity detector* can operate in several modes. In the reductive mode, halogen-bearing effluents react with hydrogen gas to produce hydrohalic acids that increase the conductivity of the cell solution. *Nitrogen/phosphorus detectors* selectively ionize N- or P-bearing effluents on a hot rubidium or cesium surface in a reducing atmosphere.

Mass analyzer detectors consist of a quadrupole or ion trap mass spectrometer dedicated to the gas chromatograph. The interface between the GC effluent stream and the mass spectrometer is a key component of most systems. This may consist of an all-glass jet separator that is differentially pumped and heated in its own oven. The GC effluent stream passes a gap before entering the MS inlet. At this location, much of the light helium carrier is pumped away, but the heavier GC peaks continue into the spectrometer.

Gas chromatography has been used by the metals industry almost since the first commercial instruments were sold. The basic steel industry, for example, has applied the technique to both liquid and gaseous mixtures associated with the production of metallurgical coke and its by-products, to blast furnace top gas, to annealing furnace atmospheres, to rolling oil emulsions, and to coatings of various types.

Most industries must face strict EPA guidelines for organic pollutant monitoring, such as Test Method 624 (Purgeables) and Test Method 625 (Base/Neutrals and Acids), which are based on GC-MS technology. Gas chromatography has also been frequently employed as a qualitative tool. Relative retention times can be used to help identify the source of spills and fugitive emissions, to help characterize process imbalances, and to monitor for toxic or flammable gases in the workplace.

Ion Chromatography

This form of chromatography, introduced commercially shortly after its development by Small and others at Dow Chemical in the mid-1970s, has revolutionized the field of anion determination. While it can be used to measure cations, the time savings for anions over alternate techniques is much more significant.

In ion chromatography, an eluent solution is pumped at high pressure through a column of ion exchange resin, then past a detector. Aqueous sample solutions are injected by means of a liquid sampling valve at the head of the column. The eluent ions, like the sample analyte ions, have an affinity for exchange sites on the resin. The resin employed is a low-capacity/ high-exchange efficiency resin—sometimes a pellicular form of resin, consisting of inert beads having a thin surface layer of exchange sites.

All the sites are occupied continuously, either by eluent ions or by sample analyte ions. As they compete for sites, the analyte ions are retarded in their movement in proportion to their affinity for the resin. As a result, they separate into distinct concentration bands. A good way to detect them is by their conductivity. But the eluent itself is also a good conductor and would ordinarily swamp the minute response of the analyte ions without some special provision.

The original solution to this problem was to place a second, "suppressor" column in line after the first. This column is used to convert the eluent to a species of low conductivity. For example, in anion analysis the eluent is frequently a dilute solution of sodium carbonate and sodium bicarbonate (a basic solution of high conductivity). The suppressor column in this case is a cation exchange resin in the hydrogen form. As the eluent and separated analytes pass through the suppressor, the sodium ions displace hydrogen ions from the resin

$$2(\text{Resin-H}^+) + \text{Na}_2\text{CO}_3 \rightarrow 2(\text{Resin-Na}^+) + \text{H}_2\text{CO}_3$$

$$\text{Resin-H}^+ + \text{NaHCO}_3 \rightarrow \text{Resin-Na}^+ + \text{H}_2\text{CO}_3$$

$$\text{Resin-H}^+ + \text{NaX} \rightarrow \text{Resin-Na}^+ + \text{HX}$$

where X is the separated anion. Carbonic acid (H_2CO_3) is weakly dissociated and has a low conductivity; thus, the measurement background is significantly suppressed. Also, the analyte anions, now converted to acids, have a stronger response since hydrogen ion as the new counterion has the highest equivalent ion conductance.

One disadvantage to this version of eluent suppression is that the suppressor column eventually becomes depleted of hydrogen ions and must be regenerated by passing dilute acid through it. Recent designs have eliminated the need for a regeneration cycle by replacing the suppressor column with semi-permeable fiber bundle devices that contain the hydrogen ion sites inside where the separator eluent flows while they are continuously regenerated by a counter-current flow of acid on the outside of the fibers.

Even more recently, a new, more rugged continuously regenerated membrane suppressor has been introduced. Non-suppressed ion chromatography schemes have also been devised, usually as "add-on" accessories to liquid chromatographs. These designs use very low-capacity resins and very dilute eluents with a high affinity for the resin. They also employ electronic means to suppress the eluent background conductivity.

Cation systems are available in all cases and are analogous to anion systems except for the use of different resins and eluents (and for suppressed designs, different suppressants). Besides conductivity detectors, two other detectors are sometimes employed. UV/visible spectrophotometry is the basis of one system. The analyte ions sometimes absorb at a characteristic wavelength. Sometimes the analyte ions are continuously reacted with a chromogenic agent as they emerge; then the colored species formed are measured. Sometimes the eluent solution absorbs at a characteristic wavelength and the analyte ions do not. In this case, the analyte species are measured as negative peaks.

The electrochemical detector is another important measurement device. It uses the oxidation or reduction of weakly conducting ionic species, such as cyanide or sulfide, in order to measure them. As the separated analyte species flows past an electrode maintained at its redox potential, it is oxidized or reduced, generating a current flow to a counter electrode.

The success of ion chromatography for the rapid and accurate determination of anions has spawned a number of loosely related techniques. Ion exclusion chromatography employs Donnan exclusion to separate weak organic acids. In a strong acid eluent, weak acids are neutral molecules that can diffuse into the pores of an ion exchange resin, while strong acids are excluded. Reversed-phase ion chromatography uses a hydrophobic packing material for the column and a hydrophilic eluent. Capillary electrophoresis uses an applied electrical field to augment the separation of ions from a sample flowing through a capillary column.

Ion chromatography and some of its offspring have proven useful in a number of metals industries. At high dilutions, the technique has been applied to plating and pickling baths, at moderate dilutions to corrosion residues and process rinse waters, and at low dilutions to surface contamination and treatment plant waters. It is, of course, invaluable for anion compliance testing of effluent water samples, leachate samples, and stack and workplace impinger samples. It also adapts readily to the determination of halides, sulfur, or phosphorus in organic materials by combusting them first in oxygen at atmospheric pressure in a Schöniger flask or at elevated pressure in a bomb calorimeter. Usually the combustion gases are absorbed in a small volume of eluent that is added to the vessel before combustion.

For reasons of space, we must pass over the other common forms of chromatography since their utility is limited in the metals business. High-performance liquid chromatography and even supercritical fluid chromatography might find use where low-volatility organic analytes become important. On the other hand, paper, thin-layer, or column chromatography might be able to solve some of the same problems with minimal capital expenditure.

A MISCELLANY OF TECHNIQUES

There remain a few more well-established measurement techniques that continue to find use in some corners of metals analysis. Some of these have always occupied specialized niches, some were once dominant and have now fallen from the mainstream, and others are dominant in other fields but only incidental to our focus. Our treatment will be necessarily brief.

Polarography

Classic d-c polarography involves applying a changing voltage between two electrodes immersed in the sample solution and measuring the current that flows through the circuit. One electrode is the indicating electrode (typically a dropping mercury type), and the other is the reference electrode (typically a saturated calomel electrode or SCE). The SCE maintains its potential and is thus nonpolarizable, while the indicating electrode acquires any potential that redox reactions impose upon it. The fall of the mercury drop at the indicating electrode is often electromechanically controlled. Redox reactions that produce polarograms (voltage versus current curves) must be diffusion based, so pains must be taken to ensure that stirring, even by convection currents, does not occur.

The technique and its many variations are inherently sensitive. The variants known as differential pulse and anodic stripping are particularly so. The problem with voltammetry (as the generic technique is known) is that it can seldom be applied unless most of the matrix has been removed by chemical separations. And while it remains an elegant and extremely sensitive approach for traces, it cannot compete in economy with, for example, graphite furnace atomic absorption, where separation is usually not required. It should be noted, however, that there is probably no better verification of the tramp level in a metal alloy than a close match in values between GFAA and, say, differential pulse polarography.

Fluorimetry

Both molecular and atomic fluorescence have been used in the analysis of metals. Fluorescence occurs when a molecule or an atom is excited by UV/visible light of a specific wavelength and then emits some of the energy as light of a different wavelength. The excitation source is often a continuum source such as a xenon arc lamp with the excitation wavelength selected by an "input" monochromator or by a series of filters. In the case of atomic fluorescence, the excitation source is often a hollow cathode or electrodeless discharge lamp.

In molecular fluorescence, the sample cell is a 1-cm quartz cuvette optically polished on all four sides. In atomic fluorescence, the sample is presented to the light beam in an argon-sheathed air/acetylene flame or in an inductively coupled plasma plume. At some angle to this arrangement (usually 90°) is a second monochromator (or series of filters) tuned to the fluorescence wavelength, followed by a photomultiplier detector. Molecular and atomic fluorescence are both sensitive techniques, but both suffer from "quenching" effects in which matrix species diminish the intensity of the measured signal.

Molecular fluorimetry can be used to measure uranyl ion (UO_2^{2+}), thallium (I), cerium (III), and certain other rare earths as "naked" aquated ions. Most work is performed with organic complexes, however. There are numerous fluorescent complexes with 8-hydroxyquinoline, morin, benzoin, and other reagents, but most are with nontransition metals since the transition elements tend to produce a quenching effect. There are many methods for aluminum, in particular. A simultaneous ICP atomic fluorescence spectrometer utilizing a circular array of hollow cathode lamps is free of the line interference problems of conventional ICP-OES, but it suffers from certain shortcomings such as the inability to determine traces of boron.

Activation Analysis

This term is a generic appellation for a large number of techniques, all of which involve bombarding a sample with high-energy particles and measuring either prompt or delayed secondary emissions. The most common projectile is the neutron. These neutrons may be produced by a nuclear reactor, by an isotopic neutron source such as ^{252}Cf or a gamma emitter mixed with beryllium, or by a Cockcroft-Walton neutron accelerator (which accelerates deuterium molecules onto a tritium target).

Reactors and isotopic sources produce neutrons with a range of kinetic energies (1 to 10 MeV), while the Cockcroft-Walton machine produces 14-MeV neutrons. The neutrons used in activation analysis are sometimes slowed (or "thermalized") by interaction with atoms in low-mass materials like H_2O or D_2O, resulting in kinetic energies of about 0.04 eV. Sometimes cadmium or a boron-bearing material is used to reduce energies into the "epithermal" range (>0.1 eV).

Often unmoderated neutrons ("fast neutrons") at 14 MeV are used. The sample is placed in the neutron beam (usually by a pneumatic tube arrangement) for a precisely measured period of time. Then it is moved to a counting station, where it is allowed to sit for another exact interval before the gamma ray spectrum is recorded. A standard is treated identically. For example, oxygen can be determined in steel by irradiation with fast neutrons: $^{16}O + {}^{1}n \rightarrow {}^{16}N + {}^{1}H$, the analyte being quantified from the characteristic decay signature of ^{16}N.

Analyte elements vary widely in their sensitivities, and the technique abounds with interference problems that sometimes can only be solved by chemical separations. At its best, however, neutron activation analysis is a definitive and extremely sensitive approach. Other types of activation analysis show similar drawbacks and advantages. Prompt gamma ray activation analysis measures the gamma spectrum produced by short-lived intermediate species immediately after thermal neutron bombardment. If charged particles like 1 to 5-MeV protons from a Van de Graaff electrostatic generator are used instead of neutrons, prompt X-rays are produced, and the technique is known as PIXE (proton induced X-ray emission analysis).

All of these instrumental methods are very useful, but immensely expensive and potentially dangerous. Generally, only the largest materials research facilities can afford or properly handle these methodologies. However, commercial analytical services using these techniques are available.

Infrared Absorption Spectrophotometry

This form of absorption spectrophotometry was not discussed in Chapter Thirteen because of its heavily organic orientation. It *is* a valuable addition to many well-equipped metals analysis laboratories, however, especially those engaged in coatings work or in the analysis of gas mixtures. Energy in the mid-infrared region (2.5 to 25 μm or 4000 to 400 cm^{-1}) is usually employed, but the infrared range extends from 0.78 to 1000 μm (or 12 800 to 10 cm^{-1}).

Unlike the absorption of electromagnetic radiation at shorter wavelengths where electronic transitions occur, in the IR region absorption of energy affects only vibrational and rotational states of the molecule. Purely rotational transitions are only observed in gases in the far IR region (>100 cm^{-1}). Rotational transitions superimposed on vibrational transitions (also only observed in gases) occur in the mid-IR.

But the main utility of the technique is the observation of vibrational transitions, which involves bending and stretching of the molecule. IR spectrophotometry is heavily used as a qualitative identification tool using a "fingerprint" of absorbance peaks that uniquely characterize structural features. It is also used as a quantitative tool using Beer's law and sometimes matrix calculations for multi-component analysis.

Older design dispersive instruments use prisms, gratings, or interference filters to select wavelengths from a continuum generated by a heated source (Nichrome wire, silicon carbide, or rare earth oxide). These are single- or double-beam instruments using various forms of detector (semiconductor photon detectors, thermocouples, thermistors, pressure-sensitive Golay detectors, and others). These instruments are being replaced by Fourier transform IR instruments, which employ a moving mirror at one arm of a Michelson interferometer to generate a scan of detector output as a function of mirror displacement (i.e., the path difference in the two arms of the interferometer).

A computer converts this interferogram into an IR spectrum. Detectors in these instruments are often of a new pyroelectric type based on a change in the electric polarization of crystalline triglycine sulfate (or a similar compound) with the absorption of IR energy. IR absorption spectrophotometry has proven useful in identifying coatings and residues on metal surfaces, for measuring the content of certain gas mixtures, for tracing the source of spills and fugitive emissions, and for monitoring weathering and thermal effects on coatings and lubricants.

THE FUTURE

Before closing our discussion of measurement techniques, we should take just a moment to speculate about the course of future developments. Such probes of likely advances are usually wildly off the mark, and there is every reason to believe that this one will be, too. However, if the reader will indulge the author here, he promises to be mercifully brief.

Total reflection X-ray fluorescence spectrometry is a new trace and surface analysis technique that may begin to challenge current methodologies in these areas. Monoenergetic X-rays from a monochromator are impinged at an extremely shallow angle (<0.1°) on a sample coated as a thin film on a flat surface. They are reflected at the same angle, and standing waves are produced above the reflection point normal to the sample surface. The nodes of the standing wave are measured by a solid state Si(Li) detector a small distance above the reflection point. Nondestructive depth profiling of thin layers is possible by varying the incidence angle.

We have already mentioned the *AC glow discharge source,* which allows the use of nonconductive samples. This seems likely to become important in both GD-OES and GDMS. The *ion trap mass analyzer* may prove useful in inorganic analysis, perhaps by linking it to a spark source or laser ablation source. This device holds ions in circular orbits until sufficient numbers are collected, then can selectively measure them. Combined ICP-OES/ICP-MS is a commercial reality. Simultaneous operation of both the optical emission and the mass spectrometer suggests the development and implementation of interactive software between them so that information unambiguously gleaned from one spectrometer can be used to automatically correct and optimize the other spectrometer.

The next step in *optical emission* and in *UV/visible spectrophotometry* appears to be a practical *Fourier transform design* for this region of the spectrum. Research grade instruments are currently available. Vibration isolation of the requisite moving mirror appears to be a major, but solvable, obstacle. Another long-time dream that may soon come true is the practical tunable *laser source* for *atomic absorption* . So far, tunable dye lasers are too limited in their wavelength range.

Current cutting edge technology will soon become commonplace. Oxygen, nitrogen, and "soluble" aluminum by optical emission and gated waveform sampling for tramp levels will spread widely in the OES field. Despite low-fluorescent yield and shallow penetration of the sample surface, work continues to extend X-ray fluorescence techniques to elements like oxygen, nitrogen, carbon, and boron. Layered synthetic crystals and long-wavelength efficient X-ray tubes have contributed significantly, and development continues.

Finally, a major analytical area in the metals production business has developed around furnace-side monitoring and robotized "container labs." Molten metal probes fall into three general categories: electrochemical solid state sensors to monitor analytes like oxygen, nitrogen, silicon, aluminum, phosphorus, and almost a dozen others; spectroscopic probes that either excite the molten metal and transport the light to a spectrometer through fiber optic bundles or generate a gas/metal aerosol that is transported to an excitation source in a spectrometer; and finally, all others.

This last includes many devices, but, perhaps most notably, a hydrogen analyzer that equilibrates the molten metal in a closed loop system of inert gas, which is then monitored for hydrogen content. The "container labs" combine computer-controlled automation technology with modern sample preparation, thermal evolution, and spectrometric instruments to create the next step after the paperless lab: the peopleless lab. So far this technology has not gotten beyond basic metal commodities, but it is certain to grow into more complex areas.

REFERENCES

Bates, J. B., *Science*, Vol. 191, No. 4222, 1976, pp. 31–37.

Beauchemin, D., *Spectroscopy*, Vol. 7, No. 7, 1992, pp. 12–18.

Crow, D. R., "Voltammetry," *Metals Handbook*, Vol. 10, American Society for Metals, Metals Park, OH, 1986, pp. 188–196.

Donahue, D. L. and Carter, J. A., "Spark Source Mass Spectrometry," *Metals Handbook*, Vol. 10, American Society for Metals, Metals Park, OH, 1986, pp. 141–150.

Ehmann, W. D. and Janghorbani, M., "Radiochemical Methods of Analysis," *Instrumental Analysis*, 2nd ed., G. D. Christian and J. E. O'Reilly, Eds., Allyn and Bacon, Boston, 1986, pp. 594–638.

Fassett, J. D. and Paulsen, P. J., *Analytical Chemistry*, Vol. 61, No. 10, 1989, pp. 643A–649A.

Fricioni, R. B. and Essig, L., "High Temperature Combustion," *Metals Handbook*, Vol. 10, American Society for Metals, Metals Park, OH, 1986, pp. 221–225.

Fricioni, R. B. and Essig, L., "Inert Gas Fusion," *Metals Handbook*, Vol. 10, American Society for Metals, Metals Park, OH, 1986, pp. 226–232.

Gijbels, R., *Talanta*, Vol. 37, No. 4, 1990, pp. 363–376.

Gross, M. L., "Mass Spectrometry," *Instrumental Analysis*, 2nd ed., G. D. Christian and J. E. O'Reilly, Eds., Allyn and Bacon, Boston, 1986, pp. 477–522.

Hinshaw, J. V., *LC/GC*, Vol. 10, No. 7, pp. 516–522.

Horlick, G., "Flame Emission, Atomic Absorption, and Atomic Fluorescence Spectrometry," *Instrumental Analysis*, 2nd ed., G. D. Christian and J. E. O'Reilly, Eds., Allyn and Bacon, Boston, 1986, pp. 315–322.

Horlick, G., *Spectroscopy*, Vol. 7, No. 1, 1992, pp. 22–29.

Jenkins, R., *Analytical Chemistry*, Vol. 56, No. 3, 1984, pp. 1099A–1106A.

Kincaid, J. R., "Infrared and Raman Spectroscopy," *Instrumental Analysis*, 2nd ed., G. D. Christian and J. E. O'Reilly, Eds., Allyn and Bacon, Boston, 1986, pp. 212–246.

Klockenkamper, R. and von Bohlen, A., *Journal of Analytical Atomic Spectrometry*, Vol. 7, 1992, pp. 273–279.

Klockenkamper, R., Knoth, J., Prange, A., and Schwenke, H., *Analytical Chemistry*, Vol. 64, No. 23, 1992, pp. 1115A–1123A.

Lingon, Jr., W. V., *Science*, Vol. 205, No. 4402, 1979, pp. 151–159.

Lochmuller, C. H., "Gas Chromatography," *Instrumental Analysis*, 2nd ed., G. D. Christian and J. E. O'Reilly, Eds., Allyn and Bacon, Boston, 1986, pp. 729–765.

Marcott, C., "Infrared Spectroscopy," *Metals Handbook*, Vol. 10, American Society for Metals, Metals Park, OH, 1986, pp. 109–125.

Melnick, L. M., Lewis, L. L., and Holt, B. D., *Determination of Gaseous Elements in Metals*, John Wiley & Sons, New York, 1974.

Merrill, R. M., "Ion Chromatography," *Metals Handbook*, Vol. 10, American Society for Metals, Metals Park, OH, 1986, pp. 658–667.

McGown, L. B., "Molecular Fluorescence Spectroscopy," *Metals Handbook*, Vol. 10, American Society for Metals, Metals Park, OH, 1986, pp. 72–81.

Siemer, D. D., "Atomic Absorption Spectrometry," *Metals Handbook*, Vol. 10, American Society for Metals, Metals Park, OH, 1986, pp. 45–46.

Skoog, D. A. and West, D. M., *Principles of Instrumental Analysis*, 2nd ed., Saunders, Philadelphia, 1980.

Supina, W. R. and Rose, L. P., *Journal of Chromatographic Science*, Vol. 8, 1970, pp. 214–217.

Warner, I. M., "Molecular Fluorescence and Phosphorescence," *Instrumental Analysis*, 2nd ed., G. D. Christian and J. E. O'Reilley, Eds., Allyn and Bacon, Boston, 1986, pp. 247–277.

Also, *Analabs Guide to Stationary Phases for Gas Chromatography*, 11th ed., J. A. Yancey, Ed., Analabs, Inc., North Haven, CT, 1977.

Part V: Quality

"The wiser men are, the more humbly they are disposed to receive the instruction of another."

—Roger Bacon (ca. 1220–ca. 1292)
—*Opus Maius*

"If a man will begin with certainties, he shall end in doubts; but if he will be content to begin with doubts he shall end in certainties."

—Francis Bacon
—*The Advancement of Learning* (1605)

16

Reference Materials, Calibration, and Validation

IN THIS LAST PART OF THE BOOK, we must address some issues that lie at the heart of our purpose as analytical chemists. Quality is not a new management revelation to the metals analyst, but has always been the essence of his task. It does take different forms, however, each with an underlying but seldom-voiced philosophy. In this chapter we will discuss one very important mechanism for bridging the gap between doubt and certainty: the application of certified reference materials to calibration and validation.

But before we can speak intelligently about how we know that an analytical procedure has produced a correct result, we must gain some insight about the method itself. Analytical techniques vary not only in their accuracy and precision, but also in their degree of independence from reference materials. This last point is not a trivial matter since in recent years the resource base for reliable wet chemically analyzed standards has become seriously imperilled. Also, we must ask some hard questions of ourselves as analytical chemists because to some degree we have it within our power to look good or bad to our superiors based on how we validate our work. Finally, we must stare in the face of the central issue—the metaphysical gap between doubt and certainty.

A HIERARCHY OF METHODS

Until we all agree that analytical methods differ at the fundamental level of "definitiveness," there is little that can be said about validation. What is presented here is the author's own construction. It is offered with the full realization that there may be other, quite distinct perceptions, but also with the firm belief that a framework of some type is essential if we are ever to establish completely sound guidelines for the validation of procedures and the verification of results.

For the metals analyst, analytical methods can be broken down into three classes: "definitive methods," which include stoichiometric and isotopic ratio methods; "primary comparative methods," which are calibrated with a pure solution standard; and "secondary comparative methods," which are calibrated with a metal alloy standard. These three classes or levels of analytical procedures represent a graded continuum from standard independence to standard bondage.

The Class I ("definitive") methods require *no* standards to achieve an analytical result. Their analytical "mechanism" derives from fundamental chemical or physical laws. One important subcategory in Class I are the stoichiometric procedures like conventional gravimetry, electrogravimetry, coulometry, and titrimetry based on normality. Here we rely on the rules by which reactants combine to form products by the exchange of valence electrons. We assume that reactions reach completion or that an equilibrium condition is reached or that we can accurately estimate the equilibrium condition.

Aside from the skill of the analyst, each stoichiometric procedure is dependent upon controllable parameters that affect accuracy. Gravimetry and electrogravimetry rely principally on an accurate weight measurement, so the primary quality control parameter is the balance calibration. Coulometry, a largely overlooked technique with limited application, is based on the measurement of the total amount of current flow required to electrogenerate a titrant in certain redox titrations. Conventional titrations are based on the measurement of reactant solution volume. In the case of coulometry, the principal control parameter is the calibration of the electronic measurement circuitry. In the case of conventional titrations, it is centered on two parameters: the titrant preparation (reagent purity, balance calibration, etc.) and buret accuracy.

Isotopic ratio methods, such as the thermal ionization and inductively coupled plasma versions of isotope dilution mass spectrometry, are also independent of standards. As discussed in Chapter Fifteen, since only the *ratio* of two isotope concentrations is measured, these methods are tolerant of factors that affect absolute concentration measurements. Since a spike of an enriched isotope is added to the sample, the associated volume measurement is a principal control parameter.

There are those who would argue that X-ray fluorescence measurements based on fundamental parameters calculations and certain activation analysis measurements belong in Class I because they can be performed without the use of standards. However, in practical application, both of these techniques in fact *do* require standards that closely match the composition of the sample if the most accurate work is required. Based on any realistic definition of "definitive," neither technique appears to belong in Class I.

Class II are the "primary comparative methods." These are procedures whose calibration is based on standard solutions of pure substances. The presumption here is that materials of sufficient purity (metals, oxides, and other compounds) are readily available and can be accurately weighed, dissolved, and diluted. These are *standards*, but they are prepared at will in any desired concentration.

With the exception of some guarantee of purity, the calibration does not depend on any "external" analysis. Methods that rely on a calibration curve prepared from pure elemental solutions include atomic absorption and molecular absorption spectrophotometry and both ICP-optical emission and ICP-mass spectrometries. Calibration by means of the method of additions and the "spiking technique" (the two-point method of additions) fall into this category as well. When pure substances (like iron wire or cobalt pellets) are weighed and used for a volumetric titer, the volumetric methods are also Class II.

Accuracy in a Class II method hinges on the assay and purity of the pure substance and on the preparation of the standard solution. Assay problems are not unheard of, even from highly respected suppliers of pure substances. Oxides may contain a variety of higher or lower oxide forms or even carbonates. Transition metal powders are notorious for surface oxygen pickup, and easily dissolved salts may adsorb moisture.

Sometimes there are answers to these problems. The oxides can be ignited to the highest oxide form. The oxygen-contaminated metal can be annealed in hydrogen. And the salts can be dried. Sometimes. And, at other times, it proves best to start over with another source material or to chemically assay the questionable standard solution (in this case, effectively dropping the method to Class III).

Standard preparation in Class II methods includes not only the weighing, dissolution, and diluting operations but also many matrix/analyte-specific judgement calls that must be carefully implemented. Thus, it must be established how closely a sample matrix must be matched with synthetic standards in order to fully compensate for interferences. And the full extent and incremental intervals of the analyte calibration must be decided upon.

The shelf-life of pure element standard solutions is an important concern. Shelf-life is to some degree dependent on concentration, with the more concentrated solutions exhibiting greater stability. A 1 mg/mL solution is the most convenient stock concentration for the majority of work in metals analysis. These solutions, if properly prepared, should remain useable for at least one year. However, solution containers with significant airspace above the liquid level (i.e., containers half or less filled) should be considered suspect, and the solutions are best discarded.

Other concentration levels, such as 5 or 10 mg/mL, are most useful for synthetic matrix preparation. Elemental standard solutions should always be thoroughly shaken before the container is opened. A portion should be poured into a clean, dry beaker or other vessel, swirled, and discarded. A second portion should be poured into the vessel and aliquots taken from it. Any excess in the vessel should always be discarded. Pipets should never be inserted into the storage container. The container should be promptly sealed after use and stored away from any heat source.

Commercial elemental standard solutions are a great convenience in a busy laboratory, but reliability can be a serious concern. Before choosing a supplier of calibration solutions, it is prudent to evaluate samples of each product using the best analytical procedures and a number of certified alloy validation standards. For the most accurate work, however, it is usually wise to carefully prepare one's own elemental stock solutions immediately before use. High concentrations of the analyte element are best weighed directly as solids on a semimicro balance, avoiding all aliquotting operations.

The "secondary comparative methods" or Class III methods are those procedures that employ analyzed alloy standard materials to establish a calibration. Within this category, methods vary widely in their "bondage" to reference materials. In some cases, it is a mere convenience to employ dissolved alloy standards instead of a synthetic matrix; in others, such as the solids emission spectrometry techniques, there are no practical alternatives.

There are great advantages in accuracy here, especially if the sample matrix can be closely matched with appropriate standards. Titration methods based on a titer from closely matching standards tend to be self-correcting for background colors or minor side reactions that influence endpoint detection. Similarly, ICP-OES work calibrated with alloy standards has all the inter-element effects neatly accounted for if samples and standards match closely. Until the advent of the fundamental parameters calibration technique, X-ray fluorescence was a "match game" of the highest order, usually requiring hundreds of standards to establish coarse relationships and a near identical match to "fine tune" a particular analysis. This work can be very accurate, but what is its price? The answer is bondage to chemically analyzed certified reference materials, which may be in short supply or completely unavailable.

The analytical chemist in industry tends to be the ultimate pragmatist under the pressure of unreasonable demands. If you happen to have a standard material that matches something you must analyze, you use it to generate a result. Never mind that some other grade of alloy—perhaps quite closely related—cannot be analyzed with anywhere near the same level of accuracy because no exactly matching standard is available. Herein lies the danger of Class III methods—to some degree they are all dependent on an increasingly rare commodity: reliable certified reference materials.

It must be emphasized that the Classes I, II, and III described above have nothing to do with the accuracy or precision of a procedure. They only reflect its relative *independence* from certified reference materials. In order to understand why this is important, let us reflect for a moment on some hypothetical situations. Suppose that a laboratory is analyzing Type 304 stainless steels by means of an X-ray spectrometer utilizing a program for stainless steels based on influence coefficients. The original set-up work was performed using a large suite of chemically analyzed and purchased standards, and "type" standards are used to "tweak" the results for most common grades.

The melt shop typically submits samples to the analytical lab after argon-oxygen decarburization, but in this hypothetical case the melting metallurgist decides that he needs a compositional check *before* AOD refining. Perfectly sound test pieces are submitted to the laboratory, which treats them as routine samples. But the results are wildly wrong because none of the calibration standards in this Class III procedure contained anywhere near the level of carbon in the submitted sample.

Next, suppose a laboratory is analyzing zinc spelter for minor and trace components by a solution-based ICP-OES technique. The analyst dissolves the samples in dilute hydrochloric acid and dilutes them to a fixed volume. Calibration and validation standard solutions are prepared by aliquotting portions of elemental stock solutions and diluting. Arsenic is not normally among the requested elements, but this time it is included in the request. The analyst simply adds an aliquot of arsenic to the calibration and validation solutions and proceeds as usual. The results show precise and accurate recovery of arsenic in the validation standards and none detected in the samples. The results, however, are grossly in error because arsenic was volatilized in the dissolution step, which the synthetic standards did not experience.

Finally, suppose a laboratory is titrating dissolved iron ore samples by the potassium dichromate redox method. A shipment from a new source contains significant levels of vanadium. Calculation of the results by normality and using a titer based on a vanadium-free standard ore yield identical results. But the test sample results are high because of vanadium interference. These examples illustrate the intended function of standards for all three classes of methods.

In the first case, a Class III method, highly dependent on closely matching standards, has been stretched beyond the range of reliability. A suitable suite of high-carbon standards added to the instrument set-up protocol would likely have handled the situation. In the second case, a Class II method was performed with perfect internal consistency, but the result was wrong because of something external to the analytical measurement "shell." A suitable certified alloy validation standard carried through the entire procedure would have uncovered the error and would have led the analyst to a new dissolution protocol. In the third case, a Class I procedure failed even though the result was apparently verified by a Class III procedure because of an unaccounted interference. Adequate knowledge about the sample matrix would have led the analyst to include appropriate separation steps, whose effectiveness could have been monitored with the use of a more appropriate standard.

What these hypothetical situations are intended to demonstrate is that serious errors can occur at all levels of independence from standards if proper calibration and validation protocols are not applied. Standards are needed at all levels—the more, the better. And the more closely they match the exact matrix of the sample, the less doubt in the analytical result will remain.

BIAS

Few subjects inspire such animated debate among analytical chemists as the statistical quantity known as bias. Many statisticians prefer the term "systematic error," although chemical analysts appear to find that label only marginally more palatable. For, in fact, to many chemists the admission that an analytical procedure yields a measurable bias implies that it is unsuitable for use. This attitude may be somewhat more prevalent among classical wet chemical analysts who believe that their work stands or falls based on the results obtained from validation standards. Instrumental analysts as a rule tend to be less ceremonious about the matter and are not usually opposed to adjusting some potentiometer or equivalent device to compensate for an observed bias. It is clear that some overview of the matter is needed if opposing views are to be reconciled. The subject, frankly, needs a little less heat and a little more light.

We analysts are always concerned about accuracy. And since accuracy is the combined effects of precision and bias, we must confront bias. If we all agree that an independent test for bias is necessary every time an analytical method is utilized, then the validation protocol must begin and end as an inviolate part of the total procedure. In other words, it is not legitimate to begin a sample set that includes a certified reference material intended as a check on accuracy and end by using that standard to adjust all of the results. Also, it is not legitimate to apply any special treatment to the validation standard.

These rules are only common sense if we are serious about validating our work, but the exigencies of an industrial environment sometimes lay temptations in our path. Too often what was originally intended as a validation standard becomes a "type correction" standard (and, of course, ends up logged as an "on the money" validation of the work). Too often a validation standard is remeasured repeatedly until a value is obtained that is within the pre-established control limits ("I had no trouble with the samples, but I had to work with the standard to get it right.").

It is human nature to want to "look good," or at least to avoid looking bad. And more than that may be at stake in an unforgiving economic climate. Is it worth jeopardizing your livelihood, hearth, and home by telling your boss that those results he wanted yesterday will take another two days because the validation standard didn't validate the sample set? Clearly, every analyst faced with such a situation must answer that question for himself. But one issue should remain clear to all concerned: By engaging your services, your employer is paying for a reasonable degree of certainty and not for just a number.

Class III methods are, by their nature, factored, adjusted, and tweaked using any or all reference materials at our disposal. But that calibration "shell," once established, must remain isolated from the validation "shell" that accompanies it. The validation standard or standards must also be different materials or the validation process is significantly weakened.

In Class II methods, sometimes there is a large and highly variable blank that needs to be characterized. Often the analyst obtains a range of blank replicates and calculates the results that each gives on a series of validation standards. If one of the blank readings gives the correct result on all of the validation standards, he uses that value for the samples as well. This is a legitimate approach if the standards match the samples and if there are a number of them representing a range of analyte concentrations. It *does* drop the standard dependence level to Class III, however, and requires that at least one standard be kept apart from this process, having been initially designated as the primary means of validation. Such an approach should not be encouraged, however, especially in the common case where blank values are expected to be under tight control. A more rigorous treatment is to always utilize a blank average and let the chips fall where they may.

Class I methods, for all their inherent independence of standards, require the most careful validation since they are probably the most subject to otherwise invisible random and systematic error. However, here, as with most of the Class II methods, adjustment of results based on a calculated bias is unthinkable because of the manipulative complexities involved in the procedures. While we can easily conceive of an X-ray spectrometer being just a tad high on chromium in just the same way every time, a man or woman titrating chromium cannot be relied upon to err in such a distinctly reproducible way. The classes of methods thus grade smoothly between the need for calibration and validation standards: Class I needs no calibration standards but requires the most validation standards, while Class III is highly dependent on calibration standards but only requires a few validation standards.

How then do we establish that an analytical procedure is free of bias? We compare the obtained average result on a validation standard with the certificate value and determine that the difference is less than that expected from random error in the method. Certified reference materials are sold with certificate values that are simply a number. In this case we have no choice but to consider it an absolute value with no associated error, even though we may know better. Other reference materials may have a certified value accompanied by an associated uncertainty.

In the first case, we calculate the uncertainty in the measurement of the validation standard from replicate determinations using: $U = \pm ts/(n)^{1/2}$, where U = the uncertainty, t = the t-test statistic for a given confidence interval (obtained from a table), s = the standard deviation of the measurement, and n = the number of replicates. For example, if we analyze a validation standard for nickel, which is certified at 16.57% Ni five times and obtain an average value of 16.61% Ni with a standard deviation of ±0.04%, we can calculate an uncertainty at the 95% confidence interval from $U = \pm(2.571)(0.04)/(5)^{1/2} = \pm 0.046\%$. Since the uncertainty is greater than the observed difference from the certified value ($16.61 - 16.57 = 0.04$), we can conclude that there is no bias (with 95% confidence that we are correct). In the case where the validation standard certificate lists an associated uncertainty with the certified value, it is sufficient to compare the uncertainty intervals and verify that they overlap.

There remain those who would argue that analytical chemists are not production line workers stamping out a product, and that we should not talk about bias in our work any more than a surgeon or a sculptor would. Certainly, we do not *expect* to see unchecked systematic error, but we must remain vigilant. One important concern is the widespread use of high-throughput instruments that tend to be designed to operate from identical physical principles. An increasing number of cooperative test programs have been utilizing this technology nearly exclusively. And one can imagine some future nightmare scenario where we all agree, blissfully, while we are all wildly wrong.

CLASSES OF STANDARDS

Anyone who has worked in the metals industry is aware that there are class categories of reference materials. There are those primary reference materials certified by recognized standardizing bodies, such as the National Institute of Standards and Technology (NIST) in the United States; there are private commercial firm reference materials; and there are "in-house" reference materials. A significant shortcoming that needs to be resolved is some objective basis for assigning confidence in different reference materials. As it stands, there is little to go on beyond the judgment of the analyst.

However, one important test of the relative merit of a given standard is its placement on the composite calibration curve of an X-ray spectrometer. This test is unusual in that it levels all values for a given analyte to one common criterion, but has proven very revealing in practice. Such curves typically utilize hundreds of standards, and a grossly deviant result stands out dramatically. The danger is, of course, that all the calibration values were obtained utilizing related technology and that systematic errors go unobserved.

There is confusion in some quarters about the meaning of certain terms that describe categories of standards. *Reference material* (RM) is a broad term that describes a substance with one or more attributes that are sufficiently characterized to merit its use in the calibration or validation of an analytical test method. A *certified reference material* (CRM) is a reference material with one or more attribute values established by technically valid methods and protocols and accompanied by a certificate issued by a certifying agency.

A "*Standard Reference Material* (SRM)" is the registered trademark for a reference material certified by the National Institute of Standards and Technology (NIST, formerly NBS) in the United States. A *primary standard* is a substance whose declared attribute values are accepted without question within established limits. A *secondary standard* is a substance whose attribute values are based in some manner upon comparison to a primary standard. The terms "primary" and "secondary" standard are used most frequently to apply to pure substances useful for preparing standard solutions, although they are also used in the broader sense to encompass metal alloy reference materials as well.

A secondary standard produced by one laboratory may be deemed a primary standard in the work of another laboratory. Within the CRM category, there is a range of standards, including SRMs, materials issued by the standardizing agencies of foreign governments, by privately owned standards companies, and by metals producers. The term "in-house reference material" is used to refer to reference materials produced by a company for its own internal use. Standards are also sometimes designated by the nature and extent of the information provided on the certificate. Thus, we hear terms such as "multi-element reference material," "element-specific reference material," "grade-specific reference material," and "drift correction reference material."

Alloy standards are issued in a variety of forms that facilitate their use. Monolithic solids are primarily for spectrometric applications, although pins are sometimes used for thermal evolution work. Chips and powders are primarily for solution chemistry and thermal evolution work, although they are occasionally used in spectrometry. The homogeneity and long-term stability (shelf life) of standards are significant issues that are properly addressed during the *preparation* of a standard material. These and other factors will be discussed in the next section.

A larger issue, mentioned above, is the degree of uncertainty associated with a standard's certified values. None of the definitions given in this section addresses this matter because no single category of standard shows consistent and demonstrable superiority in all cases all of the time. In the final assessment, the analyst cannot abrogate his own technical judgement. There will be times—hopefully, only a few—when he must question the unquestionable.

THE MANUFACTURE OF STANDARDS

Obviously, we can only skim the surface of this enormous subject since the preparation, testing, and certification of alloy reference materials encompasses broad areas of metallurgy, chemical analysis, and statistics. Once the technical need for a given standard composition has been established, an economic evaluation is often conducted since reference material production can be quite costly. A cost/benefit study will reveal the economic consequences of *not* proceeding as well as the advantages of developing the standard. If the work is justified, the alloy is either produced "from scratch" or a suitable production lot is diverted for this purpose. Sometimes the material is donated by, or purchased from, a second party.

The next step is to reduce the alloy to a suitable size for testing. This may involve forging, centerless grinding, or other operations. At some point in the reduction process, homogeneity testing is initiated. This generally involves cutting a length of bar into a series of slices and measuring an array of elements on both surfaces of each slice (coded by their original location) using X-ray fluorescence, optical emission, or both.

In optical emission work, the disk face is usually divided into four coded quadrants, and each is sparked individually. A statistical treatment of the data compares analytical measurement variability to the variability due to bar location. If a pre-established criterion for this statistic (matched to the intended needs) is satisfied, the bar is judged to be homogeneous. A random selection of the slices is then milled into chips for chemical analysis testing.

If the homogeneity tests did not include the complete array of intended elements, a pre-testing analysis should be conducted to establish approximate levels for all components and to confirm that comparable results are obtained by diverse instrumental techniques. Metallurgical condition—for example, cast versus wrought structure—is often significant for X-ray fluorescence spectrometry. Frequently, a cast calibration cannot be used to analyze a wrought sample and vice versa. Thus, it is important to specify metallurgical condition at the onset of the standards development program.

Obtaining chips for chemical certification testing (as well as for bulk preparation of a chip standard) is not a trivial exercise. In addition to all the common precautions that are associated with good sampling practice (removal of scale, oxide, and surface depletion layers, avoiding overheating, solvent degreasing, etc.), special pains should be taken to achieve an optimum and uniform chip size. If the reference material is intended to be used exclusively as a chip standard, it is permissible to sieve out and discard the fines provided that this operation is uniformly applied to all of the chips before testing begins. If the reference material is intended as a solid spectrometric standard or as both a chip and solid standard, sieving must *not* be performed. In this latter case, chemical analysts should receive instructions to attempt to select test portions that equally represent all particle sizes.

Depending on the resources available and the ultimate requirements of the program, one or more modes of certification testing are employed. In the single-laboratory approach, the entire test protocol is conducted by one laboratory utilizing its own analysts and resources. In the multi-laboratory approach, a cooperative program between laboratories is established—these may be multiple location laboratories within one large organization or a formal or informal consensus group within or between industries.

In the multi-laboratory approach, testing procedures may be specified or the participants may be instructed to employ their own best in-house procedures. An essential feature of all such certification testing is the test plan provided with the sample chips. In both single-laboratory and multi-laboratory test plans, definitive methods, numbers of analysts, numbers of replicates per analyst, and numbers of separate days on which the test is conducted may be specified. If the homogeneity of the sample material is to be confirmed as part of the testing, replicate portions of chips from randomly selected, but location-coded, areas of the solid should be provided.

The number of significant figures to be reported for each result should be specified and should consist of at least one more decimal place than is expected to appear in the certified value. Only individual, unaveraged results should be reported. Participants should also be instructed to report the exact methods used and the sample weights taken (if these were not mandated in the test plan), as well as descriptions of any problems encountered in the work.

In addition, participants must be required to report results obtained on validation standards that were analyzed at the same time and in the same manner as the test sample. This provides traceability to the certification. The validation standards must not have been used in any part of the calibration of the method. Some cooperative test coordinators provide a template form for the reporting of data. In most cases, some deadline or target date for the completion of the work is specified.

Once all the data have been assembled, the test coordinator examines the results for possible outliers. Rejection of outliers is not normally made on purely statistical grounds. Instead, the analyst or the laboratory that produced the suspected value is contacted to ascertain if there is an assignable cause that might have adversely affected the result. In some cases, the analyst or the laboratory is requested to repeat a suspected test. Once the final data set is accepted, one or several statistical treatments are applied. In addition to an arithmetic mean, within-laboratory/analyst variation (repeatability) and variation between laboratory/analyst variation (reproducibility), and tests for bias, such as those described earlier in this chapter, may be calculated.

The International Organization for Standards, known as ISO, has published a guide (ISO Guide 31) that lists all the information recommended for inclusion on the standard certificate document. This is a total of about 25 items, including: a statement of intended use; stability, transportation, and storage instructions; the attribute values and their uncertainties; the measurement techniques used; the method of standard preparation; special instructions concerning the minimum test portion that should be used; and many details about the certification program.

Revision of standard certificates is sometimes necessary due to the discovery of typographical errors or faulty data or to add additional information. The revised certificate should show the dated revision history of the standard. The changes or additions should be highlighted or marked with an asterisk, and a statement of the reason for the revision should be given. The organization issuing the standard must maintain an archival file that contains complete records for its revision history.

THE USES OF STANDARDS

It should be obvious that before a standard can be of any use the analytical procedure must be in statistical control, that is, the results obtained from replicate determinations of a homogeneous material should be precise. To check the repeatability and reproducibility of a method, *any* material of the appropriate matrix will serve provided that it contains a uniform distribution of the analyte in the appropriate concentration.[1] In practice, what often serves this purpose is a standard since few other materials have the supporting homogeneity test data.

As we saw earlier in this chapter, *calibration* with alloy reference materials defines the Class III methods: X-ray fluorescence spectrometry; arc, spark, and solid sampling plasma optical emission spectrometry; titrations based on an alloy titer; and others. These methods can be extremely accurate, but they are burdened with two problems. First, they are at the mercy of available standards. This means that either the needed standards must be for sale somewhere or the analytical laboratory must maintain the physical means and technical expertise to make its own standards. A rather sad commentary on the current times is another situation—the jealously guarded set of thinning, old standards, dating back from a day when the laboratory had wet chemical capabilities.

The second problem with Class III methods is that, unlike Class I and Class II methods, they tend to propagate systematic errors by the widespread use of the same calibration arrays. Suppose, hypothetically, that there was a positive bias for calcium in a popular and unique suite of nichrome alloy standards. The resultant calibration would bias everyone low, yet the error would be transparent. Vendor and consumer industries would nod at each other approvingly, yet both would be wrong.

It is, of course, always necessary to calibrate with sufficient standard increments to adequately define the response over the range of interest. Interpolation is safe, but extrapolation is not just dangerous, it is bad analytical chemistry.

The technology base that produces alloy reference materials is right now narrower than it has ever been. Standards in certain categories have become rare and valuable commodities, and an appropriate assortment of reliable standards (or the means to make them) may even spell the difference between financial success and failure for certain industries.

Validation is, perhaps, the key role for alloy reference materials. Here we take validation to mean evidence that an analytical method was performed properly while the unknown test samples were being analyzed. Note that this is conceptually one step removed from direct evidence that the results are correct, but it is often all that we have to go on. It is, after all, possible that something changed between the measurement of a validation standard and the measurement of a test sample. It is possible, despite best intentions to the contrary, that the sample and the standard were not treated completely identically. And it is also possible that due to its matrix the standard does not adequately represent analytical performance on the sample.

Methods vary in the degree to which they are able to be validated but not strictly by the classes described earlier in this chapter. Rather, the ease of validation is generally related to how automated and free of random error the analytical procedure is. Methods that require a great deal of human intervention are difficult to validate because men and women are not machines. One can expect, for example, an X-ray spectrometer (with proper control of long-term, short-term, and sinusoidal drift) to treat samples and standards in an identical manner. However, a human is likely to spill a little from one sample and overtitrate another. We must control such factors with replicates on both the test samples and on the validation standards.

Even where sample dissolution is the only human manipulative step, errors can occur. Suppose, for example, that the sample contains acid-insoluble analyte-bearing inclusions, while the standard is free of them. The analyst, dutifully following the necessary admonition to treat samples and standards identically, dissolves everything in acid, obtains the certified value on the validation standard, but is dead wrong on all the samples. These and other problems with validation can be handled by employing a variety of validation standards, each slightly different in matrix composition and with a range of analyte concentrations that spans the range expected in the samples. Perhaps this is easier said than done for most work because of the lack of suitable reference materials, but nevertheless it remains a goal.

At the risk of being accused of an unnecessary neologism, it seems important to consider the next step toward certainty—the *verification* of a result. We can remove doubt about validation standards by using more of them, perhaps from different sources. We can remove doubt about the analyst's or the laboratory's performance by testing them with blind (unidentified) standards or double-blind standards (disguised as unknown samples), and also by having the work repeated by other analysts and other laboratories. But the most powerful test of truth lies in the use of another method, based on different chemical and/or physical principles.

A closely matching value from both gravimetry and solution-based ICP-OES or from differential pulse polarography and graphite furnace AA (each method having been *validated* in its own right with standards) is an excellent *verification* of the result. The more different the methods, the less doubt will remain. Of course, this tactic is time-consuming and expensive. What price certainty!

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[1] The "set-up sample" in emission spectrometry similarly requires no certified analysis. It is used to adjust instrument response to "Day 1" calibration values.

Before leaving the subject of validation and verification, a few additional words need to be said about professional integrity. By allowing analysts to validate their own work rather than by the use of double-blind trials, most laboratory administrators place their faith in the ethics of their staff. And, indeed, it has been the author's experience that the vast majority of laboratory workers are scrupulously honest and forthright men and women who would no more consider intentionally altering a result than punching their boss in the nose (though both thoughts may have crossed their minds!).

However, there *are* ways to make oneself look good, by using significant figures and rounding, by selecting "easy to hit" but inappropriate validation standards, or by intentionally selecting standards with a broad uncertainty listed on the certificate. What these tactics do is make you look better than you, in reality, are. This, too, is a sublimated form of dishonesty, perhaps encouraged by the pressures of the modern workplace. The fact is that you are probably *not* going to be passed over for a raise if you have to recheck a set of samples. And, in the meantime, you may look better to yourself in the bathroom mirror.

There are other uses for standards: performance testing a newly developed or adopted method; evaluating a newly trained analyst before assigning him production work on a procedure; evaluating a new or spot-checking a currently used commercial lab; settling interlaboratory discrepancies; and defining and monitoring tolerance limits for an established method. Control-chart monitoring is a well-established way to ensure that a routinely employed analytical procedure remains within control limits. Control charts are applicable whenever the same type of sample is analyzed by the identical procedure on a regular basis. The standard selected for use may be a certified reference material, an in-house standard, or even an abundantly available production sample known to be homogeneous with respect to the analyte. If control charting is widely applied, it is wasteful to employ CRMs for this purpose when other suitable material is available.

Control charts take several forms. The simplest is a plot of the value obtained on the control standard which is analyzed at regular intervals along with production samples. If the value obtained on the control standard falls between the upper control limit and the lower control limit, the values obtained on the production samples are accepted as valid. If it does not, the reason is investigated and corrected and the entire analytical sequence is repeated. Other types of control charts plot the standard deviation from replicates of the control standard. Sometimes the range limits or the difference between duplicates of the control standard are plotted. Such monitoring of the standard's precision is accepted as providing evidence that the precision of measurement of the associated production samples is in control. Control charts are less useful where the sample mix and the analytical methodology is varied. But even the so-called finesse lab that performs a thousand different test procedures does *some* things routinely. And it is precisely there where control charts are useful.

CODA

These days management types tend to talk a lot about quality assurance, quality control, and quality assessment, the former encompassing the latter two. None of this is news to the metals analyst, who has been wrestling with these issues for over a century. The new awareness about quality in production circles stems from foreign competition, which is forcing industry to relearn things they knew a hundred years ago. The analytical chemist never forgot the quality imperative because his product is not an automobile or a steel billet, it is a number. And he stands or falls on how good it is.

REFERENCES

Caulcutt, R. and Boddy, R., *Statistics for Analytical Chemists*, Chapman and Hall, London, 1983.

ISO Guide 30: "Terms and Definitions Used in Connection with Reference Materials," ISO/REMCO N223.

ISO Guide 31: "Contents of Certificates of Reference Materials."

Mesley, R. J., Pocklington, W. D., and Walker, R. F., *Analyst*, Vol. 116, 1991, pp. 975–990.

Miller, J. C. and Miller, J. N., *Statistics for Analytical Chemistry*, 2nd ed., John Wiley & Sons, New York, 1988.

Spectrochimica Acta, Special Issue, Reference Materials and Reference Methods, Vol. 46B, No. 12, pp. 1571–1652.

Taylor, J. K., *Standard Reference Materials, Handbook for SRM Users*, U.S. Department of Commerce, Washington, DC, 1985.

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Statistics and Specifications

STATISTICS AND SPECIFICATIONS are, in a sense, both completely unrelated and intimately connected. Analytical chemists are almost always "out of the loop" when it comes to specifications. We hear about them in corporate memos and in trade consensus publications, but rarely does anyone ask us for our opinion. Specifications are almost always based on property data and production exigencies. Rarely does anyone bother to ask "can the lab do that?"

Part of the problem stems from the erroneous perception by the laboratory's clients that analyte concentration is not a factor in the accuracy of the result: "If you could give me a good number for manganese at 0.013%, why can't you do the same at 19.50% Mn?" And part stems from the erroneous perception that matrix is unimportant: "If you could give me a good number for chromium in stainless steel, why can't you do the same in cobalt-base alloy?"

But even more fundamental are conceptual differences about what constitutes *the result*. A specification is a limit for some attribute of a commodity, such as a concentration limit for an elemental component. It is almost always expressed as an absolute number, such as a minimum or a maximum, or as an absolute range of numbers, totally innocent of any experimental uncertainty. The laboratory's client asks "What number did the lab get?" and not "What range of uncertainty is associated with the lab result?"

Thus, the dilemma arises when the analytical laboratories dutifully report their precision data. What we hope to demonstrate in this chapter is that it is imperative that the laboratory's clients take an intimate interest in the precision of test methodology because it is inseparable from their own pressing concerns about the product and the process.

PRECISION

No reasonable person would expect any complex set of operations performed by a human being to yield exactly the same result every time. Conditions vary, starting materials vary, and even an olympic champion has a bad day. And so, in the search for certainty, our only recourse is to replicate our work in the belief that the arithmetic average of our raw data is a better estimate of the truth than any individual result. Although hundreds of books have been written about the subject, this simple truth lies at the heart of statistics.

Of course, there are multifold things we can do with our data once we begin replicating test methods: we can reject outliers, estimate expected precision, compare the means or the precision of two procedures, and much more. One can get carried away with statistics—just as one can get carried away with computers—and lose track of the chemistry. But there is a core of very useful techniques that need to be discussed here.

The *standard deviation* of a test result is the most common and utilitarian estimate of the expected spread in the numbers. It is defined as: $s = \pm[\Sigma(x_i - \bar{x})^2/(n - 1)]^{1/2}$, where s = the standard deviation, x_i = an individual result, $\bar{x}$ = the mean of all results, and n = the number of replicates.

The square of the standard deviation is called the *variance*. The variance of measured quantities can be added or subtracted just like the quantities themselves. Thus, the variance in a spectrophotometric measurement and the variance in the blank can be subtracted. Taking the square root of the difference yields the standard deviation of the corrected absorbance reading. Often it is useful to combine the variances found by the same analytical procedure on a variety of samples. The *pooled variance* (v_p) is calculated from $v_p = \Sigma[\Sigma(x_i - \bar{x})^2]/\Sigma(n - 1)$, and the *pooled standard deviation* (s_p) is simply obtained from $s_p = (v_p)^{1/2}$. The pooled standard deviation is sometimes used as a rough measure of an analytical method's overall effectiveness.

Another important quantity is the *relative standard deviation* (RSD), also known as the coefficient of variation (CV). It is equal to $(100s)/\bar{x}$. This can be a very revealing quantity if it is calculated over a range of concentrations. For any given method, the RSD begins at a high value at the low end of the analyte concentration, drops to a low value at the optimum concentration range, then rises as the method exceeds its bounds. These quantities are all simple estimations of random errors in a procedure. They provide the insight that tells the analyst that his work is in statistical control and allow him to make meaningful bias tests such as those which were described in the last chapter.

Sometimes it becomes necessary to compare methods, analysts, or laboratories in regard to the variability of their results. "Eyeballing" data is sometimes a useful way to make such comparisons, but large data sets, which provide the best basis for judgment, usually swamp our perceptions. Here, statistical treatments provide the best answer. The simplest approach is to compare the means of the two data populations. This is accomplished with the *two-sided t-test*. First, we calculate a pooled standard deviation from the standard deviations (s_1 and s_2) of the two data sets (provided that s_1 and s_2 are not greatly different from one another):

$$s_p = \pm\{[(s_1)^2(n_1 - 1) + (s_2)^2(n_2 - 1)]/(n_1 + n_2 - 2)\}^{1/2}$$

where s_p = the pooled standard deviation, s_1 and s_2 are the standard deviations, and n_1 and n_2 are the population sizes of the two data sets. Then the value of t is given by

$$t = (\bar{x}_1 - \bar{x}_2)/s_p[(1/n_1 + 1/n_2)]^{1/2}$$

where $\bar{x}_1$ and $\bar{x}_2$ are the means of the two data sets. The value of t in this case has $(n_1 + n_2 - 2)$ *degrees of freedom*, a value that expresses the number of deviations (a data point subtracted from the mean) used in the calculation. We calculate t, then look up a critical value of t from a two-sided t-distribution table (to be found in the back pages of nearly every book on statistics), using the calculated number of degrees of freedom and a selected confidence interval (usually we use 95%). If the calculated value of t is greater than the table value, we have found evidence (at the 95% confidence level) that the difference between the two means is significant. Conversely, if the calculated value of t is less than the table value, no significant difference between the two means was found.

Another useful statistical approach in comparing data populations is to compare their standard deviations (instead of assuming that they do not differ significantly, as we did above). This is done with the *two-sided F test*, using the expression: $F = (s_1)^2/(s_2)^2$, where s_1 and s_2 are the standard deviations of the two populations; but they must be inserted in the equation so that F is greater than 1.

We calculate F, then look up a critical value of F from a two-sided F-distribution table of the appropriate confidence interval (generally 95%). To find the critical value of F, we must use the number of degrees of freedom of s_1, which is $(n_1 - 1)$ and the number of degrees of freedom of s_2, which is $(n_2 - 1)$, where n_1 and n_2 are the respective population sizes. These two-sided (or "two-tailed") t and F tests we have just described are used when we have no prior knowledge about which direction the difference between the means or the standard deviations should trend toward. If we have such knowledge—say we expect analyte loss due to volatility or analyte pickup from labware contamination in one of the two methods—we would calculate t or F just as described above, but we would use a one-sided table to look up the critical value.

One interesting variation on the t-test provides a useful way to compare the means from two methods using no special replicate runs but only the results obtained by both methods on a variety of different samples, representing a variety of different analyte concentrations (but ranging over only one or two orders of magnitude). This is the *paired t test*.

Suppose Method A is a well-established procedure in your laboratory. It has proven performance data at all common analyte levels and for all common sample matrices. It is rather slow, however. And so you have just developed Method B, which is twice as rapid and seems just as good. To check out Method B, you establish a plan in which all routine samples will be analyzed by *both* methods for a period of two weeks. At the end of that period, you examine the two sets of data, which represent a range of analyte concentrations and sample matrices (for example, see Table 17-1). You take the difference between each pair of numbers, average these differences, and calculate the standard deviation of the differences. Then, using the simplified expression for t, derived from that which we used in Chapter Sixteen,

$$t = \bar{x}(n)^{1/2}/s$$

where $\bar{x}$ is the mean (+0.04 in the example), n is the number of replicates (6), and s is the standard deviation (0.0996), we can calculate that t in this case is +0.984. Since t has $(n - 1) = 5$ degrees of freedom, we can find the critical value for t at the 95% confidence interval in a two-sided t-table: 2.45. Since 0.984 is less than 2.45, there is no significant difference in the means derived from the two methods.

Our established confidence in Method A thus implies a similar confidence in the results from Method B. The paired t-test assumes that all error in both methods is independent of concentration and thus must be limited to one or two orders of magnitude. When many orders of magnitude of concentration must be investigated, the results from the two methods are plotted on an x-y coordinate axis (the points should be fairly evenly spaced, with the method expected to be more reliable plotted on the x-axis). A regression line is calculated, as well as standard deviations and confidence intervals for the slope and intercept. If the slope interval overlaps 1 and the intercept interval overlaps 0, no significant difference in the two methods has been found (see Table 17-2 in which linear regression is illustrated for the treatment of calibration data).

The technique known as *analysis of variance* (ANOVA) allows the extraction of detailed precision information concerning specific aspects of a data population. In treating the results of a structured experiment, it can separate random analytical error from the error associated with some con-

TABLE 17-1—Example illustrating the use of the paired t-test.

Sample No.	Method A	Method B	Difference	$\lvert d\rvert$	d^2
1	13.55	13.60	−0.05	0.09	0.0081
2	11.90	11.78	+0.12	0.08	0.0064
3	14.14	14.09	+0.05	0.01	0.0001
4	10.23	10.29	−0.06	0.10	0.0100
5	17.41	17.32	+0.09	0.05	0.0025
6	12.67	12.78	−0.11	0.15	0.0225
			Mean ($\bar{x}$): +0.04		Σd^2: 0.0496

$s = \pm [0.0496/(6 - 1)]^{1/2} = \pm 0.0996$

$t = (\bar{x} - \mu)(n)^{1/2}/s$; $\mu = 0$ (null hypothesis: average difference between pairs is zero)

$t = \bar{x}(n)^{1/2}/s = (0.04)(6)^{1/2}/0.0996 = 0.984$

Degrees of freedom = $(n - 1) = 5$

Table value for t at 95% confidence: 2.45

$0.985 < 2.45$; therefore, there is no significant difference in the means at the 95% confidence level

TABLE 17-2—Linear regression.

$a = \bar{y} - b\bar{x}$, where $\bar{x}$ = average analyte concentration; $\bar{y}$ = average measured analytical signal; b = the slope of the curve; and a = the intercept of the curve.

From the analytical data used to prepare the calibration curve:

$$b = \Sigma(x - \bar{x})(y - \bar{y})/\Sigma(x - \bar{x})^2$$

$$a = \bar{y} - [\Sigma(x - \bar{x})(y - \bar{y})/\Sigma(x - \bar{x})^2]\,\bar{x}$$

Correlation coefficient:

$$r = \Sigma[(x - \bar{x})(y - \bar{y})]/\{[\Sigma(x - \bar{x})^2][\Sigma(y - \bar{y})^2]\}^{1/2}$$

$$s_{y/x} = \{\Sigma[(y - \hat{y})^2]/(n - 2)\}^{1/2}$$

where $\hat{y}$ = the y residuals (the *calculated* values of y for each experimental x).

Standard deviation of the slope:

$$s_b = s_{y/x}/[\Sigma(x - \bar{x})^2]^{1/2}$$

Standard deviation of the intercept:

$$s_a = \{\Sigma(x^2)/n[\Sigma(x - \bar{x})^2]\}^{1/2}$$

Confidence interval of the slope = $b \pm ts_b$

Confidence interval of the intercept = $a \pm ts_a$

Degrees of Freedom = $(n - 2)$

trolled factor, such as the analyst or the laboratory performing the test, an instrumental or chemical parameter that is varied, or even the test methodology used when different procedures are compared. It can also be used to isolate random analytical error from some other uncontrolled factor, as when samples are taken from random locations in a nonhomogeneous lot and each is analyzed in replicate.

All these examples represent "one-way ANOVA" in that the error due to one factor (controlled or random) is mathematically highlighted against a background of the total random analytical error. One very important use of this powerful statistical technique is in the estimation of repeatability and reproducibility intervals for a method. *Repeatability* is the short-term within-laboratory variance, generally derived from a single analyst, utilizing the same equipment in a short period of time. The *repeatability interval* (sometimes symbolized as $R1$ and sometimes as r) is often defined as the maximum expected spread in replicate results within a laboratory by a single analyst using the same equipment, exceeded only 5% of the time.

Reproducibility is the variance between laboratories. The *reproducibility interval* (sometimes symbolized as $R2$ or R) is the maximum expected spread in test results between two laboratories, exceeded only 5% of the time. Mathematically, $R1 = 2(2)^{1/2}[s_w/(m)^{1/2}]$, where s_w = the within-laboratory standard deviation, and m = the number of replicates that were averaged to obtain a test result (if raw data were reported, $m = 1$); and $R2 = 2(2)^{1/2}[(s_L)^2 + (s_w/m)]^{1/2}$, where s_L = the between-laboratory standard deviation. The calculation of an ANOVA treatment appears daunting at first glance, but, in fact, it is a simple, if tedious, sequence of quite common arithmetical operations. Anyone reasonably facile in a scientific programming language can easily write a program to perform the calculation, and spreadsheets also lend themselves to the calculation.

Table 17-3 illustrates the mathematical sequence with a small data set. The first item to highlight is the quantity m, which is the replicate basis of the treatment. If raw data is used, m is set equal to 1; if duplicates are averaged, m is set equal to 2, and so on. The value of m should reflect standard practice or what will become standard practice in the laboratory once the method is sanctioned for routine use. With a computer program set up to do ANOVA calculations, it is a simple and highly illustrative exercise to calculate $R1$ and $R2$ for raw data, then average duplicates and repeat the calculation, then average triplicates and repeat the calculation again. In most cases, $R1$ and $R2$ converge to small values quite dramatically, demonstrating the precision advantage of replicate averages.

Another aspect of Table 17-3 to consider is the data of Laboratory 6, which appears to be rejectable as an outlier. One implicit assumption of all that has been said so far here and in most statistical discussions is that the data follows a normal distribution. If we accept this assumption as an article of faith, we have a strong argument for applying a test for outliers. However, such a credo may be hard to swallow with a small data set such as those that analytical chemists normally encounter.

The evidence is usually simply not overwhelming that any given aberrant-appearing value is justifiably rejectable in the absence of an assignable cause, such as a spilled sample or an overtitrated endpoint. Statisticians are sanguine about outlier tests; good analytical chemists usually approach them with trepidation. With a small data set, after all, you may be rejecting the only correct value, and most experienced analysts can recall at least one episode where that was, in fact, the case. Except for their use in massive data sets from instrumental studies, outlier tests should be regarded with suspicion. However, it is appropriate here to at least mention the most popular protocol, the Dixon test

$$Q = [(\text{suspect result}) - (\text{nearest result})]/[(\text{largest result}) - (\text{smallest result})]$$

One calculates the value of Q and compares it to a table of critical Q values for a given confidence interval. If the calculated value exceeds the critical value, the suspect result is rejected. In the case of the suspect value in Table 17-3, the Dixon test is inappropriate unless it is applied to the laboratory averages, in which case the data of Laboratory 6 are rejectable.

But in the absence of sound proof of analytical error, is there sufficient justification to reject the data from Lab 6? They might, after all, be the only laboratory that accounted for some unapparent but critical aspect of the determination. This brings us to the matter of analytical judgment, which transcends the statistical analysis of data. Statistics is a valuable tool to the metals analyst, but it can be a siren that leads even a good analyst of sound judgment onto the rocks of error. A classic example of this effect is the correlation coefficient, calculated commonly from calibration curve data. The *correlation coefficient* is defined as

$$r = \Sigma[(x - \bar{x})(y - \bar{y})]/\{[\Sigma(x - \bar{x})^2][\Sigma(y - \bar{y})^2]\}^{1/2}$$

where x and y are all data points, and $\bar{x}$ and $\bar{y}$ are the means of all x's and y's, respectively.[1] When a least-squares treatment

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[1] The point defined by $(\bar{x}, \bar{y})$ is called the *centroid* of the calibration curve.

TABLE 17-3—Example of an ANOVA calculation: $m = 3$ (i.e., each value of x is the average of three replicates).

Lab No. (p)	Wt% C (x) $n = 1$	Wt% C (x) $n = 2$	Wt% C (x) $n = 3$	Σx	Σx^2	x^2 $n = 1$	x^2 $n = 2$	x^2 $n = 3$
1	0.0278	0.0275	0.0266	0.0819	0.0067076	0.0007728	0.0007562	0.0007075
2	0.0262	0.0275	0.0284	0.0821	0.0067404	0.0006864	0.0007562	0.0008065
3	0.0276	0.0252	0.0263	0.0791	0.0062568	0.0007617	0.0006350	0.0006916
4	0.0285	0.0292	0.0277	0.0854	0.0072931	0.0008122	0.0008526	0.0007642
5	0.0256	0.0271	0.0275	0.0802	0.006432	0.0006553	0.0007344	0.0007562
6	0.0224	0.0220	0.0230	0.0674	0.0045427	0.0005017	0.0004840	0.0005290
7	0.0278	0.0267	0.0260	0.0805	0.0064802	0.0007728	0.0007128	0.0006760

Mean ($\bar{x}$) = 0.0265

$\Sigma(\Sigma x) = 0.5566$

$\Sigma(\Sigma x^2) = 0.0444528$

$\Sigma(x^2) = 0.0148301$

Correction term: $C = [\Sigma(\Sigma x)]^2/pn = (0.5566)^2/21 = 0.3098035/21 = 0.0147525$.

Sum of the squares for total: $\text{SST} = \Sigma(x^2) - C = 0.0148301 - 0.0147525 = 0.0000776$.

Sum of the squares between labs: $\text{SSL} = 1/n\{\Sigma[\Sigma(x^2)]\} - C = 1/3(0.0444528) - 0.0147525 = 0.0000651$.

Sum of the square within labs: $\text{SSW} = \text{SST} - \text{SSL} = 0.0000776 - 0.0000651 = 0.0000125$.

Mean square between labs: $\text{MSL} = \text{SSL}/(p - 1) = 0.0000651/6 = 0.0000108$.

Mean square within labs: $\text{MSW} = \text{SSW}/p(n - 1) = 0.0000125/7(2) = 0.0000008$.

Repeatability: $\text{SW} = (\text{MSW})^{1/2} = (0.0000008)^{1/2} = 0.00089$.

Reproducibility: $\text{SL} = [(1/n)(\text{MSL} - \text{MSW})]^{1/2} = [(1/3)(0.000108 - 0.0000008)]^{1/2} = 0.00182$.

Repeatability interval: $R1 = 2(2)^{1/2}[\text{SW}/(m)^{1/2}] = 2(1.414)[0.00089/(3)^{1/2}] = 0.00145$.

Reproducibility interval: $R2 = 2(2)^{1/2}[[(\text{SL})^2 + (\text{SW})^2]/m]^{1/2} = 2(1.414)[[(0.00182)^2 + (0.00089)^2]/3]^{1/2} = 2(1.414)[(0.0000033 + 0.0000007/3]^{1/2} = 0.00529$.

(see Table 17-2) is used to calculate the equation of the line that best represents the calibration curve, one typically also calculates the correlation coefficient with the implicit belief that the closer the calculated value is to 1, the closer the fit of the data points. While this is often true, it does *not* constitute proof since there are many alternate situations that produce apparently linear balanced relationships while the individual data points fall far outside of a straight line. And that is the nature of statistics—a valuable but dangerous tool that must never be applied without thought about the problem and the consequences of a statistical treatment.

SPECIFICATIONS

In the introduction to this chapter, we defined a specification as a limit or a set of limits for some attribute of a commercial commodity. Here the attribute we are concerned with is nearly always some part of its elemental composition. While there are some exceptions, for the most part specifications do not recognize the existence of analytical error. And so the type of statement a metals analyst is forced to deal with takes forms such as "0.3 ppm bismuth max.," "1.0% silicon min.," and "chromium: 21.50 – 22.00%." These are absolute limits—a separate paradigm, as it were, from the world of analytical realities, where each generated number of necessity is associated with either a characterized or an unknown uncertainty.

The conflict between these separate worlds dates back to the earliest days of the metals industry, but it was initially transparent because laboratories seldom measured replicates or performed statistical studies. If the single determination result proved to show the material "out of spec," it would probably be "rechecked" (a curious redundancy!). And if the second result turned out to be "in spec," the first would often be dismissed as undefined analytical error. This is not only bad statistics, it is bad science. And yet it is an unfortunate fact that even today some laboratories operate this way.

The problem between analytical laboratories and specification people emerges clearly when replicates are routinely determined and when the analytical error has been statistically characterized. Figure 17-1 illustrates the difficulty presented by absolute limits and analytical uncertainty. It also serves to show how the concept of an analytical control limit can resolve the problem. In Fig. 17-1, the dots represent the reported analytical results, and the associated vertical bars represent the analytical error of the results. In both examples shown, Results A, B, and C appear to meet the specification, and only D is "out of spec." In fact, the material represented by B and C should also be rejected based on this test since the error associated with those points overlaps the specification limit.

The laboratory can provide a guide for itself, however, by inserting analytical control limits within the specification limits. These are established by measuring off the width of the method error from the specification limit. Hopefully, what remains of the range will be a practically achievable target. Very narrow specification ranges or very low maximum specifications often will make this approach unrealistic. The analyst's only recourse then is to report uncertainties with his results. None of this makes the lab's clients very happy.

In the case of the B and C results, the client has in his hand two numbers that clearly meet the material specification, and yet the analyst is declaring the material rejectable based on analytical error. The fact is the material *may* be out of specification or it may not be. When the error bar overlaps the specification limit, there is simply no way of telling unless additional laboratory work, possibly employing a different analytical procedure, is performed. The goal of such additional lab work has to be to *narrow the error bar,* not to obtain one analytical result within the range of the analytical control limits.

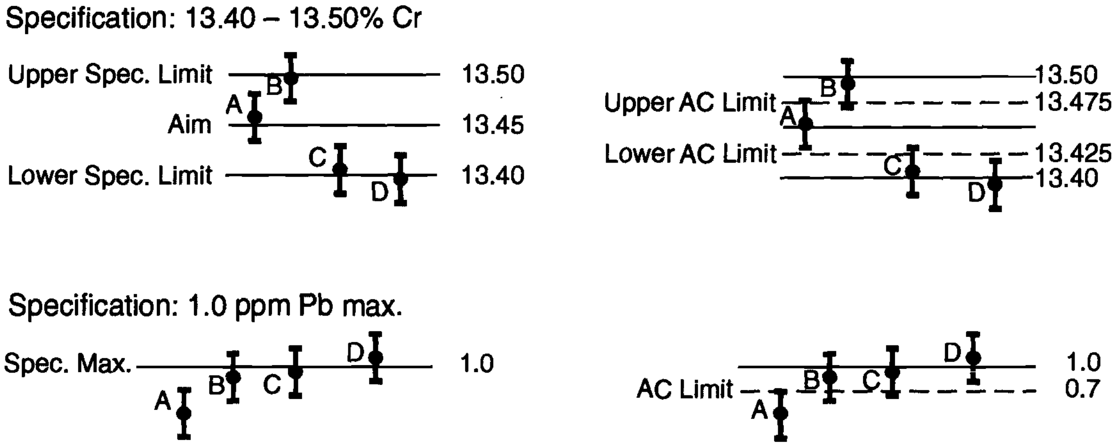

FIG. 17-1—Specification limits and analytical uncertainty (AC = analytical control).

There is another unfortunate practice involving specifications that crops up occasionally at some metal producers. A material found to be narrowly out of specification is resubmitted to the laboratory repeatedly (sometimes as a blind sample) until an "in spec" value is obtained. The "in spec" value is accepted, and all the other generated data are scrapped. This is not only bad science, it is tantamount to fraud. It is similarly fraudulent to "recheck" in such a manner "in spec" values that are outside the analytical control limit. Some specifications include explicit rules as to when and how a recheck analysis may be requested. Such provisions are designed to prevent the kind of abuses just described. It is, however, always legitimate to repeat a detailed statistical study designed to accurately define the error bar.

Clearly, the rejection of a large lot of material based on an out-of-specification compositional analysis is not a trivial matter. In the case of high-value commodities of complex matrices, a lot of money is riding upon the accuracy of some very difficult analytical chemistry. Here, as with sampling, a dialogue between the laboratory and its clients is the most salutary approach. Where the analytical chemist can provide input into matters such as compositional aims and ranges, he should actively seek to do so.

Metallurgists sometimes purposely "melt-in" at the high end or the low end of an elemental range because of processing or economic considerations. Rarely do they consider the analytical problems this causes when result uncertainties begin to overlap the range limits. For the sake of all concerned, a strong case can usually be made for narrow melting ranges near the center of the specification limits.

Input on the specifications themselves is another matter, perhaps best handled by intercommittee liaison in consensus organizations like ASTM. Analytically unrealistic specifications are of no use to anyone and should be discouraged wherever a receptive ear can be found. Bad specifications include ranges that are too narrow, "maximum" levels that are too low, and scientifically and legally indefensible expressions such as "all other impurities." This last is endemic among high-purity metals specifications and may stem from the days when emission spectroscopists visually scanned photographic plates. But what lab (or law department) is willing to defend a product as "impurity-free"?

REPORTING CONVENTIONS

The way analytical results are averaged, rounded, and reported is not a trivial concern. Some aspects of this matter are based on statistical rules, and some reflect an analytical philosophy that should be consistent within a laboratory or a network of related laboratories. Most chemists know that rounding a result should be the *last* step in any calculation, and that when the last rounded digit is a *five*, by statistical convention one rounds the previous place to the *even* number. Rounding *before* averaging seems an innocent enough practice on the surface of the matter—certainly, it is sometimes convenient—but it is always wrong and can lead to a serious error in the reported result. Consider the following list of results averaged both ways:

	Raw Data	Rounded Data
	0.0016	0.002
	0.0015	0.002
	0.0016	0.002
	0.0012	0.001
	0.0013	0.001
Averages:	0.001	0.002

The practice of rounding to the *even* number when the last digit is a five is purely arbitrary but should be consistently observed. It avoids the biasing of results that occurs in such cases if values are rounded up (or down).

At a deeper level, one can discern the presence of reporting philosophies at the interface of statistics and specifications, especially at low-analyte concentrations. I have termed these the "conservative," "literal," and "statistical" approaches in an attempt at describing their respective characters.

These reporting styles are most clearly contrasted in terms of the *quantitation limit* of an analytical procedure. This is the concentration below which a quantitative result is not reported. Note that we are speaking of a quite different number than the *detection limit*, which may be orders of magnitude lower. Statisticians have not provided clear guidance in this area, leaving some considerable room for personal proclivities.

One statistical convention places the detection limit at three standard deviations above the average blank signal and the quantitation limit at ten standard deviations above the average blank signal. We can call this approach "statistical" (although many statisticians would not defend it). In averaging replicates, the "statistical" chemist takes a straight average and dutifully reports it (provided it is above the noise-defined quantitation limit):

	Found, %
	0.00015 0.00013 0.00004
Average:	0.00011
Report:	0.0001 (statistical)

If the straight average is below the quantitation limit, the "statistical" chemist reports "less than" the predetermined value for the quantitation limit. But he or she becomes "literal" or "conservative" when the average requires a rounding decision. For the sake of some examples, let us assume the quantitation limit for a method has been established at 0.0001%:

Found, %	Found, %	Found, %
0.00006	0.00007	0.00007
0.00002	0.00010	0.00010
0.00003	0.00006	0.00006
Ave.: 0.00004	0.00008	0.00008
Rep.:<0.0001(statistical)	<0.0001(literal)	0.0001(conservative)

The "literal" chemist accepts any average below the quantitation limit as mandating the use of the "less than" term, while the "conservative" chemist rounds any value whose last digit is greater than five to the next highest value (in this case 0.0001%). The "conservative" chemist follows no statistical rule, but sets the reporting limit based on a worse-case scenario. At the concentration levels we have been using for illustration, we are generally dealing with a "maximum" level specification for a harmful contaminant. Suppose the "conservative" chemist had to deal with our original example:

	Found, %
	0.00015 0.00013 0.00004
Average:	0.00011
Report:	<0.0003 (conservative)

You might call this the "HPMBR" position ("high point might be right"). Rather than accepting an average from such a wide spread of values, the "conservative" chemist selects the most damaging result of the set and reports a quantitation limit result just above this level. An analogous "low point might be right" approach would be used in the case of a minimum specification.

An interesting situation develops when a data set is generated that includes one or more readings with no discernible analyte signal. Here, the "literal" chemist uses the detection limit to define "none detected" (often abbreviated as "N.D."), while the "conservative" chemist uses the quantitation limit to define this condition. The "statistical" chemist would treat the zero reading as a number in calculating the average. The "conservative" chemist is likely to opt for a "less than" expression that hedges on the matter, while the "literal" chemist takes the data at face value:

Found, %	Found, %	Found, %
0.0006	0.0006	0.0006
0.0005	0.0005	0.0005
N.D.(<0.0002 = DL)	N.D.(zero)	N.D.(<0.001 = QL)
Ave.: 0.0004	0.0004	0.0004
Rep.: <0.0006(Literal)	0.0004(Statistical)	<0.001(Conservative)

Such a great amount of trace work in metals is being done these days that these issues, which would have aroused slight interest a few decades ago, are now very much the concern of many metals analysts. When analytical laboratories must routinely operate near the noise limit of instruments, they must pick a reporting style that satisfies their clients and themselves, document it, and stick with it consistently.

This discussion also points to the need to perform regular detection limit and quantitation limit studies, especially with techniques like ICP-OES, where such values are known to change daily. The laboratory's clients are likely to be confused by changing limit values that accompany "N.D." ("none detected"), but having to supply a detailed explanation may be better than offering no clue as to what "N.D." represents.

As an example, in the case of solution work by ICP-OES, a reasonably conservative set of limits is conveniently obtained by taking ten replicate measurements of a valid blank solution. The 3-sigma value (three times the standard deviation) is the *detection limit*, which is the *lowest raw data value recorded* and is the value accompanying "N.D." and quoted as "less than" when no evidence of analyte signal is obtained. The 10-sigma value (ten times the standard deviation) is the *quantitation limit*, which is often the *lowest average value reported*. Any values from measured signal below this level are reported as "less than" the quantitation limit.

Finally, there is the "sticky" question of the effect of the specification limits themselves on analytical reporting conventions. Like most human beings, metals analysts want to be perceived as doing a good job, they want to please their clients, and they want to minimize the amount of extra work they have to do. But untold problems can result from making unsupported claims for methods and instrumentation. If you are asked if you have a procedure that can be used to monitor a 0.3-ppm maximum bismuth specification, you had better be sure of it before you answer in the affirmative. After all, you must meet this challenge not just today, but tomorrow and a year from now. And you may have to meet it with other alloy matrices and with non-ideal samples.

Without a thorough initial investigation and an on-going program of detection and quantitation limit monitoring, as well as validation standard monitoring, you cannot be sure that the required signal has not drowned in a sea of noise. From the opposite perspective, it is improper to deliberately withhold information when the analytical data support reporting more significant figures than the specification requires. Admittedly, this *can* lead to bewildered clients if the extra digit must be dropped from later data due to deteriorating sensitivity.

RANGE STATISTICS

Before closing this chapter, we should say a few words about an extremely rapid and efficient way to make statistical calculations. Formally called *nonparametric methods*, these statistical tests differ from all those previously discussed in that they do not assume a normal distribution of the data population. In fact, they make *no* assumptions about the population distribution. Strictly speaking, nonparametric tests deal with medians and "interquartile ranges" and not with means and standard deviations; however, if no statistician is looking over your shoulder, some of these tests in the form described here can be useful and reasonably accurate. This subject is very broad and will only be touched upon here. As with all the topics in this chapter, the reader is referred to any standard text on statistics for much greater detail.

A rapid estimate of the standard deviation of a set of results can be obtained from

$$s_r = (x_h - x_l)/(n)^{1/2}$$

where s_r = the standard deviation for the range, x_h = the highest point in the data set, x_l = the lowest point in the data set, and n = the number of replicates. The test works best over the interval $4 < n < 12$. A simple t-test to validate an analysis, such as that described in Chapter Sixteen, can be approximated from

$$t_r = |\bar{x} - \mu|/(x_h - x_l)$$

where t_r = the test statistic, $\bar{x}$ = the average result, and μ = the certified standard value.

Similarly, a test to compare two methods, analysts, or laboratories can be derived from

$$t_L = 2|\bar{x}_A - \bar{x}_B|/[(x_{hA} - x_{lA}) + (x_{hB} - x_{lB})]$$

where t_L = the test statistic, $\bar{x}_A$ and $\bar{x}_B$ are the means of the two data sets being compared, and x_{hA} and x_{hB} are the high points and x_{lA} and x_{lB} are the low points of the populations. An equivalent F test to compare standard deviations can be approximated from: $F_r = (x_{hA} - x_{lA})/(x_{hB} - x_{lB})$ (or its inverse, whichever is >1). Appropriate tables with comparison values for these statistics should be available in most thorough statistics texts.

LEMMA

Mark Twain said: "There are lies, damn lies, and statistics," but he also said: "When in doubt, tell the truth." The fact is that statistical treatments are sometimes consciously and sometimes unconsciously abused, but when they are honestly and thoughtfully applied they are an invaluable tool. The best advice for the metals analyst is to study and use these aids *critically*. They will never be the final answer for us because our tasks are too complex and our data sets are too small. We dare not surrender completely to these tides, but we must swim our course guided by technical judgment and common sense. If these currents can support us we must use them. If not, we must resist.

REFERENCES

Analytical Methods Committee (Royal Society of Chemistry, UK), *Analyst*, Vol. 113, 1988, pp. 1469–1471.

Annual Book of ASTM Standards, Vol. 03.05, American Society for Testing and Materials, Philadelphia, 1993, Designation E 173.

Annual Book of ASTM Standards, Vol. 03.06, American Society for Testing and Materials, Philadelphia, 1993, Designation E 1282.

Becker et al., *Use of NIST Standard Reference Materials for Decisions on Performance of Analytical Chemical Methods and Laboratories*, NIST Special Publication 829, National Institute of Standards and Technology, Gaithersburg, MD, 1992.

Caulcutt, R. and Boddy, R., *Statistics for Analytical Chemists*, Chapman and Hall, London, 1983.

Hirsch, R. F., *Analytical Chemistry*, Vol. 49, No. 8, 1977, pp. 691A–700A.

Mandel, J. and Lashof, T. W., *Journal of Quality Technology*, Vol. 19, No. 1, 1987, pp. 29–36.

Mark, H. and Workman, J., Jr., *Spectroscopy*, Vol. 11, No. 2, pp. 38–42.

Miller, J. N., *Analyst*, Vol. 116, 1991, pp. 3–14.

Miller, J. N., *Analyst*, Vol. 118, 1993, pp. 455–461.

Miller, J. C. and Miller, J. N., *Statistics for Analytical Chemistry*, 2nd ed., John Wiley & Sons, New York, 1988.

Taylor, J. K., *Standard Reference Materials, Handbook for SRM Users*, NIST Special Publication 260-100, National Institute of Standards and Technology, Gaithersburg, MD, 1985.

Youden, W. J., *Industrial Quality Control*, May 1959, pp. 24–28.

18

Good Laboratory Practices

LIKE MOST IDEAS THAT BECOME widely disseminated, the original meaning of "good laboratory practices" has been somewhat altered. Today most people associate the phrase with "safe laboratory practices," which carries only part of the original meaning. Certainly, good laboratory technique is *safe*, but it is also *effective* in its intended purpose. So we will return to that total concept with a miscellany of suggestions that pertain to metals analysis. Like so much that has gone before in this volume, we can only scrape at the surface of this subject, hopefully unearthing some nuggets that will prove useful.

CLEANING LABWARE

Before medicine became aware of the need for asepsis, chemists knew that an accurate analysis required clean labware. Properly cleaning vessels used for inorganic analysis is not a job that can be left to untrained personnel. Like packing one's own parachute, the task is best handled by the analyst who has used the vessels and is about to use them again. Only he or she knows what contaminants may be present from the last use and what substances must be absent for the next use.

Some of the more difficult residues left on glass beakers and flasks are *oxides of titanium, niobium, and tantalum and titanium phosphate*. These white residues resist most common cleaning methods. TiO_2 is particularly difficult as the rainbow-hued monolayer that sometimes forms. All of these residues can be removed by adding a small amount of sulfuric acid, covering with a watchglass (which can also be freed of these contaminants in this way), and heating to strong fumes of SO_3. The vessel is cooled to room temperature; any excess acid is cautiously poured out into cold running water; and the vessel and watchglass are rinsed thoroughly. This is followed by a scrubbing with a good laboratory detergent and a second thorough rinse. Stubborn areas may have to be scrubbed with an abrasive plastic scouring cloth; for others, a beaker or flask brush may be sufficient.

Tungsten and molybdenum oxide residues can be removed easily with a strong caustic solution such as 25% (w/v) NaOH. *Tin oxide* not only contaminates beakers and flasks but is also frequently left on graduates and storage bottles that have been used for stannous chloride solutions. It succumbs to concentrated hydrochloric acid. *Mercury* leaves stubborn black and gray stains that dissolve readily in concentrated nitric acid with the evolution of NO_x. Sometimes a tiny drop of metallic mercury forms after this treatment. The remaining acid should then be diluted and decanted away. More water is added to remove residual acid by decanting, and then the mercury drop is transferred to a mercury waste storage container.

Iron, chromium, and other common transition metals leave residues that are sometimes hard to detect visually. However, if chromyl chloride has been evolved during an analysis, the outside of the vessel is likely to be coated with prominent brown stains. Most common transition metal residues dissolve readily in concentrated hydrochloric acid. Stains on the outside of a vessel can be removed using rubber gloves and an absorbant paper moistened with 1:1 $HCl:H_2O$. Filling a vessel with HCl and letting it stand a few moments is usually sufficient for inside contamination by the common transition metals. For trace work, 1:3 $HCl:H_2O$ has been recommended as a better choice than concentrated HCl since it has been alleged that the concentrated acid activates sites on the vessel walls, which leads to accelerated trace ion adsorption.

Organic residues can be handled in a number of different ways. Sometimes a simple rinse with an appropriate solvent, followed by detergent scrubbing, is sufficient. Stubborn residues are best handled by soaking (sometimes overnight) in chromic acid (a solution of CrO_3 or $K_2Cr_2O_7$ dissolved in concentrated sulfuric acid). If the vessels have been rinsed in methanol or ethanol, the analyst must be careful that no residual alcohol makes its way into the chromic acid. As little as one drop of methanol or ethanol can reduce several liters of chromic acid. (In fact, this reaction is so sensitive that it is the basis of several breath analysis colorimetric tests for inebriation.)

Volumetric labware—pipets, burets, and volumetric flasks—should not be filled with or immersed in chromic acid, nor should other vessels that will be used for low chromium determinations. This is because chromium residues, which may be difficult to remove, will be left behind. In these cases, concentrated sulfuric acid is a good substitute. There is also a chromium-free additive for sulfuric acid sold as a commercial product.

Glass frit crucibles are a special problem when gravimetric work has been completed. Nickel dimethylglyoximate, aluminum 8-hydroxyquinolate, selenium, and tellurium metal residues will all dissolve in freshly prepared 1:1 $HCl:HNO_3$. Platinum crucibles are typically cleaned by fusion with potassium pyrosulfate, the melt cautiously poured out into a dry metal waste vessel and the cooled crucible boiled in 1:1 HCl: H_2O. Zirconium crucibles are cleaned by boiling in 1:1 HCl: H_2O after use.

An ICP torch and nebulizer chamber must also be cleaned regularly to prevent or minimize clogging and "memory" effects. The best approach is to disassemble the entire device and soak the torch and glass parts of the nebulizer in freshly prepared 1:1 HCl:HNO_3. After several minutes, the torch and nebulizer chamber are transferred to a container of distilled water. The 1:1 HCl:HNO_3 mixture is cautiously disposed of by transferring it in small portions to running water in a hood sink. Any plastic parts of the nebulizer can usually be cleaned by soaking in distilled water (and, if necessary, passing a "cat's whisker" wire through the liquid and gas orifices). Seldom will the torch tip come completely clean, but minor discoloration has not been known to present serious problems. Permanent restriction of the torch tip orifice is a serious problem, however, and usually requires replacement.

Polytetrafluoroethylene (Teflon) laboratory vessels present a special problem due to the electrostatic charge that they tend to accumulate. After washing them thoroughly and putting them away in a clean drawer or on a clean shelf, one often finds that they have accumulated a layer of dust when they are removed for their next use. They can be "neutralized" with an antistatic radioactive source kept near them during storage or they can be simply wiped out with a clean towel before use.

TRANSFERRING SOLUTIONS

The "quantitative transfer" was, at one time at least, the essence of analytical technique. It remains an essential skill for any work with dissolved samples. Surface tension and the *Coanda effect* are both a bane and an asset in the transfer of liquids from one vessel to another. This refers to the phenomenon of a liquid following the outside surface of a vessel when it is being poured, resulting in sample loss. The same boundary layer effect can be used to advantage when a stirring rod placed against the vessel lip is used to direct the flow. Some analysts find great advantage in vessels with Teflon-coated rims. Others believe that they can better manipulate the liquid to their advantage without the Teflon coating.

When transferring solutions to narrow-mouthed vessels, such as small-capacity volumetric flasks, it is prudent to use an appropriately sized funnel. One or more spacer lifts should be employed to prevent the formation of an air seal, which may prevent the funnel from draining or may cause the solution to be blown out of the funnel by escaping air. Such lifts can be manufactured by forming a U-bend in short lengths of 2-mm glass rod.

When an alloy sample has been dissolved in acid and the solution cooled, the first step in transferring the solution is to rinse down the beaker watchglass with a stream of distilled water. This common procedure can be an important source of error since water will spatter when it contacts the acid solution and droplets can fly out of the beaker. It is best to hold the watchglass at a shallow angle just above the beaker mouth while directing a stream of water onto its inner convex surface. This will tend to catch and retain any backsplash. Such precautions are absolutely essential when determining major amounts of analyte.

If one were determining iron, say, at the 50.00% level, consider the following scenario. Suppose the beaker contained 50 mL of sample solution and one drop was lost. We can take an average drop as 1/20th of a milliliter, or 50 μL. This amounts to an error of one part per thousand. Thus, even before measurement, our iron value has been reduced to 49.95%. At the 80.00% iron level, our pre-measurement concentration would be reduced to 79.92%. Of course, low and trace level analyte determinations are much more tolerant of physical sample loss. But they are much more sensitive to contaminant pickup from reagents, labware, and the laboratory environment.

DILUTING AND ALIQUOTTING

Like the care required in quantitative transfer, diluting and aliquotting are more critical for major amounts of analyte. This is not to suggest a tolerance for sloppy technique at any concentration level, but merely to emphasize that above the 10% analyte level most analytical requirements tighten down considerably. It is not generally considered unreasonable to expect to confine analytical error to less than 0.1% of the amount present between 10 and 80% for certain analytes. Such stringent demands require great attention to detail.

Volumetric flasks should be diluted to just below the line, mixed thoroughly, then allowed to stand for 4 to 24 h to allow any heat from an acid-water reaction to dissipate. Of course, acid solutions vary greatly in the heat of dilution generated when they are mixed with water. Diluted sulfuric acid solutions are quite hot and take considerable time to cool. Rushing the cooling process with an ice bath or a running water bath is not generally a good idea because of the possibility of under- or overcooling. Final dilution to the mark and a second thorough mixing should occur just before the analytes are measured or aliquots are taken. Minute bubbles or foam at the meniscus will not do, and steps must be taken to break them up by rapping the flask or by other means before final dilution. Thorough mixing consists of at least 20 complete inversions of the volumetric flask, allowing enough time on each for the air bubble to completely traverse the length of the vessel. Some borosilicate volumetric flasks contain a bulge in the neck above the line as an aid to proper mixing.

In some analytical situations, it proves permissible to tolerate a moderate amount of particulate matter in a volumetric flask. The volume error associated with the particles is rarely a significant problem so long as no analyte is contained in the particles. In such cases, it is highly advisable to allow all the particles to settle completely after mixing before any aliquots are taken or any measuring is performed. Aliquotting or measuring a solution containing analyte-bearing particulates is *not* recommended, although analysts have been known to get away with this approach when the results are not especially critical. Magnetically stirring the solution as it is being aliquotted or measured is the best technique, but the general practice should be discouraged.

If the laboratory is known to experience even minor temperature shifts over a 24-h period, it is important to dilute and then aliquot, both within a short space of time. Pipets are not the most accurate way to take an aliquot (for example, better work can usually be performed with an appropriately sized buret, or by weight, using a top loading balance), but pipets remain the most convenient approach. The initial dilution volume, pipet size, final dilution volume, and any subsequent volume partitioning should be sized and arranged to minimize error. Suppose, for example, that you have dissolved a 1-g sample of a 70% nickel-base alloy for nickel analysis and need to obtain a portion of the solution that contains between 50 and 100 mg of nickel. Numerous choices present themselves, but let us consider four alternatives.

A. Transfer the solution to a 100-mL volumetric flask, dilute to the mark, mix, and remove a 10-mL aliquot by pipet.
B. Transfer the solution to a 200-mL volumetric flask and remove a 20-mL aliquot.
C. Transfer to a 500-mL volumetric flask and remove a 50-mL aliquot.
D. Transfer to a 1-L volumetric flask and remove a 100-mL aliquot.

In Chapter Two, we discussed volumetric glassware tolerances. These (typically Class A) tolerances represent systematic error within a published range. In the case of our four alternatives:

Pipet Size, mL	Tolerance, mL	Volumetric Flask Size, mL	Tolerance, mL
10	0.02	100	0.08
20	0.03	200	0.10
50	0.05	500	0.20
100	0.08	1000	0.30

We can calculate the systematic error propagation for each route as follows:

A. Volume range for 10-mL pipet: 9.98 to 10.02 mL.
Volume range for 100-mL volumetric flask: 99.92 to 100.08 mL.
Range for aliquot factor: (99.92/10.02) to (100.08/9.98) or 9.972 to 10.028 or 10.000 ± 0.028.

This represents a 0.28% error and would, by itself, broaden a "true" value of 70.00% to the range: 69.80 to 70.20%.

B. Volume range for 20-mL pipet: 19.97 to 20.03 mL.
Volume range for 200-mL volumetric flask; 199.90 to 200.10 mL.
Range for aliquot factor: (199.90/20.03) to (200.10/19.97) or 9.980 to 10.020 or 10.000 ± 0.020.

This represents a 0.20% error and a nickel range of 69.86 to 70.14%.

C. Volume range for 50-mL pipet: 49.95 to 50.05 mL.
Volume range for 500-mL volumetric flask: 499.80 to 500.20 mL.
Range for aliquot factor: (499.80/50.05) to (500.20/49.95) or 9.986 to 10.014 or 10.000 ± 0.014.

This represents a 0.14% error and a nickel range of 69.90 to 70.10%.

D. Volume range for 100-mL pipet: 99.92 to 100.08 mL.
Volume range for 1000-mL volumetric flask: 999.70 to 1000.30 mL.
Range for aliquot factor: (999.70/100.8) to (1000.30/99.92) or 9.9890 to 10.0110 or 10.000 ± 0.011.

This represents a 0.11% error and a nickel range of 69.92 to 70.08%.

Thus, it should be evident that decisions about which aliquotting scheme to choose are important to the ultimate result. These systematic errors are "built in" to the equipment we choose to employ and are added onto any random or systematic manipulative errors that we contribute as analysts.

The importance of choosing the proper aliquotting scheme is greatest wherever the highest accuracy is required. These are typically (but are not confined to) applications at analyte concentrations above 10%. Consider one more example, this time at trace concentration levels: Suppose you want to prepare 100 mL of a 1-ppm aluminum solution from a stock standard solution of 1.000 mg Al/mL. Consider three alternatives in this case:

I. Take a 100-μL aliquot of the stock solution (with a micropipet) and transfer it to a 100-mL volumetric flask. Dilute to the mark and mix.
II. Take a 1-mL aliquot of the stock solution, transfer it to a 100-mL volumetric flask; dilute to the mark and mix. Then take a 10-mL aliquot of that solution, transfer it to a 100-mL volumetric flask; dilute to the mark and mix.
III. Take a 10-mL aliquot of the stock solution, transfer it to a 1-L volumetric flask; dilute to the mark and mix. Then take a 10-mL aliquot of that solution, transfer it to a 100-mL volumetric flask; dilute to the mark and mix.

Which alternate preparation will show the lowest systematic error (all other errors being assumed to be equal)?

Pipet Size, mL	Tolerance, mL	Volumetric Flask Size, mL	Tolerance, mL
0.1(micro)	0.0005	100	0.08
1	0.006	1000	0.30
10	0.02		

Systematic error in this example is calculated from a formula for multiplicative relationships:

$$1 \text{ ppm Al} = (0.1 \text{ mg Al}/0.1 \text{ L})$$

$$(y_e/y) = (a_e/a) + (b_e/b) + \cdots$$

where

y = the calculated quantity,
y_e = the error on the calculated quantity,
a, b, etc. = the method parameters, and
a_e, b_e, etc. = the errors on the method parameters.

I. $(y_e/1) = (0.0005/0.1) + (0.08/100) = 0.0058$
$y_e = 0.0058$
Thus, the resultant solution is 1.0000 ± 0.0058 ppm Al.

II. $(y_e/1) = (0.006/1) + (0.08/100) + (0.02/10) + (0.08/100) = 0.0096$.
$y_e = 0.0096$
Thus, the resultant solution is 1.0000 ± 0.0096 ppm Al.

III. $(y_e/1) = (0.02/10) + (0.30/1000) + (0.02/10) + (0.08/100) = 0.0051$.
$y_e = 0.0051$
Thus, the resultant solution is 1.0000 ± 0.0051 ppm Al.

Two things that are not obvious emerge here. First, if properly used, micropipets are not as bad an approach as some may have suspected. That disclaimer is important, however, since the least bit of solution adherence in the tip can be disastrous for the result. Second, choosing a multiple dilution scheme is not always better than a single dilution approach. In Alternative II, all the bother was rewarded with nearly a doubling of the error in the direct approach of Alternative I.

Before leaving this general subject, it should be pointed out that the calculations employed here are specific to systematic errors. Random errors are added, subtracted, multiplied, and divided by a completely different set of rules in which method parameter standard deviations are converted to variances by squaring before any calculations are performed.

Accurate diluting and aliquotting requires scrupulously clean volumetric labware, a steady hand and a keen eye in adjusting the meniscus level, and periodic checks on the accuracy of air-driven or positive displacement micropipets. Micropipets are easily checked by weighing aliquots of water in glass-weighing bottles (preferably on a semi-microbalance). Follow the manufacturer's instructions on maintenance procedures (these may involve dissembling the device and greasing certain threaded parts).

One relatively recent development is the use of electronic top-loading balances for dilution and aliquotting by weight. This approach is extremely accurate and lends itself readily to robotics applications. For aliquotting small volumes volumetrically, a microburet is unsurpassed in accuracy. For aliquotting large volumes, the most accurate volumetric approach is to overfill a dry volumetric flask, take the meniscus down to the line with a dry dropping pipet, then transfer the liquid and flask rinsings to the receiving vessel.

Finally, with all this talk about accuracy, a few words must be said about those situations where only reproducibility matters. In adding an internal standard to a series of samples or in removing sample aliquots for use with the method of additions (multi-point or two-point), only the consistency of the aliquot size matters. Most mechanical and electronic pipeting devices excel in reproducibility.

SYNTHETIC SOLUTION STANDARDS

In Chapters Three and Fifteen, we touched upon this important subject, but there is even more to be said. Mixed element calibration and validation solutions are probably more widely utilized today than at any time in the past due to the dominance of ICP-OES and the rapid growth of ICP-MS. The ability to utilize customized standards, prepared to order as it were, is a great boon in convenience, but this approach, as we have seen, can be fraught with unseen error. If the calibration and validation solutions were prepared incorrectly or if they have deteriorated, they can result in undetected bias. Check standards will appear to validate the results, but the results will be wrong. It bears repeating here that it is always best to include some chemically analyzed alloy standards, even if only poor matches to the matrix are available, rather than placing all trust in synthetic calibration and validation. This same precaution also applies when pure substances are directly weighed, dissolved, and analyzed in order to calibrate or validate a determination at high concentration levels.

Most laboratories maintain extensive stocks of elemental standard solutions, either prepared in-house, purchased, or both. In Chapter Three we described in detail common preparation schemes for many of these solutions. In nearly every case there are alternative schemes that generally result in a different solution matrix. Similarly, many commercial elemental standard solutions are available in several different solution media. Combining aliquots of these solutions without any thought to the potential reactions that may occur between them is clearly negligent. Also, there is a distinct possibility that the vessel utilized may play a role in inappropriate side reactions. Finally, and particularly at low concentration levels, the *order* in which aliquots are added to a mixture may be critical to success or failure.

Chloride is, perhaps, the most tolerant medium for mixing elemental standards. The alkali metals, the alkaline earths, the rare earths (except cerium), titanium, zirconium, hafnium, vanadium, niobium, chromium, molybdenum, manganese, iron, cobalt, nickel, copper, zinc, cadmium, aluminum, indium, tin, and gallium can all be combined in hydrochloric acid solution. However, to avoid certain problems with double-salt formation, it may be wise to ensure that the members of this group that exhibit many oxidation states be utilized in their lowest stable oxidation state. Nitrate is the medium of choice for the next largest group: silver, lead, mercury, antimony, arsenic, selenium, rhenium, bismuth, and thallium (iron, cobalt, nickel, copper, chromium, zinc, and cadmium can be included here, as well). Combinations of chloride and nitrate are usually required for gold, platinum, palladium, and tellurium.

Stopping here for a moment, we can already delineate several important incompatibilities. Silver, lead, and mercury cannot be combined with any chloride-bearing solutions since they will precipitate. If the final solution is to be heated, arsenic, selenium, and rhenium cannot be mixed with a chloride medium since they are likely to be partially volatilized. Moving on to fluoride as a medium, we find titanium, zirconium, hafnium, niobium, tantalum, tungsten, and rhenium standard solutions. Sulfate medium standards include cerium, titanium, niobium, zirconium, and hafnium. A caustic medium is used for molybdenum, tungsten, and silicon.

The rare earths are clearly incompatible with fluoride, the alkaline earths with fluoride and sulfate, and both of these groups, as well as the transition metals, are incompatible with caustic. Obviously, one must not mix elemental standards without considerable planning. It is, of course, desirable to take maximum advantage of those elements that allow some latitude in the medium used. Thus, if one needs a nickel and silver mixture, it is necessary to start with a nickel standard solution prepared in nitric acid. But if one needs a tantalum and calcium standard mixture, one had better carefully rethink his calibration plan since such a mixture would require special complexing agents.

Consider another situation. Suppose you need to calibrate the ICP-OES instrument for aluminum, niobium, and tantalum. At first, you are a little concerned about the aluminum precipitating as AlF_3 in the dilute fluoride medium of the other two elemental standards. Then you realize that this reaction is unlikely in the dilute hydrochloric acid medium that you will employ. So you prepare the mixture and calibrate the instrument with it, but your aluminum results on alloy standards run low. The reason is that you employed a borosilicate glass volumetric flask to prepare the standard mixture and the dilute hydrofluoric acid from the niobium and tantalum elemental standards leached some aluminum from the glass. Your samples, of course, contained no hydrofluoric acid and yielded low aluminum results.

Effects such as this can produce significant errors even with diminishingly small concentrations of HF. A reasonable alternative is to prepare the calibration solution in a plastic volumetric flask. In other cases another choice, which suggests itself in all cases of elemental incompatibility, is to prepare separate calibration solutions for the interacting elements. Most ICP software programs allow many separate calibration solutions for groups of elements. Of course, the sample solutions may suffer from some of the same element incompatibilities as do element calibration mixtures and may have to be specially complexed or chemically separated to produce an accurate set of results.

The order of addition of certain elements can *sometimes* be used to circumvent potential problems by utilizing dilution to prevent precipitation. For example, it *is* possible to prepare a mixed calibration solution of, say, lanthanum and niobium by adding the lanthanum first, then a considerable volume of dilute hydrochloric acid, then a small aliquot of HF-bearing niobium standard solution. If the solution is diluted, mixed, and used in a relatively short period of time, the lanthanum and niobium concentrations are likely to be correct.

Other important considerations in the matter of synthetic solution standards are the age of the elemental standard solutions and the amount of air space above the liquid in the closed container. Expired commercial solutions (which should all be labeled with an expiration date) or any elemental standard solution that was prepared over a year ago should be considered suspect. Bottles of any age that are more than half empty are also suspect because of water vapor loss each time they are opened. "Stale" elemental standards tend to get more concentrated and, if used for calibration, tend to throw results low.

In the specific case of ICP-OES, it is possible to suggest some specific guidelines for the means and manner of calibration. For analyte concentrations below 100 ppm and when a two-point calibration is deemed appropriate, it is often best to use a reagent or partial matrix blank for the low point (0 ppm analyte) and a similarly prepared high point standard at approximately 1.5 times the expected analyte level. For analyte concentrations between 100 and 300 ppm, a blank and high point *at* the expected analyte level is often best. For analyte levels above 300 ppm, usually a bracketting technique is most effective (low point just below and high point just above the analyte level) with a special blank correction, if needed.

The frequency of recalibration during an ICP-OES run is most often determined by the extent of long-term drift in the instrument readings. As a rough rule-of-thumb, a validation standard should be measured after every eight sample readings and the instrument recalibrated as needed. Sometimes it is appropriate to recheck a series of eight or less sample readings by measuring them again in reverse order after a recalibration. The average of duplicates from the two sets of readings is often a better estimation of the truth than either alone. In the case of severe drift, it may be necessary to decrease the eight sample criteria to four, or even one.

HOMEMADE SUPPLIES

Unlike certain organic labs that require the services of a full-time glassblower, most metals analysis facilities make do with commercially available equipment. There are a few invaluable items that no one sells, however, and it proves worth the time and effort to manufacture them in-house. One of these is the boiling rod, which is inserted into a beaker to prevent the contents from bumping when a solution needs to be boiled on a hotplate. The boiling rod is made from 6-mm glass tubing cut to an appropriate length (say, 15 cm). An oxymethane hand torch or bench burner is needed to attain sufficient temperature. The tube is heated at a point about 2 cm from one end until the glass fuses into a solid mass. The other end is then simply sealed. When cool, the open end is roughed on a piece of abrasive paper. This helps to nucleate incipient steam bubbles when the boiling rod is in use. With a little practice, an analyst can produce a hundred of these in about an hour—a sufficient supply for many years of use.

Inexperience with the oxymethane torch is a problem these days, however. The analyst should consult a good text on the subject, such as *Creative Glass Blowing—Scientific and Ornamental* by J. E. Hammesfahr and C. L. Strong, W. H. Freeman and Co., San Francisco, 1968. While he or she is at it, the analyst can make a batch of customized stirring rods—thin short ones for 100 and 150-mL beakers and huge baton-sized ones for stirring a solution in a 4-L beaker, as well as everything in between. These are simply made by fusing the ends of suitable lengths of glass rods of the appropriate diameters with the oxymethane torch. When cool, the fused ends should be abraided to provide nucleation sites.

A simple Fisher or Mekker burner is all that is required to manufacture glass "lifts" for watchglasses and funnels. These are simply short pieces of 2-mm glass rod bent into U-shapes. They are handy for lifting watchglasses for the rapid evaporation of solutions and to prevent funnels from sealing to the mouth of small vessels, thus preventing a "vapor lock" of solution. Short cut lengths of 10-mm glass rod are handy to keep small Erlenmeyer flasks from resting flat on the bottom of a boiling water bath (say a 2-L beaker), thus preventing bumping.

If one wishes to do chloride/fluoride system ion exchange, it is necessary to manufacture the plastic ion exchange columns. Polystyrene or (better) polymethylmethacrylate tubing is cut to length, and a one-hole, waxed rubber stopper with polyethylene tube and stopcock is inserted in the bottom and sealed in place first with paraffin, then with an acid-resistant sealant, and secured with wire and clamps.

Sand baths for use on hotplates are flat trays welded together from steel sheet. They are sized to hold a row of 600 or 800-mL beakers across the width of a hotplate. The raised sides are about 5 cm high. In use, they are filled with coarse sand. They are useful when hotplate temperatures may damage labware (e.g., Teflon) or when contact with hot metal may be a problem (e.g., platinum will form an alloy layer). The sand bath acts to distribute heat evenly to vessels partially embedded in it. A small-scale substitute suitable for crucibles are the aluminum ice cube trays (minus the dividers) from an old refrigerator.

Some labs utilize heating and cooling blocks of aluminum drilled to hold crucibles of various sizes. Some manufacture customized heating and cooling baths with lids designed to hold vessels of various sizes. Other equipment, such as beaker and crucible tongs, funnel and separatory funnel racks, and drying racks are sometimes custom built.

CONTROLLING LABORATORY HAZARDS

If the analyst is not keenly aware that he is working in a hazardous environment, he should immediately seek another career. That is not to say that the risk of harm is beyond control or by any means imminent or inevitable. In fact, properly run metals analysis laboratories may be expected to run indefinitely without a serious or even a minor injury.

Safety authorities recognize three means of controlling hazards: engineering, administration, and protective equipment. The first of these is the preferred approach and should be applied wherever possible. Engineering means designing a work environment that is inherently safe: hoods remove toxic vapors, electrical outlets are properly grounded, buildings are designed for proper air exchange and for emergency evacuation. Administration means the in-place standard operating procedures that instruct lab personnel on policy issues related to safety: toxic substance handling and disposal, health and safety inspections and audits, an emergency response plan. Protective equipment includes respirators, "air packs," safety glasses and goggles, face shields, gloves, ear protectors, and much more. It is clear that no laboratory can operate safely without the proper meshing of the engineering, administration, and worker personal protection plans.

In the United States, the Occupational Safety and Health Administration (OSHA) was established within the Department of Labor by the Williams-Steiger Occupational Safety and Health Act of 1970. Under the act, the National Institute of Occupational Safety and Health (NIOSH) within the Department of Health and Human Services was charged with prescribing the regulations, standards, and criteria for workplace safety, which OSHA enforces. In 1990, a new federal regulation code (designated CFR1910.1450) for occupational exposure to hazardous chemicals in laboratories became effective. Among the provisions of this document was the requirement that a written chemical hygiene plan for laboratories be fully implemented by 31 July 1991. Each employer was charged with appointing a chemical hygiene officer to provide technical guidance in the development and implementation of the plan, which must include standard operating procedures, control measures, and training for the use of hazardous substances in the laboratory.

The regulation also recognizes the need for special protection for work with particularly hazardous materials (such as select carcinogens) and requires that additional measures be taken in such cases. An extensive appendix to this document was extracted from *Prudent Practices for Handling Hazardous Chemicals in Laboratories* (a report by the National Research Council—available in its entirety from the National Academy Press, 2101 Constitution Ave., N.W., Washington, D.C. 20418).

It is evident that the technical, administrative, and legal considerations involved in laboratory safety are too large a subject for detailed treatment here. The reader is referred to the regulation and the reference cited above, as well as to those references cited at the end of this chapter, for information critical to the safe operation of a laboratory. We *can*, however, briefly highlight some generally recognized features of hazard control in laboratories.

General Principles

Laboratory workers should treat all chemicals and laboratory equipment as potential hazards. Skin contact is an important danger that must not be treated lightly. In particular, hand, eye, and face protection must be appropriately used. Hands should never be cleaned with solvents or other chemicals, but contaminated skin should be thoroughly washed with soap and copious water immediately upon contamination and again before leaving the laboratory. Any behavior that might startle or distract a coworker is dangerously inappropriate in a laboratory.

One should assume that any chemical of unknown toxicity is toxic and that any mixture is more toxic than its most toxic component. Never use mouth pipetting techniques; always employ a suction bulb instead. Use a hood when working with any substance with a published threshold limit value (TLV) of less than 50 ppm or with chemicals whose reaction could generate such a substance. Confine long hair and loose clothing and wear leather shoes. Do not eat, drink, smoke, chew gum, or apply cosmetics in a laboratory. Do not store food, drink, tobacco, or cosmetics anywhere in the laboratory.

Keep the laboratory clean and uncluttered, with purchased and prepared solutions properly labeled, categorized, and dated. Inspect gloves before each use and wash them before removal. Seek information and advice about unfamiliar hazards. Plan appropriate protective procedures and obtain and position all needed protective equipment before beginning any laboratory operation. Inform management of any personal prosthetic device (such as a hearing aid, contact lenses, or a pacemaker) that may require special precautions for safe work in the laboratory.

Management Responsibilities

It is the duty of management to provide adequate safeguards, appropriate training, and access to needed information in order to minimize risk of injury in the laboratory. The engineering aspects of the physical plant must provide fume hoods and other ventilation devices to prevent worker exposure to harmful airborne substances, adequate egress in the event of emergency, as well as adequate alarms, controls, and emergency response devices, as required. Engineering also involves the safe layout of the laboratory facility, including the placement of sinks, eyewash stations, emergency showers, fire extinguishers, fire alarms, airborne monitors, properly ventilated stockrooms, emergency and first-aid equipment, exit signs, and other devices.

The administrative responsibilities of management are centered upon the chemical hygiene plan, which should establish policy for work procedures in the laboratory, as well as for reagent procurement, distribution, and storage, for environmental monitoring, housekeeping, medical surveillance, first-aid, and emergency medical treatment, the use of personal protective apparel and equipment, accident and medical record keeping, the posting of emergency signs and labels, emergency procedures, training programs, the availability of literature and advice, a waste disposal plan, and other policy issues.

The features of a chemical hygiene plan must include provisions for regular chemical hygiene inspections and health and safety audits by the designated chemical hygiene officer and/or his designees. It may also describe the function and duties of an emergency response team. It should include a complete evacuation plan, a spill control plan, and procedures for the post-event analysis of accidents and near accidents. Safety training should be provided as a regular and continuing part of the chemical hygiene plan.

Limiting Exposure

The American Conference of Governmental Industrial Hygienists (ACGIH) has been publishing *threshold limit values* (TLVs) for industrial chemicals since 1947, but since 1970 many TLVs now carry the force of law as limits for airborne worker exposure. TLVs are also known as 8-h time-weighted averages (TWAs) since they are the maximum time-weighted average exposure to a single toxic material for any 8-h shift of a 40-h work week that current knowledge indicates will produce no ill effect in a normal worker. TLV levels are invalidated if the worker has been exposed to the same substance by another route (say, skin contact) and do not apply to hypersensitive individuals or pregnant women. Moreover, there may be synergistic effects in the case of toxic mixtures. High temperatures, prolonged overtime, alcohol or drug abuse, and other factors may also invalidate TLVs. TLVs are commonly expressed as parts-per-million by volume in air or as milligrams of vapor and/or aerosol per cubic meter of air.

The ACGIH also defines *short term exposure levels* (STELs) for certain substances for which levels above the TLVs can be safely tolerated by a normal individual if most of the working day is spent below the TLV. "Short term" is defined as a 15-min exposure. No more than four such exposures are permitted per day and there must be a minimum of 60 min between exposures. For acutely toxic materials, the ACGIH has also defined the *ceiling limit*, which is the exposure level which must not be exceeded at any time. These values are indicated by a "C" prefix. *Permissible exposure limits* (PELs) are established as law by OSHA—they may be a time-weighted average or a ceiling limit. OSHA also defines a lower, *action level*, which requires an employer to initiate certain required procedures, such as exposure monitoring, medical surveillance, and additional training programs.

Skin contact exposure is a significant concern for corrosive and toxic substances. While an experienced worker may feel confident that he understands the relative dangers involved, he may be unaware that certain substances are absorbed readily through the skin, some in sufficient amounts to be dangerous in either an acute or a chronic sense. The only sensible practice is to use gloves and other equipment to avoid all contact of chemicals with the body. If contact occurs accidentally, wash the area of contact thoroughly with soap and copious amounts of running water. Scrupulous observation of rules prohibiting food, drink, tobacco, and cosmetics use in laboratories are safeguards against accidental ingestion of harmful substances.

Chemists are occasionally exposed to noise hazards (such as in arc/spark spectroscopy laboratories) and to airborne dust hazards (such as in grinding or polishing operations for sample preparation). Limiting these types of worker exposure can be accomplished with earplugs (or noise barrier "ear muffs") and with properly designed respirators, respectively.

Types of Hazards

Laboratory hazards include acute and chronic toxic exposure, burn hazards from corrosive substances and from high-temperature equipment, shock hazards from electrically powered equipment, hazards from the potential for fire and explosion, hazards associated with cryogenic substances and from pressurized and vacuum equipment. There are also dangers from falls and from mechanical equipment.

The danger from chemicals mandates an understanding of several different systems for classifying and labeling chemicals. The U.S. Department of Transportation (DOT) system consists of a color-coded diamond containing an icon symbol and a descriptive term: "flammable liquid," "flammable gas," "compressed gas," "corrosive," "poison," "radioactive," "explosive," or "oxidizer." The DOT system, which is designed for use in the transport of hazardous substances, may utilize one or more such labels for a given chemical.

The National Fire Prevention Association (NFPA) system is more complex. It consists of a diamond divided into four quadrants. Numbers in the upper three quadrants indicate the degree of severity of three categories of hazard. The "west" (blue) quadrant is the emergency health hazard, the "north" (red) quadrant is the fire hazard, and the "east" (yellow) quadrant is the chemical reactivity hazard. The relative scale for each ranges from 4 (extreme hazard) to 0 (no unusual hazard). The "south" (white) quadrant is for extra information (for example, a "W" with a line through it indicates that water should not be utilized in the event of a fire). The NFPA system was designed to assist fire fighters in extinguishing chemical fires. Its limitations are the omission of chronic health hazards and precautionary details.

Reagent chemical manufacturers, like J. T. Baker and Fisher Scientific, and large corporations that utilize many bulk chemicals in production facilities have devised their own systems of chemical hazard classification. OSHA Standard 29CFR1910.106(a) classifies "flammable" and "combustible" liquids by their *flashpoint temperatures* (the minimum temperature at which an ignitable vapor is emitted, as tested by the Tagliabue, Pensky-Martens, or Setaflash Closed Tester Methods). Table 18-1 lists these classes with some examples.

Other types of chemicals have been classified, as well. For example, NFPA Code 43A-1980 for the Storage of Liquid and Solid Oxidizing Materials recognizes four classes of oxidizer. *Class 1*: "causes an increase in the burning rate of combustible Materials"—it includes 8 to 27.5% H_2O_2, $MgClO_4$, <60% $HClO_4$, and $AgNO_3$. *Class 2*: "moderately increases the burning rate or may cause the spontaneous ignition of combustible materials"—it includes 27.5 to 52% H_2O_2, Na_2O_2, $\leq 50\%$ $Ca(OCl)_2$ solutions, and chromic acid. *Class 3*: "causes a severe increase in the burning rate; will undergo self-sustained

TABLE 18-1—Flammable and combustible liquids [from OSHA Standard 29CFR1910.106(a)].

Class	Category	Flash Point, °C	Examples
I	Flammable	<37.8	
IA	Flammable	<22.8 (and b.p. <37.8°C)	Diethyl ether, N-pentane
IB	Flammable	<22.8 (and b.p. >37.8°C)	Cyclohexane, acetone
IC	Flammable	37.8-22.8	2-butanol
II	Combustible	60.0-37.8	Kerosene
III	Combustible	> or = 60.0	
IIIA	Combustible	93.4-60.0	Pine oil
IIIB	Combustible	> or = 93.4	Glycerine

decomposition when catalyzed or exposed to heat"—it includes 52 to 91% H_2O_2, 60 to 72.5% $HClO_4$, $NaClO_3$, and $(NH_4)_2Cr_2O_7$. *Class 4*: "explosive reaction when catalyzed or exposed to heat, shock, or friction"—it includes >91% H_2O_2, NH_4ClO_4, NH_4MnO_4, K_2O. In NFPA Code 43C-1980, the separate storage category of gaseous oxidizers (including Cl_2, N_2O, and O_2) is treated.

The safe storage of hazardous chemicals in the laboratory is the subject of a book edited by D. A. Pipitone (*Safe Storage of Laboratory Chemicals*, John Wiley & Sons, New York, 1991). Essential parts of safe chemical storage are the proper segregation of potentially reactable compounds, proper ventilation and fire control measures, proper labeling, and thoughtful planning to minimize potential accidents and to control the spread and severity of injury and damage in the event of a mishap.

The revised OSHA standard on hazard communication (29CFR1910.1200) published in 1987 requires employers to maintain and provide free access for employees to Material Safety Data Sheets on chemicals stored at the facility, to ensure that containers in storage are properly labeled with the chemical identity and appropriate hazard warnings, and to provide training and information on personal protection in the event of sealed container leakage. There are additional provisions for those cases where a chemical storeroom is used to dispense chemicals. Specifically, a separate written hazard communication document for the storeroom operation is required, as well as procedures for insurance that dispensed chemicals are properly labeled with identity and hazard warnings. *Material Safety Data Sheets* (MSDSs) are provided by reagent manufacturers and distributors. OSHA guidelines are used for the hazard communication data that they contain. Some employers have implemented an on-line database that includes MSDS information for all chemicals used at the facility. Another essential feature of chemical storage is *inventory control*, which can also be greatly facilitated by the development of an on-line database. Both MSDS records and a current inventory of chemicals must be submitted to state emergency response commissions, local emergency planning committees, and local fire departments.

The types of hazards present in a laboratory work environment can be summarized in a brief overview. An appropriate hazard communication program should be designed to address each of them.

A. *Toxic hazards*—acute toxicity, chronic toxicity, embryotoxins, allergens (gases, liquids, solids).
B. *Chemical burn hazards*—acids, bases, dehydrating agents, oxidizing agents, among others.
C. *Flammability hazards*—Class A: ordinary combustible material (wood, cloth, paper); Class B: flammable liquids and gases; Class C: energized electrical equipment; Class D: combustible metals (e.g., Mg, Zr, Ti, Na).
D. *Reactivity and explosion hazards*—peroxides, perchlorates, chlorates, nitrates, bromates, chlorites, iodates, compounds containing acetylide, azide, diazo, halamine, nitroso, and ozonide functional groups, among others.
E. *Pressure/vacuum hazards*—gas cylinders, vacuum Dewar flasks, vacuum desiccators, vacuum fusion analyzers, gas sampling bulbs, among others.
F. *Cryogenic hazards*—liquified gases.
G. *Asphyxiation hazards*—gas cylinders, liquid gas cylinders.
H. *Thermal hazards*—muffle furnaces, induction furnaces, resistance furnaces, drying ovens, etc.
I. *Electrical hazards*—analytical measurement instruments, furnaces, pumps, etc.
J. *Physical hazards*—pumps, centrifuges, saws, drill presses, milling machines, grinders, other moving or rotating machines, cuts, falls, etc. Also, dust, noise, intense light sources, ionizing and nonionizing radiation from various sources.

SPILL CONTROL AND EMERGENCY PLANNING

The chemical hygiene plan should include planned actions for anticipated accidents and emergencies. This must include an evacuation plan with assigned rally points and group captains, ambulance stations, and methods for rapid communication with local fire, police, and hospital authorities, as well as corporate security, safety, hygiene, and medical officials. It should also include instructions for dealing with less serious emergencies, with clear guidelines for distinguishing between those situations that require evacuation and those that do not. All laboratory personnel should be trained in the location and use of fire alarms and fire extinguishers and in the route of evacuation in the event of an alarm.

There are commercial kits available for dealing with various types of chemical spills. It is a matter of policy under what circumstances they are utilized by a trained emergency response team or by laboratory personnel. Such kits should be available in close proximity to areas where the corresponding hazardous substances are commonly stored and used. Every worker in the laboratory should be familiar with their location and use. Kits are available for acid spills, caustic spills, mercury spills, and formaldehyde spills. Some acid spill kits are unsuitable for hydrofluoric acid spills, while others are. Each type of kit should be clearly labeled as to its intended purpose, and instructions for use should be prominently visible.

Mercury spills are sometimes difficult to handle because of the element's tendency to form small particles that lodge in crevices. In the case of mercury spills, special equipment such as vacuum devices, mercury sponges, amalgamating powders, and mercury vapor absorbants are important additions. Neutralizing sprays are available for acid and base spills. Absorbant pillows, dikes, and booms may be useful in containing large spills. Various types of granular absorbants are also available. Sealable plastic bags and plastic shovels, plastic brooms, brushes, and scoops may all be needed. Personal protective gear that should be available includes gloves, safety glasses, goggles, face shields, protective garments and boots, appropriate respirators, and self-contained breathing equipment.

CHEMICAL WASTE DISPOSAL

One of the rationalizations often heard for the dropping of classical chemical techniques from the industrial workplace is the group of burdensome regulations that now must be met for the disposal of chemical waste. In fact, the total amount of waste generated by even the largest and busiest chemical analysis laboratory is vanishingly small compared to that generated by even the smallest steel mill or smelter. Nevertheless, laboratory wastes must be handled by means that satisfy all federal, state, and local laws, and which present no undue hazard to the personnel involved.

The Environmental Protection Agency (EPA) was formed in the 1970s by executive order after the passage of the Environmental Protection Act. The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, also known as the "Superfund") was passed in 1980 to respond to past environmental damage. It was reauthorized in 1986 as the Superfund Amendment and Reauthorization Act (SARA). Laws enacted to prevent future damage to the environment include the Clean Air Act, the Resource Recovery and Conservation Act (RCRA), and the Emergency Planning and Community Right-to-Know Act. Some EPA regulations that apply to waste disposal include those dealing with Hazardous Waste (40CFR Parts 160-265), Emergency Planning and Notification (40CFR Part 355), and Hazardous Substance Reporting (40CFR Part 370). Under the law many laboratories may qualify as small quantity generators, either "conditionally exempt" or nonexempt, based on the amount of hazardous and acutely hazardous waste they generate and store on-site.

The laboratory's chemical hygiene plan should contain provisions for the proper disposal of all classes of chemical waste that are generated. Useful guides are the text, *Prudent Practices for Disposal of Chemicals from Laboratories* (by the National Research Council, National Academy Press, Washington, DC, 1983) and the Chapter, "Procedures for Disposing of Chemicals in Laboratories" in *Prudent Practices for Handling Hazardous Chemicals in Laboratories* (by the National Research Council, National Academy Press, Washington, DC, 1981).

Disposal to a sanitary sewer system by drain dumping must be a thoughtful act, limited to small quantities of permitted substances. If sewer systems discharge directly into waterways, even more stringent restrictions apply. In the special case of an on-site treatment facility, important restrictions to drain dumping still prevail. Drain dumping, when permitted, is always confined to select water-soluble compounds and must be accompanied by copious amounts of cold running water. Flammable compounds must be diluted to the point where they are no longer a fire hazard. Acids and bases must be diluted to the pH 3 to 11 range. Two or more chemicals must not be allowed to mix in drains. All toxic, malodorous, lachrimatory, or explosive materials must be disposed of by other means. Many laboratories have established regular pick-up schedules for stored, segregated solid and liquid waste. These are transported to a central location where they may be batched with similar waste from other corporate departments and ultimately dispositioned by one or more means.

Segregated solvents may be distilled for recovery or incinerated, either in-house or by contract with an outside agent. Acids may be neutralized or reclaimed by any of several processes. Approved waste haulers may be contracted to remove these and other forms of waste as well. It is important that safe and appropriate containers be used for the collection, interim storage, and transport of lab wastes and that written waste segregation rules be strictly adhered to. Special disposal situations may involve the treatment of unwanted solid, liquid, or gaseous chemicals in the laboratory following the instructions for a specific compound given in *Prudent Practices for Disposal of Chemicals from Laboratories*.

POSTSCRIPT

We suggested at the outset that good laboratory practices *were* safe laboratory practices. Admittedly, this statement begs the question to some degree, but there is a very relevant sense in which it is not circular semantics. A clean and orderly laboratory with procedures in place to minimize hazards is the best starting point for good analytical chemistry. The total concept of "good laboratory practices" is really quite large, encompassing all that we have included in Part V of this book and more. What we have chosen to cover here emphasizes actual laboratory manipulations, their requirements, and their consequences. The metals analyst is a citizen and community member, as well as a scientist. And one of the consequences of his work involves its effect on the environment. Hopefully, that effect will always be benign. I remember a teacher years ago who admonished the quantitative analysis class never to use tap water in their procedures because: "That stuff's hardly fit to *drink*!"

REFERENCES

Annual Book of ASTM Standards, Vol. 03.05, American Society for Testing and Materials, Philadelphia, 1993, Designation E 50.

Annual Book of ASTM Standards, Vol. 03.06, American Society for Testing and Materials, Philadelphia, 1993, Designation E 416.

Bretherick, L., *Handbook of Reactive Chemical Hazards*, 2nd ed., Butterworths, London, 1979.

Fire Protection Guide to Chemical Hazards, 6th ed., National Fire Prevention Association, Boston, 1975.

Guide to Safe Handling of Compressed Gases, Matheson Gas Products, East Rutherford, NJ, 1982.

National Research Council, *Prudent Practices for Disposal of Chemicals from Laboratories*, National Academy Press, Washington, DC, 1983.

National Research Council, *Prudent Practices for Handling Hazardous Chemicals in Laboratories*, National Academy Press, Washington, DC, 1981.

Nielsen, J. M., *Solvents and Safety*, General Electric Corp., Schenectady, NY, 1980.

NIOSH-OSHA Pocket Guide to Chemical Hazards, U.S. Government Printing Office, Washington, DC, 1987.

Safe Storage of Laboratory Chemicals, D. A. Pipitone, Ed., John Wiley & Sons, New York, 1991.

Sax, N. I. and Lewis, Sr., R. J., *Dangerous Properties of Industrial Materials*, 7th ed., Vols. I–III, Van Nostrand Reinhold, New York, 1989.

Young, J. A., Kingsley, W. K., and Wald, Jr., G. H., *Developing a Chemical Hygiene Plan*; American Chemical Society, Washington, DC, 1990.

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Good Administrative Practices

By analogy to good laboratory practices, we can delineate administrative procedures that facilitate the function of a metals analysis laboratory. The focus here, as well, are quality issues, for without an organizing effort the most technically competent labs will appear to flounder. This is also, perhaps, the best place to characterize the different "personalities" and styles of operation that a metals lab can acquire since the administrative function molds that to a large degree.

THE CORPORATE ENVIRONMENT

No analytical lab that the author is aware of operates in an economic vacuum. There are always budget constraints and fiscal agendas that usually have little time or concern for laboratory operations, which may be regarded as high overhead service functions. Even in commercial laboratories, where the product *is* the analysis, technology takes a backseat to the balance sheet. And in academic and government labs, as well, funding concerns are never very far away. This is *reality*, and the laboratory administrator must deal with it on a daily basis. He or she must often play defender to retain and advocate to expand the function of the laboratory. The relationship of the lab administrator to the corporate environment is critical to the health and survival of the laboratory.

The laboratory manager often represents the efforts of numerous workers to the people who sign the paychecks, and the impression he or she leaves reflects on the entire operation. This individual has an obligation to represent interests beyond their own career advancement and to promote the utility of the analytical function where it can serve corporate goals. In some small "high-tech" industries, analytical chemistry may represent one third of the total work force. In commercial labs, it may reach 90%. But, more typically, the analytical function is a vanishingly small part of the total payroll. In such a situation, just getting attention may be a large problem. Corporations and operating divisions within corporations also have unique styles, which may change with time. The laboratory administrator must translate the real technical needs and concerns of the analytical function for absorption by this corporate context. Similarly, he or she must represent the management structure to the laboratory personnel. This should be done honestly and openly, with no personal agenda involved.

MATERIAL AND DATA FLOW

If one were to flowchart the operation of metals analysis laboratories, each instance is likely to be unique in some respects, but certain basics are usually shared. In broad outline, the laboratory sample arrives at the facility's doorstep, as it were, and is processed into a test sample. Portions of the test sample are analyzed by various techniques, generating estimates of the sample's component concentrations. These results are collated into a report that is sent (physically or electronically or both) to one or more destinations. The unused remainder of the test sample is stored in the laboratory for a predetermined length of time for use in the event of recheck requests (and potentially as legal evidence). A copy of the test report and all associated typed, handwritten, and software entries associated with the work are also stored for a predetermined length of time. Any unused portion of the original laboratory sample may also be stored.

A large, busy lab is likely to be receiving a steady stream of highly diverse samples from many different sources. The laboratory's "doorstep" may be cluttered with metal alloys, ores, slags, plating solutions, acid-pickling bath samples, lubricating oils, process rinse waters, treatment plant effluent waters, stack impinger samples, and annealing furnace atmosphere samples. Each of these is accompanied by a unique array of requested analytes and a unique roster of individuals requiring the analytical report. Other imperatives may accompany the lab sample: maximum holding times (for water samples), the presence of preservatives, the need to keep the sample refrigerated or frozen (as in the hydrogen analysis of low-alloy steels), process deadlines, target dates, shipping dates, or, perhaps, some value on a relative priority scale. Of course, there are always any number of identifying codes.

One of the first things that needs to be decided is what constitutes the minimum work unit for the laboratory. Most labs, especially those with a laboratory information management system (LIMS) regard each sample received as the minimum work unit, and thus each sample receives an assigned laboratory identity code. Labs without an LIMS and bar code generator may find such an approach cumbersome, especially in situations where a large number of similar samples are submitted together. Suppose an engineer submits 25 machined parts of T-304 stainless steel and requests a complete analysis on each in the hope of identifying the three original heats that were utilized and also to correlate minor variations in composition with part wear. He has already coded them A through Y. Rather than assign 25 unique lab IDs, some laboratories would treat this request as one large job, assigning it one unique lab ID, requiring 25 complete sets of results and utilizing the submitter's ID numbers.

There are several distinct ways to configure an LIMS. The largest and most complex systems are managed by a mainframe computer and can accommodate almost any number of terminals. Smaller systems can be handled by a local area network (LAN) of personal computers managed by a file server and a database executive. The cost of an LIMS can range over several orders of magnitude, beginning at minimal configurations for about the price of, say, an FAA spectrophotometer, on up to millions of dollars. Such expenditures are justified by a return in efficiency, with the size and complexity of the system scaled to the work throughput of the laboratory.

There are layers of utility possible with commercially available software packages, but not all can be used to advantage in all laboratory situations. In its ultimate expression, an LIMS is linked to a larger corporate network. It acknowledges receipt of the lab sample, assigns it an identifying code, generates bar code labels, assigns and specifies standard operating procedures for all sample preparation and analysis tasks, receives results from keyboard entries and directly from interfaced instruments, and generates a report for the lab manager's approval. Upon approval, it routes copies of the report to the appropriate locations on the corporate network and assigns an archival storage location for excess sample.

Other tasks that such a system can perform are numerous. Management reports of various types can be generated to trace individual and group performance, to calculate analytical service costs, to apportion lab client charges, and to monitor activity level by alloy grade, by project, or by department. If validation work and individual replicates are entered, the system can be used to produce a continuously updated tolerance table against which new work is weighed for acceptance or flagged for recheck. The LIMS can also manage a regular program of interlaboratory testing, comparing results from different laboratories against a corporate tolerance table and archiving the data for future audits and accreditation programs.

One of the big advantages of an LIMS is the ability to access work in progress on an on-line basis, so that preliminary reports can be issued and approaching target dates can be monitored. Retrieval of archived reports and the location of archived samples is another asset. The relational database can be queried by numerous protocols: by lab code or any other identifying number, by alloy grade, by client, by submission or report date, and for some systems by the exact or approximate reported composition, The LIMS can also be the repository for various regularly needed information, which will be available at any terminal on-line: standard operating procedures, available reference materials, alloy specifications, instrument maintenance logs, and calibration records.

All of this is a great aid to the management of a busy laboratory but of only marginal assistance to the analysts. It eliminates some of the paperwork (which should not have been a large part of the analyst's task at any rate), and it provides ready access to information that would otherwise have to be manually extracted from hardcopy files. However, in poorly configured systems, the LIMS may actually add to the analyst's burden by requiring long keyboard entries with inflexible and error-prone protocols. A LIMS is not a panacea, and it is not for every lab. It is primarily a management tool for high-throughput laboratories. And its value lies in how closely it is tailored to the work flow of the organization. Unless a ground-up systems design approach is utilized in the initial planning—a process that should involve every potential user—the LIMS can create as many problems as it solves.

Computers and automation aside, a metals analysis laboratory today functions in much the same manner as it always has. The instruments are faster, more sensitive, and more accurate than ever before, and there are far fewer people. But the material and data flow are much the same. Quality assessment audits now highlight features that have always been a part of effective laboratory work flow. Sample custody requirements, for example, emphasize accountability that the material being analyzed is the material that was sampled. Chain of custody documentation may be required for some or all samples, and the laboratory manager may have to be prepared to testify that the sample results, in fact, represent the laboratory sample received. Custody protocols are mandatory for regulatory testing of environmental samples and are sound quality control practice for *all* samples.

Recording and storing data is another important feature of the work flow. It is a matter of lab policy as to how long analytical records are kept, although liability evidence suggests that 30 years is not excessive and may be too brief in some cases. At any time after a final report has been issued, it should be possible to (relatively easily) reconstruct all the work that was done, including the names of the analysts, the methodology employed, the dates on which each determination was performed, the raw data replicates, the calibration data, the calculations employed, and the results obtained on all validation standards.

Labs differ in how they require record keeping, and automated systems have reduced the amount of handwritten entries and manual calculations required, but at the very least there should be some archived individual analyst record that corresponds to each determination in the archived final report. Some labs require signed and witnessed carbon copy pages from lab notebooks to be permanently filed, with the notebooks themselves to be turned in for filing when filled or upon termination of employment. Analysts must be schooled to use only permanent ink, to make no erasures, and to cross out errors with a single line, initialed and dated. Hardcopy data obtained directly from instruments—computer printouts, calculator tapes, recorder plots—should be clearly marked with the sample identification code, the analyst's name, the date, and any other relevant information. These may be stored in files, bound in notebooks, or even microfilmed. Software data records should be routinely downloaded onto floppy disks or magnetic tape cassettes that are write-protected, identified, and stored in a secure area away from magnetic fields.

Laboratory matters involving litigation or potential litigation require special attention. One individual should be assigned to the task, and all work should be performed by him or under his direction. A special bound and page-numbered notebook should be devoted to recording all work. The sample or samples should be handed to the person in charge of the work and kept in his custody. It is unwise to enter the work on an LIMS unless the laboratory is prepared for the possibility that the entire LIMS database may be seized as evidence and scrutinized. Testing procedures used should be the best available umpire methods with every step documented. All calibrations, printouts, and calculations should be dated, initialed, and retained. The person assigned to this work should consult with the attorney handling the case before any work is performed. He must be able to testify on all technical aspects of the work should the case come to trial.

LABORATORY STYLE

At the outset we suggested that laboratories have "personalities," and it is probably worth a moment to discuss this remark even though it pertains to an area full of intangibles. Here we are not referring to the nature of the lab's business or even to the urgency of its task (control lab versus research lab, say), although both of these may influence the form that a lab's "personality" takes. Regulatory requirements, corporate policies, the age and academic credentials of the workers, and the lab's organizational structure may all play a role, but in sum a lab's personality is a composite of the personalities of the people who work there. And no single personality usually has more influence on this cumulative effect than that of the lab manager. That is not to say that the lab's personality is an undistorted reflection of the lab manager's personal style. In fact, a strong-willed "micro-manager" sometimes engenders a floundering, directionless organization, while "laid-back" types may find themselves in charge of an efficient analytical engine.

Laboratories differ in the speed and efficiency with which they handle routine work, in the flexibility and adroitness with which they respond to new challenges, and in the overall level of accuracy that is accepted as a norm. These traits are superimposed on prevailing attitudes or resignations toward matters like new equipment purchases, career advancement, the resolution of nontechnical problems, and communications with outside departments. We can broadly distinguish the "Henry Ford" lab, geared up for speed and efficiency, from the "Thomas Edison" lab, ready to take on any assignment and welcoming the unusual. The former takes as its primary goal an iterative refinement of existing procedures, accepting new approaches primarily as time savers, and only after cautious comparisons. The latter manifests an "I can do anything" attitude, seeking opportunities to highlight its versatility and discouraged by an excessive diet of the routine.

The "Henry Ford" lab may be heavily outfitted with high-speed instrumentation, but is easily thwarted by an unusual request. "We don't have a channel for that element" is a frequent disclaimer. The "Thomas Edison" lab may be able to determine almost any component in almost any matrix, but the man-hour cost will be high, and large batches of samples would require a prohibitive amount of time. "We're going to have to authorize overtime to handle that request" is likely to be heard at some time or other.

We have avoided any reference to accuracy in describing these two styles because both types of laboratory can exhibit a broad range of performance. There *are* characteristic traps that each is prone to fall into, however. The "Henry Ford" lab tends to be standard dependent and may become locked into inappropriate validation schemes that do not adequately challenge the full range of their tasks. The "Thomas Edison" lab may be seduced into believing that if *matching* validation standards are unavailable then *no* validation is needed. Both types of laboratory can find excuses for shunning replicates; ironically, to some ears these may sound similar: "we don't have the time"/"takes too long" and "we'll just get the same number"/"we don't make mistakes." A good personality for a metals analysis laboratory is, of course, a blend of both styles that avoids these pitfalls. Perhaps this is the ideal that will remain an unattainable goal: a laboratory that is all things to all clients while maintaining the highest standards of the profession.

QUALITY CONTROL

A popular topic in management circles is *quality assurance*, an embracing concept that includes both *quality control* and *quality assessment*. "Quality control" stands for the sum of all those in-place protocols whose aim is to ensure that what is supposed to happen, does in fact happen when a product or a service is produced. It includes notions of customer or client satisfaction, dependability, and cost control. "Quality assessment" stands for any and all means available to monitor the effectiveness of the quality control process. In the case of a service function, like metals analysis, there is a bit of a semantic dilemma here. In a metals-producing facility the analytical laboratory, itself, *is* a *quality control* function on the alloy *products*, and validation standards, control charts, and other checks on lab performance are *quality assessment* programs. There is another sense, though, narrowing the focus on the laboratory, in which the *service* is *quality controlled* by means of standards and charts, and this whole process is *quality assessed* by means of audits, interlaboratory testing, double-blind studies, or other means. Here let us keep to this latter sense and outline a few relevant details on controlling the quality of analytical measurement that have not yet been discussed.

Standard operating procedures (SOPs) are written formalized protocols for all laboratory activities. They include sample preparation and analytical methodology, as well as administrative functions. Most lab audits and accreditation programs insist on thorough SOP coverage of lab functions, and so they have become a part of the work experience of most analysts and managers. SOPs should follow a consistent format to aid in cross-referencing. They should include a step-by-step procedure for each required operation and specify appropriate quality control measures. Copies of the appropriate SOPs should be stored at the workplace where they are utilized. These are *controlled distribution documents*, signed and approved by management with revisions appropriately numbered and dated.

Outdated versions of such documents are collected or destroyed when revisions are issued. Deviations from an SOP are possible with formalized management approval. There are other types of controlled distribution documents that may or may not be referred to as "SOPs." These include corporate and laboratory tolerance tables and formalized conventions for rounding values, the number of significant figures reported, and detection limit and quantification limit protocols.

A well-constructed array of SOPs and related documents ensures that quality-damaging aberrations do not creep into the analytical process.

Equipment metrology is concerned with the calibration and maintenance of balances, micropipets, spectrophotometers, muffle furnace controllers, and other devices. These are essential aspects of the analytical process that are normally considered outside the province of an analytical procedure. Equipment calibration and maintenance may be provided by laboratory personnel, by corporate personnel outside the laboratory, or by service from an outside firm. In a typical case, all three sources are utilized. Where possible, traceability to a NIST or other primary standard should be employed. A maintenance schedule that includes such calibration should be established in every applicable case, and formal records of each calibration/maintenance service should be kept, including any necessary repairs or modifications. Repair and maintenance records for equipment that does not require calibration should also be kept. It is appropriate to tag certain equipment, such as analytical balances, with a calibration approval date. The tag or label may also include the date of the next scheduled calibration.

Validation and control chart records provide documented evidence that the analytical process was in control when a given sample measurement was produced. Tabulated and dated records of results on certified reference materials are an invaluable resource, not only for traceability, but to establish a dynamic monitor of expected tolerances. Some laboratories have established a software spreadsheet wherein results on standards are routinely entered and calculated precision and bias tolerances are correspondingly updated. Control charts of various kinds are also often managed by software and can provide graphical trend insights that may otherwise escape notice. It is often possible to avert disruptive down-time by nipping a bias trend in the bud, as it were.

Other records have a quality control function as well. Calibration and validation standards, pure elements and compounds, and commercial solution standards that are utilized in the operation of a laboratory must have certificates or other proof of authenticity, and these must be available in a readily accessible form. An auditor may ask to see such documentation. Therefore, it behooves the lab manager to ensure that files are current and that no undocumented materials remain on the shelves.

Handling errors is an important part of a quality control program. Procedures should be in place for all likely contingencies. In particular, a "recheck" protocol is critical since there is a temptation to recheck values that: (a) show a material to be out of specification; (b) show the test-originating laboratory to be wrong; or (c) otherwise jeopardize the security or aspirations of the test originator. If the validation standards validate the analytical procedure and if the analyst perceives no extraneous circumstances that might have affected the sample test, there is no reason to recheck a result. And none should be performed. Performing inappropriate rechecks skews the database of an analysis and can lead to serious error. In the case of suspected analytical or sampling error, rechecks are always appropriate, but a rigorous treatment requires that all previous data be rejected and reported values be generated from a complete set of new replicates, sometimes from a completely new sample.

Commercial laboratories are sometimes utilized to supplement the work of a metals analysis laboratory, either for determinations of analytes or matrices for which no capability is maintained, or to relieve an excessive workload. In this event, it becomes important to qualify the outside service with single- or double-blind standards and possibly to audit their operation. An audit involves a visit to the commercial lab, inspection of their facilities, examination of their standard operating procedures, interviews with lab personnel, and observation of routine operations. It is the ultimate goal of accreditation programs to diminish or eliminate the need for regular customer audits; however, it is likely some commercial lab clients will continue to want to make their own judgments about the work they are paying for.

Specifying instrument purchases is an important feature of quality control since a laboratory becomes "wedded" to its selection and that decision affects the accuracy of its work. An excellent source of information for large instrument purchases are the following ASTM Standards: ASTM Guide for Describing and Specifying the Spectrometer of an Optical Emission Direct-Reading Instrument (E 1507); ASTM Practice for Describing and Specifying the Excitation Source in Emission Spectrochemical Analysis (E 172); ASTM Practices for Describing and Specifying the Spectrograph (E 356); ASTM Practice for Describing and Specifying a Wavelength-Dispersive X-Ray Spectrometer (E 1172); and ASTM Practice for Describing and Specifying Inductively-Coupled Plasma Optical Emission Spectrometers (E 1479). Large instrument purchases are typically written in the form of a contract in which the instrument manufacturer agrees to meet certain performance criteria. Sometimes a corporation's legal staff is involved in the transaction.

Verifying software performance may be a requirement by the laboratory's auditors. This means determining that the computer programs utilized by the laboratory do what they purport to do. There is no painless way to rigorously fulfill this quality requirement. The simplest course is to thoroughly validate the method with certified reference materials; however, some auditors may be satisfied with nothing short of hand-calculating a selected set of results and determining that the extant computer program yields identical results. Back-up copies of the current version of all software must be stored in some secure area free of magnetic fields. The modern laboratory is full of "black boxes" that chug out analytical results. This makes some auditors and some analysts nervous. And perhaps it should.

QUALITY ASSESSMENT

The primary means of determining that a laboratory's quality control programs are effective is feedback from its clients. Such feedback can be encouraged by initiating a survey that requests candid responses. In particular, the lab manager should seek responses that focus on specific deficiencies rather than broad complaints like "too slow." If the clients are dissatisfied, there is a problem—it may be analytical, but it also may be administrative—and the answer will usually lie in one of the quality assessment plans that should be in place.

Internal audits are an essential feature of a quality assessment program. They may be initiated by the lab manager or by a quality assurance officer of the corporation. Like safety audits, they may involve an unannounced inspection of routine laboratory activities. They may require traceability evidence for validation work and for calibration materials, interviews with analysts, and notebook perusals.

External audits are taken quite seriously by most corporations. Usually the date and time of the audit are known ahead of time and a lab "walk through" is scheduled at some point in the proceedings. Surprises usually come when auditors ask to trace a routine analysis to its ultimate validation source. This may include locating the certified reference material certificates, the certificates of purity of the elemental standard materials used, the notebooks of the analysts, and other sources.

Interlaboratory studies are an important source of quality assessment since good correspondence of results between laboratories, especially those that utilize different techniques, reflects positively on both operations. Sometimes an interlaboratory study is conducted between laboratories within a corporation and sometimes as a cooperative program between companies. The protocols involved in such tests may be formal and complex or informal and simple. If the laboratory is merely requested to use its best or its routine procedure for a specified sample determination, the test is usually termed a *round robin*. Testing of this type is useful in evaluating and comparing laboratories. It is also important in the certification of reference materials, where confidence in establishing a standard value may derive in part from obtaining similar results by diverse techniques.

Very formal testing protocols, such as those described in ASTM designations E 173[1], E 1601[2], and E 691[3], and in ISO 5725[4], are utilized in evaluating an analytical procedure. In this case, a highly detailed draft of the procedure is provided and must be exactly applied to the same set of samples by all participants. All types of interlaboratory studies, whatever their intended purpose, can potentially be applied in a quality assessment program. For this reason, among others, lab managers should encourage active participation of their staff in industry consensus programs and in the cooperative testing programs of standardizing bodies like NIST. In addition, any organization with more than one analytical laboratory needs some regular program of comparison among them, not as a finger-pointing exercise, but in a cooperative spirit to intercept drift before it becomes serious. Such a program need not be so exhaustive that it becomes burdensome, but it should adequately challenge the analytical systems of all the participating laboratories.

Proficiency testing is a specialized form of interlaboratory testing in which identical samples are analyzed by many laboratories, usually using a specified procedure. The managing agency (or its subcontractor), usually for a fee, mails out a set of samples at regular intervals and receives the results from the participants. When all results are in, a statistical workup of the complete data is mailed to all participants. The participating laboratory can identify its own data in the context of the entire data set, but all the other laboratories remain anonymous.

One good graphical treatment that can be employed is the *Youden plot*, provided that two similar samples are utilized. In this presentation, values for one sample are plotted on the x-axis and values for the other on the y-axis. A horizontal line with half the points above it and half below is drawn parallel to the x-axis. A vertical line with half the points to its right and half to its left is drawn parallel to the y-axis. If only random error was present in the data set, the points would be equally distributed in the four quadrants thus formed. Commonly, however, the points are concentrated in the upper right and lower left quadrants, indicating that most laboratories show a high bias on both samples or a low bias on both samples. A 45° diagonal straight-line plot through the lower left and upper right quadrants represents systematic error. The distance of any point from this diagonal is a measure of its random error. Proficiency testing programs are a valuable investment for all laboratories since they furnish proof that a facility is performing on a par with its peers. It is important that such a program include some certified reference materials as a guard against undetected systematic error, especially when a comparative method is specified.

Accreditation and certification programs are fee-based audits by firms or government agencies that specialize in evaluating the capabilities and documented procedures of laboratories. These programs are expensive, but are increasingly becoming part of the price of doing business. Typically, a lab's quality and standard operating procedure manuals are mailed to an auditor for study before he or she actually visits the facility. The scheduled visit may extend over several days and involve inspection of equipment, observation of work procedures, and interviews with workers and management. Failure to pass such a certification is usually not a final judgment, but a reaudit may require major or minor changes to operations or documentation.

Accreditation, once achieved, must be renewed with a reaudit at periodic intervals, usually every one or two years. Accreditations and certifications vary in depth and refinement, sometimes based on the technical knowledge of the auditor or the auditing team. Merely specifying that detailed written procedures are followed exactly is not in itself a guarantee of quality. However, performance-based criteria that examine validation and traceability records, and in particular a practical working knowledge of analytical chemistry by the auditor, lead to true quality assessment.

OTHER ADMINISTRATIVE FUNCTIONS

Lab managers spend a certain amount of time involved in economic matters, such as department budgets, man-hour costs, purchasing, negotiations for major equipment purchases, service contracts, and other details. Another area involves personnel issues: salaries, performance evaluations, training, injury and exposure records, grievances, and promotions. Then there is the large area of safety and environmental responsibility that was discussed in the last chapter.

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[1] ASTM Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals.

[2] ASTM Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method.

[3] ASTM Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method.

[4] International Standard: Precision of Test Methods—Determination of Repeatability and Reproducibility by Inter-Laboratory Tests.

All of these activities make demands upon the time of the lab administrator; some can be partially delegated and some cannot. And yet, it is essential that time be found for both the science and the people who are doing it. It is important to keep the lines of communication open and clear, to know when a technical dialogue is needed. No metals analysis lab can run for very long on automatic pilot.

REFERENCES

Annual Book of ASTM Standards, Vol. 03.05, American Society for Testing and Materials: Philadelphia, 1993, Designations E 172, E 173.

Annual Book of ASTM Standards, Vol. 03.06, American Society for Testing and Materials: Philadelphia, 1993, Designations E 356, E 1172, E 1479, E 1507, E 1601.

Annual Book of ASTM Standards, Vol. 11.01, American Society for Testing and Materials: Philadelphia, 1993, Designations D 3856, D 4840.

Annual Book of ASTM Standards, Vol. 14.02, American Society for Testing and Materials: Philadelphia, 1993, Designation E 691.

Goldberg, R., Finnerty, W., Somani, K., Berthrong, P., and Birnbaum, N., *American Laboratory*, March 1987, pp. 114–118.

Harris, H., *ASTM Standardization News*, April 1993, pp. 44–51.

ISO Guide 25 and ISO Standard 5725, International Organization for Standardization (available from: American National Standards Institute, New York).

Liscouski, J. G., *American Laboratory*, March 1987, pp. 98–103.

Matson, J. V., *Effective Expert Witnessing*, 2nd ed., CRC Press, Boca Raton, FL, 1994.

Mesley, R. J., Pocklington, W. D., and Walker, R. F., *Analyst*, Vol. 116, 1991, pp. 975–990.

Miller, J. C. and Miller, J. N., *Statistics for Analytical Chemistry*, 2nd ed., John Wiley & Sons, New York, 1988, pp. 86–87.

Ouchi, G. I., *LC-GC*, Vol. 1192, 1993, pp. 101–110.

Taylor, J. K., *Standard Reference Materials: Handbook for SRM Users*, NIST Special Publication 260-100, National Institute of Standards and Technology, Gaithersburg, MD, 1985.

Youden, W. J., *Industrial Quality Control*, May 1959, pp. 24–28.

Also: User manuals—Lab Vantage (Laboratory MicroSystems, Inc. Troy, NY), Net Ware (Novell, Inc., Provo, UT).

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Personnel

THERE IS BUT ONE SUBJECT yet to cover—the most important quality factor of all: people. The best-equipped laboratory in the world is worthless without a qualified, trained, and motivated staff to operate it. Perhaps the "container" (robotic) labs will one day challenge this state of affairs in some industries, but until that day arrives management must continue to hire, train, and motivate human beings to work as metals analysts. And in those labs that must deal routinely with the nonroutine, it is unlikely that even future heuristic computer systems can eliminate the workforce. In fact, based on the heavy dependence on reference materials by much of industry, there is reason to believe that the near future may see some increase in personnel as classical techniques are recreated, phoenix-like, from their own ashes.

People are now and will continue to be the key factor in the success or failure of any analytical chemistry function. No quality control plan, however elaborate, can supersede the simple fact that the analyst is always the final arbiter of what is "good enough." If he or she has not been properly trained and motivated, "good enough" for the analyst will not be good enough for the client, and the lab's work will be rated poor. As we hope to now illustrate, training does not mean credentials, and motivation does not mean intimidation. The need for instruction, inducements, and job enrichment has not been lost on successful employers.

LABORATORY ORGANIZATION

The organization of personnel in a laboratory should reflect not only the nature and complexity of the workload but also the talents and personalities of the individuals who toil there. As with the chemistry itself, so with the personnel responsibilities: "There is more than one way to skin a cat." An arrangement that works just fine with one group of people may be a disaster with another group. Restructuring the organization to accommodate a fastidious individual by moving him away from a "free spirit" whose lab bench is a jumble is the kind of flexible structuring we are talking about. There are other examples: the team players versus the loners, the "young lions" versus the "old guard"; and then there are the gadgeteers, the computer jocks, and all the other assorted denizens of a laboratory, each with unique skills and abilities. The effectiveness of each can be optimized if the lab organization is flexible enough to accommodate some variations in personal style and use them to advantage.

The laboratory may be a highly structured hierarchy or a loose and free-wheeling system of overlapping duties and responsibilities. Neither is a guarantee of efficiency or of chaos. However, if the system of organization is a poor match with the people involved, chaos is the more likely outcome. Typically, there is one individual with overall responsibility for the metals analysis laboratory. He or she may be called a director, a manager, a supervisor, or, often, the chief chemist. Some guides [such as ASTM Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water (D 3856)] recommend a minimum of a baccalaureate degree in science or engineering or equivalent and five years of laboratory experience as minimum requirements for such a position.

In hiring for such positions these days, preference often falls on M.S. and Ph.D. degreed applicants, although many non-degreed individuals have served with distinction in such positions. The laboratory manager may delegate many of his duties informally to one or more individuals, but, more typically, there is at least a second level of authority with formal recognition. This category may consist of one to six or more individuals with titles like group leader, assistant manager, assistant supervisor, or assistant chief chemist. There may also be titles that recognize technical achievement or seniority, but do not emphasize administrative responsibility. These include: research associate, senior chemist, senior scientist, principal chemist, and others.

Many salaried job categories for junior analysts are divided between those that are exempt from overtime pay and those that are "nonexempt." Exempt titles might include: assistant chemist, associate chemist, and chemist, while nonexempt titles might include: analyst, technician, and technical specialist. Some of the latter titles are also frequently applied to hourly laboratory workers. What all these titles mean in terms of duties and compensation varies widely.

The laboratory manager generally assumes direct responsibility for the long-term direction of the work plan and the development of quality assurance systems for monitoring laboratory performance. He or she approves all standard operating procedures, develops an operating budget, and appraises the performance and career development of each laboratory worker. Other duties may include intra- and intercorporate activities such as audits, accreditation, interlaboratory testing, industry consensus work, and liaison with other departments in the company. In some situations, the lab manager is also the chemical hygiene officer for the facility and may have direct responsibility for all purchasing and physical plant maintenance.

Duties that are typically relegated to assistants or senior staff include training activities, routine performance monitoring of analytical data, development of new or modification of existing analytical methods, and writing new and modifying existing standard operating procedures. Sometimes assistants or senior staff participate in the appraisal of performance and salary review of junior staff. Often they are involved in planning and negotiations for new equipment purchases and in audits, safety reviews, and corporate liaison activities.

In these times, the metals analyst has many responsibilities beyond his expected on-time quality result. He may be developing a new analytical procedure for anticipated needs in his "spare time." And he may have been saddled with administrative tasks such as mailing samples to commercial labs, modifying LIMS software, writing purchase orders, calibrating equipment, handling service contracts, or arranging instrument repairs. These extra responsibilities are not always reserved for degreed or salary exempt technical staff but may be shared with technically trained salary nonexempt personnel.

Some laboratories, unfortunately, encourage a degree caste system with the lines of work assignments strictly defined by academic credentials. This is inappropriate for several reasons: first, college training, by itself, at any degree level is inadequate preparation for work in a metals analysis laboratory; second, non-degreed personnel, just like degreed personnel, need to be able to demonstrate the full extent of their talents and to be rewarded for their best efforts; and third, no laboratory can afford to allow abilities to lie fallow.

A further word needs to be said about academic training since laboratory organizations have quite distinct perceptions in this regard. These perceptions may reflect the attitude of the laboratory manager or they may derive from that corporate style that we mentioned in the last chapter. In some process control laboratories, there is a long-standing tradition of offering starting analyst positions to hourly workers in the labor force. These individuals are selected for their intelligence and enthusiasm, rarely for their academic training. Most of these workers render a good account of themselves in these positions provided that they receive adequate training. There are many examples of such individuals advancing to laboratory manager and to other management positions within an organization.

In some process control and in most research laboratory environments, the lowest entry level position in the analytical lab requires a two-year associate degree in chemical technology or some closely related physical science curriculum. Some large laboratories have developed a close working relationship with a local junior college, wherein especially bright graduates are brought to the attention of the corporate personnel department or the lab manager. Inexperienced individuals with an associate degree are most often hired as salary nonexempt analysts. B.S., M.S., and Ph.D. chemists, with or without experience, are traditionally hired as salary exempt workers with a title and responsibilities that reflect their academic training and their practical experience. Economic adversities have fostered ethical abuses at times, however. The underemployed chemist and the "rent-a-chemist" cast a pallor on the industrial scene when they represent a wage or benefits squeeze as a matter of corporate policy or (worse) as an ambitious ploy by middle management.

A few metals analysis laboratories are engaged in method development that far exceeds the adapting of literature references or industry standard methods to a corporation's immediate needs. The design and construction of process monitoring and control instrumentation, major modifications to commercial instrumentation in order to improve or adapt performance, analytical methods based on fundamental studies, and other investigations may benefit from the highest levels of academic training and experience. However, wise managers know that a challenge accepted with enthusiasm often yields better results than the condescending glance from an ivory tower. Sometimes work of this kind benefits greatly from contractual liaison with a university or a national laboratory.

The work of bachelor and master degree level chemists in a metals analysis laboratory runs the gamut from the most routine to the most esoteric in any and all combinations. Generally, some fluency with computers and with statistics is always required and available. At much more of a premium are good laboratory manipulative skills, which some schools no longer cultivate. A good laboratory manager must walk a tightrope here, as in so many other matters, by keeping his or her professional staff intellectually challenged and technically sharp, while ensuring that everything that needs to be done gets completed on time. To abrogate any part of this responsibility is a disservice to both the chemist and the corporation.

A chemist is a problem-solving resource who will find no nurture in a steady diet of the routine. When he is needed—really needed—will he be ready? Or has prolonged neglect turned a scientist into a technician? And the routine means not only running carbon determinations, it also means administrative paperwork (or keyboard entries) that are more properly handled by nontechnical personnel.

That is not to say that the routine is not the life blood of the metals analysis laboratory. It is. The range might run from 100% routine analysis for a process control laboratory (say, in a basic steel mill) to 85% in a finesse lab in an R & D department. By "routine" we mean in-place methods requiring no special work or development. Of course, these estimates say nothing about the relative complexity of the total task. The control lab may run 10 elements or 50, and the finesse lab may have hundreds of standard operating procedures. Most of this "routine" work is performed by non-degree or associate degree personnel in the control lab environment, but today anywhere from 25 to 75% of this type of work is performed by professional staff in the typical finesse lab.

Finally, we have the sample preparation and clerical duties that are typically assigned to personnel who are not scientifically trained. The sample preparer may be a machinist with training and experience in an industrial machine shop. Special on-the-job training may be required to acquaint this person with chemical terms, acid pickling, and special cleanliness requirements to avoid sample contamination. The clerk should be familiar with computers but will have to be trained on the software used by the laboratory or on the paperwork procedures in use. These individuals should be encouraged to interact freely with the technical staff to ensure the free flow of information in both directions.

It is interesting, even amusing, to read accounts of steel control lab operations in the early part of the twentieth century (try *Technical Analysis of Steel and Steel Works Materials* by Frank T. Sisco, McGraw-Hill, New York, 1923, Chapters IV and V). Every detail of the chemical control operation was worked out in precise detail: the placement of equipment, the space allotted to each man, the material flow, the timing, even the hiring and advancement. It was an assembly line that discouraged even the most minor deviation or change. The chief chemist was an autocrat who presumably ruled with an iron hand over a rather unsophisticated work force.

It is unlikely that any labs that even remotely fit this mold remain today. But there are some lessons of efficiency that can be re-learned from these laboratories of the past. For example, Sisco discusses such topics as optimum sample set size and fostering amicable rivalries, which, properly translated for the present, may still have a place in some high-throughput, operationally lean laboratories of today.

TRAINING

The hiring process ends when an individual with a given set of academic credentials and employment experience starts their first day on the job. We will not address hiring practices except to emphasize that the applicants and the employer have corresponding ethical responsibilities—the first, to represent themselves honestly and honorably, and the second, to represent the available position in the same manner, including an honest assessment of the potential for advancement. Seldom does a new man or woman, however experienced, begin a new job in a metals lab completely prepared to fulfill all the required duties. At the very least there will be a break-in period to familiarize the new analyst with office procedures, sample and alloy coding, and laboratory routine. More often, some form of training will be required before a new person can come fully up to speed in an unfamiliar environment. And inexperienced workers may require a detailed training program extending over many months, or even years, to achieve the level of performance required.

Training is approached somewhat differently in different organizations. Some labs supplement on-the-job training with formal programs in specialized areas such as safety procedures, computer usage, experimental design, statistics, and major analytical disciplines like optical emission and X-ray fluorescence spectrometry. These formal programs can be prepared and conducted by in-house personnel or purchased as a packaged program and conducted by professional training companies either on- or off-site. Many such courses are available on video or audio cassettes and in programmed learning packages for self-study. There are also valuable computer-based tutorial programs.

On-the-job training in metals analysis, as in most professions, is by far the most important form of training. Exactly how it is conducted varies considerably, however. The most formal programs begin with the trainee reading the SOP or other write-up of the method and observing the procedure as conducted by an experienced analyst. This is followed by the trainee conducting the procedure while being observed and guided by the experienced analyst. Finally, the trainee solos (always with the opportunity to seek help and advice).

A blind set of standards is sometimes used to decide if he or she is ready to assume responsibility for the procedure. This decision is sometimes announced in a report or memo that includes the results of the blind standard study. Often the entire process is much less formal with the same intent and result. Sometimes a senior analyst will simply work with a new employee and inform the lab manager when he or she believes that the new hire is ready to assume a new responsibility.

Formalized on-the-job training usually implies that the procedure is one expected to be needed frequently. But what about training for the rare requirement? Most lab managers tend to avoid this issue. If adequate SOPs do not exist, the conventional wisdom is to rely on the ingenuity and experience of employees to quickly pick up what they need to know. In some labs, those procedures that are needed only very infrequently become the exclusive province of the most senior analysts, who may need to employ them two or three times per decade. The problem is that these people eventually retire. In some cases, it may become necessary to call them back from retirement as consultants in order to fulfill a rare request, and, hopefully, to train someone in the procedure.

The alternative is "reinventing the wheel" or perhaps employing different technology. Labs that go to these lengths generally end up with a formal standard operating procedure, even though the requirement may never arise again. The most reasonable course is to maintain an open technical environment among the laboratory workers so that specialized arcane knowledge and skills do not tend to accumulate in isolated individuals but rather become available tools for all to use. Cross training of jobs in the metals analysis lab is one of the most important administrative activities. It allows flexibility in work scheduling for the lab manager, and it provides job enrichment for the employee, who naturally takes pride in mastering a new skill and thus increasing his or her value to the employer.

An active cross-training program should be maintained on an available-time basis for all but the most experienced and thoroughly trained analysts. Moreover, within the constraints of workload demands, a serious effort should be made to maintain and nurture acquired skills by rotating job assignments. It is true that some very talented analysts feel threatened by change. In these cases, the lab manager is tempted to avert his eyes and allow these individuals to continue to excel in their comfortable niche. But such an approach may prove to be a disservice to both the individual and the company. The lab manager has an obligation to concern himself or herself with the career development of each person in their charge. And if this means helping someone to overcome personal inertia or hangups, an effort in this direction should be made.

Sometimes the best start for a cross-training program is formal classroom and laboratory instruction at a university, a technical society sponsored seminar series, or an instrument manufacturer's training facility. This must be soon followed by on-the-job training at work. As with all training, continuity is very important. One of the best ways of ensuring training continuity while minimizing the impact on work efficiency is to assign each trainee one or two 4-h blocks of time each week to learn a new job. The trainer should be expected to report monthly or quarterly on the trainee's progress. It is important that such training remain focused. The trainer should be held accountable to a training plan with milestone points and a projected completion date. Scheduling aids, such as Gantt charting, may be useful here.

A laboratory that sustains a high level of cross training will encounter a number of problems. Chemists become very possessive of equipment at times, especially of complex, finely tuned instruments. There are also personality conflicts and work habit differences. Some individuals may even feel threatened by the prospect of having to show someone else *their* job. The prudent lab manager will persist in his course, however, weathering these storms as they arise. The benefits of such a program far outweigh the difficulties if a laboratory is to build for the future.

There are also what might be termed specialty training requirements that may directly involve the laboratory manager and his staff. Most organizations have some form of safety training program. It may be managed by a corporate safety department, by the chemical hygiene officer, or by the laboratory manager. Safety training often involves regularly scheduled safety meetings in which relevant issues are discussed. It may also involve scheduled "hands-on" training in the use of fire extinguishers, self-contained breathing equipment, and other safety devices, as well as fire drills. In some cases, the chemistry lab is expected to lend its expertise to other departments in a corporation by preparing and conducting seminars and courses on chemical safety.

Sometimes analytical chemistry personnel provide other types of courses—the basics of optical emission or X-ray fluorescence for electricians who must install such equipment and provide routine repair and maintenance on it is one example. A general information course on the chemical analysis of metals is another possibility. Such a program would be of use to all who employ the laboratory's services. Finally, a few companies maintain a formal program that involves moving new-hire professionals between departments to provide them with a perspective on the overall organization before they assume their permanent assignment (Bethlehem Steel's "looper" program was the model for many similar systems).

The metals analysis laboratory is sometimes one step in such a program. During their tour of duty, metallurgists learn the essentials of certain chemical and instrumental procedures, sample requirements, work-flow, and information flow. Most importantly, they learn the services that the metals analysis laboratory can provide for them in their ultimate position with some appreciation for the complexity of and time needed for each task.

MOTIVATION AND EVALUATION

The laboratory that requires constant monitoring and close supervision is usually just getting organized or has been poorly assembled. A well-trained and properly motivated staff should be able to efficiently handle 95% of routine tasks and the majority of special tasks with no input from supervision. Here we will briefly discuss the motivation of personnel and its opposite side—the evaluation of performance. For these two seemingly separate management activities are, in the final analysis, intimately connected. Motivation—to perform faster and more accurately, to be more technically creative, to take initiatives for the benefit of the organization and for personal development—is the input. Evaluation—of job performance, of career development—is the output.

Those who believe that all motivation is self-motivation usually also manage by intimidation. Inevitably, such a course proves counter-productive, engendering bitterness and dissatisfaction in the workforce. People—especially bright, technically creative people—are encouraged by courtesy and familiarity with management. A "we're-in-this-together" attitude is the best approach, not only because it works, but also because it is true.

Remuneration is important, but not of primal importance in motivating most people. If the only communication you have with your boss is a slip of paper with your raise on it, you probably will be a dissatisfied employee. Promotion is a much more important incentive because of its visibility. Many people respond to a title change whether they admit it or not. A wise lab manager will campaign for many layers of titles in his organization and administer promotions fairly and objectively. The most effective motivator for most laboratory workers, however, is probably the proper challenge. A challenge is *proper* if it is based on a *realistic* assessment of the "do-able." Some workers respond best to the efficiency challenge: "Can you have the results by five o'clock?" Others respond best to the technical challenge: "We need a new method for trace levels of lutetium." These are new requests, not demands, it should be made clear. And it is essential that the need be explained in realistic terms.

Nearly everyone responds better to a challenge if someone takes the time to detail out the reason for the need. Praise for an accomplishment or a new level of performance is absolutely essential. Despite protests to the contrary, no one is immune to praise. And no one wants to feel that their best efforts go unnoticed or are taken for granted.

These steps for a lab manager are, of course, only common sense, but they will go a long way to prevent good workers from becoming bad workers. The evaluation process is designed to distinguish the two. It must be based on objective criteria, whatever physical form it takes. Evaluation programs are a matter of corporate policy. Recent trends have been to involve employees in establishing performance criteria for themselves. Participative management of this sort can be very useful if the process involves no management coercion or hidden agendas by the employee. The evaluation process should be an opportunity for frank discussion of work performance and career development. The results should be a thoughtful, honest, and objective assessment, free of "politics" and preconceptions. And the linkage to compensation increases and promotions, as well as to disciplinary action, should always be made clear.

The laboratory manager has an obligation to maintain professionalism and avoid favoritism. He or she functions most effectively as a transmitter, not as an amplifier, of corporate policy. He or she must motivate by example, gratitude, courtesy, challenge, and reward. The worker, too, has an obligation to comport himself or herself ethically and professionally. Within the bounds of this enjoiner, the employee also owes a loyalty to his employer—to support the corporate needs and strategies as they are understood; to protect confidential information; and to return a fair day's work for a fair day's pay.

REFERENCES

Annual Book of ASTM Standards, Vol. 11.01, American Society for Testing and Materials, Philadelphia, 1993, Designation D 3856.

Sisco, F. T., *Technical Analysis of Steel and Steel Works Materials*, McGraw-Hill, New York, 1923.

Afterword

"I do not know whither my pen will run; it will use up all my paper if I don't stop it."

—Regiomontanus (Johan Müller) (1464)

THERE IS A CERTAIN *hubris* involved in a work of this sort. The subject is very broad, indeed, and, despite the extremely valuable suggestions of many reviewers, all the errors and inadequacies have probably not been corrected. For these shortcomings I offer my sincere apologies, and I welcome all comments and suggestions for future revisions of this volume.

In a sense, the preparation of this text has been analogous to the development of an analytical procedure, for there is no analytical method that makes no assumptions, ignores no possible sources of error, or that corrects for every contingency. Science, art, and life always incorporate some elements of compromise. This is probably as it should be since we always seem happier when our goal exceeds our grasp.

There *are* many satisfactions, however. In its most refined forms, the analysis of metals rivals some of the most complex and challenging of industrial assignments. For this, the analyst often receives little credit for success and all the blame for failure. And yet there is a secret perquisite akin to a computer programmer's rush when the last bug has been excised. It is that moment when the replicates check and the validation standards are right on the money—a high that the office-bound executive will never know.

Glossary

The terms listed below are part of the jargon of the metals analyst. They have been used freely in this book, in some cases without definition. As an aid to understanding, definitions are provided here. Some are close to standard English usage; others are from the *patois* of the working analyst.

absorption, n. 1. the incorporation of one substance with another. 2. the assimilation of energy (as, e.g., electromagnetic radiation).

acid anhydride, n. the compound that results from the removal of H_2O from an acid. (Thus, SO_3 is the anhydride of H_2SO_4.)

adsorption, n. a chemical or physical process in which one substance adheres to the surface of another.

aliquant, n (archaic). an irrational fraction of the test solution (e.g., 3 mL out of 100 mL).

aliquot, n. a quantitative portion of the test solution (originally reserved for a rational fraction of the whole).

amphoteric, adj. having both acidic and basic properties, as e.g., the aqueous Al^{3+} ion. (Also known as *amphiprotic.*)

analyte, n. the sample component that is quantified.

azeotrope, n. a constant boiling mixture of two or more liquids.

bandpass, n. the range of electromagnetic wavelengths that can pass a barrier, as, e.g., an optical slit.

BEC, abbrev. for Background Equivalent Concentration, a term often used in plasma optical emission spectrometry to denote apparent analyte concentration due to the sum of background and interferences.

carrier, n. 1. an element intentionally added to a solution to serve as a coprecipitant. 2. in chromatography, the gas or liquid that serves to transport the sample through the column and detector.

chemisorption, n. the absorption of one substance by another involving the formation of chemical bonds.

chromophore, n. a reagent that forms a colored compound or complex with the analyte.

Coanda effect, n. the property of a fluid in motion that causes it to adhere to a surface.

coordination number, n. the number of ligand-forming sites available on a molecule.

coprecipitant, n. an element or species that forms an insoluble compound at the same time and in the same manner as the analyte, serving as an aid to complete analyte precipitation.

critical temperature, n. the maximum temperature at which a gas can be liquified by the application of pressure.

decant, v.t. to pour off a top liquid layer, leaving a solid phase beneath undisturbed.

deliquescent, adj. having the property of certain salts that spontaneously absorb and partially dissolve in atmospheric moisture.

dry filter, v.t. to filter a solution beginning with a dry funnel, filter paper, and collection vessel.

earth acids, n. 1. a loosely used term that refers to certain elements of Groups IV, V, and VI. 2. those elements that tend to precipitate as hydrous oxides in dilute acid solution— commonly, niobium, tantalum, titanium, and tungsten; sometimes also, molybdenum, zirconium, hafnium, and tin.

effluent, n. that which flows out, as, e.g., a gas chromatographic peak or a column chromatographic eluate.

efflorescence, n. salt deposits that remain after liquid evaporation.

eluate, n. the effluent from a chromatographic column that contains a species of interest.

eluent, n. a liquid used to desorb one or more species from a solid phase chromatographic column.

endothermic, adj. taking up heat, as certain chemical reactions.

eutectic, n. a mixed salt or metal alloy composition that is the lowest melting combination of its components.

exothermic, adj. giving off heat, as certain chemical reactions.

external indicator, n. in titration, an endpoint indicator used with a drop of solution removed from the titration vessel (e.g., on a spot plate). This approach is now rarely used.

flashback, n. an accidental explosion of a flame atomic absorption burner.

formal, adj. (abbreviation: F), 1. expressed in concentration units of apparent equivalents per liter (archaic). 2. expressed in half-cell potential units of experimentally measured voltage.

fume, v.t. to heat a solution containing non-gaseous mineral acids to evolve the acid anhydride vapor.

gangue, n. a low value or worthless rock phase accompanying an ore.

hydration, n. the incorporation of water molecules in a chemical species.

hydrolysis, n. 1. any reaction involving water. 2. reaction with water to form an insoluble hydrous oxide precipitate.

hydrophillic, adj. (Lat.: "water-loving") having the property of a substance or chemical group that dissolves in or is wetted by water.

hydrophobic, adj. (Lat.: "water-fearing") having the property of a substance or chemical group that is immiscible in or is not wetted by water.

hygroscopic, adj. absorbing moisture from the atmospheric environment.

IEC, abbrev. for Inter-Element Correction, a term often used in spectrometry to denote an empirically derived constant used to compensate for spectral overlap.

ignite, v.t. to heat, usually at a high temperature.

internal indicator, n. in titration, a substance added to the test solution that changes color at the analyte endpoint.

iodimetric, adj. 1. referring to any redox titration involving direct or indirect oxidation with iodine. 2. (archaic) referring to those redox volumetric procedures involving direct titration with iodine solution.

iodometric, adj. (archaic) referring to those redox volumetric procedures involving indirect titration with iodine generated in situ in the sample solution (typically, by the reaction between iodate and iodide ion).

laboratory sample, n. the sample that is submitted to the laboratory.

leach, v.t. 1. to dissolve a cooled, solidified molten salt fusion in water or other reagents. 2. to remove an analyte selectively by treating a particulate solid test portion with acid or other solvent—a process of questionable rigor, which leaves some portion of the particles undissolved.

lean, adj. in flame atomic absorption, a fuel-deprived/oxidant-abundant gas mixture and the flame it produces.

ligand, n. the metal cations or other species that attach to certain molecules at specific sites to form coordination compounds.

lot, n. a recognized unit of production or shipment expected to have uniform properties.

matrix, n. the composite of sample components that are not being quantified, especially the major components (cf., **analyte**).

meniscus, n. the curved interface of a liquid column with the air above it. Buret and pipet readings are taken tangent to the curve.

molar (abbreviation: *M*), adj. expressed in concentration units of moles per liter or gram-atoms per liter.

normal (abbreviation: *N*), adj. expressed in concentration units of equivalents per liter.

occlude, v.t. to absorb and retain one substance in another, e.g., to coprecipitate.

police, v.t. to remove all traces of a precipitate from a vessel quantitatively, especially with the use of a rubber policeman.

policeman, n. a rubber paddle-like device that is attached to a rod for use in the quantitative removal and transfer of precipitates from a vessel.

pyrophoric, adj. tending to ignite spontaneously, especially by reaction with atmospheric oxygen.

rich, adj. in flame atomic absorption, a fuel-abundant/oxidant-deprived gas mixture and the flame it produces.

sparge, v.t. to bubble a gas through a liquid.

stoichiometric, adj. pertaining to chemical reactions in which reactants combine in predictable whole number proportions.

tare, v.t. to weigh an empty vessel so as to remove its value from a previous or subsequent weighing.

tautomer, n. an isomer of a compound that differs from it in the position of a double bond and a hydrogen atom. Such forms are in equilibrium with each other.

test portion, n. the unit of test sample used in a single analytical determination.

test sample, n. the sample, prepared from the laboratory sample, from which test portions are removed.

titer, n. in titration, an empirically derived factor for converting titrant volume to weight of analyte.

triturate, v.t. to grind to a fine powder, as with a mortar and pestle.

Bibliography

THE FOLLOWING BOOKS ARE recommended for reference and further study. Some have been used in the preparation of this text; most treat specific subject areas in greater detail; all contain much useful information. While this list is not intended to be comprehensive, it may provide a useful starting point for the metals analyst. Hopefully, those titles that are out of print can still be found on library shelves.

GENERAL TOPICS

These references encompass broad subject areas and analytical methodology. In addition to the titles listed below, recent editions of *Lange's Handbook of Chemistry* (McGraw-Hill, New York), the *Handbook of Chemistry and Physics* (CRC Press, Boca Raton, FL), *The Merck Index* (Merck & Co., Inc., Rahway, NJ), and *The MIT Wavelength Tables* (The MIT Press, Cambridge, MA) are highly recommended.

Chemical Methods

Analytical Chemistry of the Manhatten Project, C. J. Rodden, Ed., McGraw-Hill, New York, 1950.

Bock, R., *A Handbook of Decomposition Methods in Analytical Chemistry*, John Wiley & Sons, New York, 1979.

Boltz, D. F., *Colorimetric Determination of Nonmetals*, Interscience Publishers, New York, 1958.

Cheng, K. L., Ueno, K., and Imamura, T., *CRC Handbook of Organic Analytical Reagents*, CRC Press, Boca Raton, FL, 1982.

Dolezal, J., Povondra, P., and Sulcek, Z., *Decomposition Techniques in Inorganic Analysis*, Elsevier, New York, 1966.

Erdey, L., *Gravimetric Analysis*, Parts I-III, G. Svehla, Translator, I. Buzas, Ed., Pergamon Press, New York, 1965.

Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd ed., John Wiley & Sons, New York, 1953.

Johnson, W. C., *Organic Reagents for Metals*, Chemical Publishing Co., New York, 1955.

Kodama, K., *Methods of Quantitative Inorganic Analysis*, Interscience, New York, 1963.

Lundell, G. E. F. and Hoffman, J. I., *Outlines of Methods of Chemical Analysis*, John Wiley & Sons, New York, 1938.

Melnick, L. M., Lewis, L. L., and Holt, B. D., *Determination of Gaseous Elements in Metals*, John Wiley & Sons, New York, 1974.

Morrison, G. H. and Freiser, H., *Solvent Extraction in Analytical Chemistry*, John Wiley & Sons, New York, 1957.

Reagent Chemicals, 6th ed., American Chemical Society, Washington, DC, 1981.

Rieman III, W. and Walton, H. F., *Ion Exchange in Analytical Chemistry*, Pergamon Press, New York, 1970.

Sandell, E. B., *Colorimetric Determination of Traces of Metals*, Interscience Publishers, New York, 1959.

Schilt, A. A., *Perchloric Acid and Perchlorates*, GFS Chemical Co., Columbus, OH, 1979.

Schilt, A. A. and McBride, L., *Standard Substances and Solutions*, GFS Chemical Co., Columbus, OH, 1983.

Shugar, G. J., Shugar, R. A., and Bauman, A. L., *Chemical Technician's Ready Reference Handbook*, McGraw-Hill, New York, 1973.

Standard Methods of Chemical Analysis, Vol. I: *The Elements*, 6th ed., N. H. Furman, Ed., Robert E. Krieger, Malabar, FL, 1962.

Standard Methods of Chemical Analysis, Vol. II, Parts A and B: *Industrial and Natural Products and Non-Instrumental Methods*, F. J. Welcher, Ed., D. Van Nostrand, Princeton, NJ, 1963.

Sulcek, Z. and Povondra, P., *Methods of Decomposition in Inorganic Analysis*, CRC Press, Boca Raton, FL, 1989.

Welcher, F. J., *The Analytical Uses of Ethylenediamine Tetraacetic Acid*, D. Van Nostrand, Princeton, NJ, 1958.

Physical Methods

Bertin, E. P., *Principles and Practice of X-ray Spectrometric Analysis*, 2nd ed., Plenum, New York, 1975.

Birks, L. S., *X-ray Spectrochemical Analysis*, Interscience Publishers, New York, 1969.

Boumans, P. W. J. M., *Line Coincidence Tables for Inductively Coupled Plasma Emission Spectrometry*, Vols. I and II, Pergamon Press, New York, 1980.

Flame Emission and Atomic Absorption, Vols. 1-3, J. A. Dean and T. C. Rains, Eds., Marcel Dekker, New York, 1975.

Fuller, C. W., *Electrothermal Atomization for Atomic Absorption Spectrometry*, The Chemical Society, London, 1977.

Harvey, C. E., *Spectrochemical Procedures*, Applied Research Laboratories, Glendale, CA, 1950.

Inductively Coupled Plasma Emission Spectroscopy, Parts I and II, P. W. J. M. Boumans, Ed., John Wiley & Sons, New York, 1987.

Jenkins, R., Gould, R. W., and Gedcke, D., *Quantitative X-ray Spectrometry*, Marcel Dekker, New York, 1981.

Slickers, K., *Automatic Emission Spectroscopy*, Bruhlsche Universtatsdruckerei, Geissen, Germany, 1980.

Winge, R. K., Fassel, V. A., Peterson, V. J., and Floyd, A., *Inductively Coupled Plasma Emission Spectroscopy*, Elsevier, New York, 1985.

Safety

Bretherick, L., *Handbook of Reactive Chemical Hazards*, Butterworths, London, 1979.

Committee on Hazardous Substances in the Laboratory, Assembly of Mathematical and Physical Sciences, National Research Council, *Prudent Practices for Handling Hazardous Chemicals in Laboratories*, National Academy Press, Washington, DC, 1981.

Committee on Hazardous Substances in the Laboratory, Commission on Physical Sciences, Mathematics, and Resources, National Research Council *Prudent Practices for Disposal of Chemicals from Laboratories*, National Academy Press, Washington, DC, 1983.

Fire Protection Guide on Hazardous Materials, 6th ed., National Fire Protection Association, Boston, 1975.

Guide to Safe Handling of Compressed Gases, Matheson, East Rutherford, NJ, 1982.

Nielsen, M. J., *Solvents and Safety*, General Electric Corp., Schenectady, NY, 1980.

Safe Storage of Laboratory Chemicals, 2nd ed., D. A. Pipitone, Ed., John Wiley & Sons, New York, 1991.

Sax, N. I., *Dangerous Properties of Industrial Materials*, 5th ed., Van Nostrand-Reinhold, New York, 1979.

Young, J. A., Kingsley, W. K., and Wahl, Jr., G. H., *Developing a Chemical Hygiene Plan*, American Chemical Society, Washington, DC, 1990.

Miscellaneous

Barr, W. E. and Anhorn, V. J., *Scientific and Industrial Glass Blowing and Laboratory Techniques*, Instruments Publishing Co., Pittsburgh, 1949.

Caulcutt, R. and Boddy, R., *Statistics for Analytical Chemists*, Chapman and Hall, New York, 1983.

Division for Architectural Studies of the Nuffield Foundation, *The Design of Research Laboratories*, Oxford University Press, London, 1961.

Hammesfahr, J. E. and Strong, C. L., *Creative Glass Blowing—Scientific and Ornamental*, W. H. Freeman & Co., San Francisco, 1968.

Handbook of Analytical Chemistry, L. Meites, Ed., McGraw-Hill, New York, 1963.

Laboratory Planning for Chemistry and Chemical Engineering, H. F. Lewis, Ed., Reinhold, New York, 1962.

Matson, J. V., *Effective Expert Witnessing*, 2nd ed., CRC Press, Boca Raton, FL, 1994.

Metals Handbook, 9th ed., Vol. 10: *Materials Characterization*, American Society for Metals, Metals Park, OH, 1986.

Miller, J. C. and Miller, J. N., *Statistics for Analytical Chemistry*, 2nd ed., John Wiley & Sons, New York, 1988.

Munce, J. F., *Laboratory Planning*, Butterworths, London, 1962.

Pitard, F. F., *Pierre Gy's Sampling Theory and Sampling Practice*, Vols. I and II, CRC Press, Boca Raton, FL, 1989.

Taylor, J. K., *Standard Reference Materials, Handbook for SRM Users*, NIST Special Publication 260-100, National Institute of Standards and Technology, Gaithersburg, MD, 1985.

Zief, M. and Mitchell, J. W., *Contamination Control in Trace Element Analysis*, John Wiley & Sons, New York, 1976.

COMMODITIES

These texts are narrowly focused on analytical chemistry for a specific matrix. Many provide necessary detail that is absent in a more general volume. In addition to these titles, the most recent *Annual Book of ASTM Standards*, Vols. 03.05 and 03.06, and the *Suggested Methods for Analysis of Metals, Ores, and Related Materials* (American Society for Testing and Materials, Philadelphia) are highly recommended.

Iron and Steel

ASTM Chemical and Spectrometric Test Methods for Steel, American Society for Testing and Materials, Philadelphia, 1992.

Donaldson, E. M., *Some Instrumental Methods for the Determination of Minor and Trace Elements in Iron, Steel, and Non-ferrous Metals*, Monograph 884, Energy, Mines, and Resources, Canada, 1982.

Gregory, E. and Stevenson, W. W., *Chemical Analysis of Metals and Alloys*, 2nd ed., Blackie & Son, London, 1942.

Johnson, C. M., *Rapid Methods for the Chemical Analysis of Special Steels, Steel-Making Alloys, and Graphite*, 2nd ed., John Wiley & Sons, New York, 1914.

Lundell, G. E. F., Hoffman, J. I., and Bright, H. A., *Chemical Analysis of Iron and Steel*, John Wiley & Sons, New York, 1931.

Sampling and Analysis of Carbon and Alloy Steels, U.S. Steel Corp., Reinhold, New York, 1938.

Standard Methods of Analysis of Iron, Steel, and Ferroalloys, 4th ed., United Steel Companies, Ltd., Sheffield, UK, Lund, Humphries & Co., London, 1951.

Precious Metals

Beamish, F. E., *The Analytical Chemistry of the Noble Metals*, Pergamon Press, New York, 1966.

Beamish, F. E. and Van Loon, J. C., *Recent Advances in the Analytical Chemistry of the Noble Metals*, Pergamon Press, New York, 1972.

Bugbee, E. E., *A Textbook of Fire Assaying*, 3rd ed., John Wiley & Sons, New York, 1940.

Shepherd, O. C. and Dietrich, W. F., *Fire Assaying*, McGraw-Hill, New York, 1940.

Van Loon, J. C. and Barefoot, R. R., *Determination of Precious Metals, Selected Instrumental Methods*, John Wiley & Sons, New York, 1991.

Aluminum

Churchill, H. V. and Bridges, R. W., *Chemical Analysis of Aluminum*, Aluminum Co. of America, New Kensington, PA, 1935.

Copper

Elwell, W. T. and Scholes, I. R., *Analysis of Copper and Its Alloys*, Pergamon Press, New York, 1967.

Nickel

Lewis, C. L., Ott, W. L., and Sine, N. M., *The Analysis of Nickel*, Pergamon Press, New York, 1966.

Lewis, C. L. and Ott, W. L., *Analytical Chemistry of Nickel*, Pergamon Press, New York, 1970.

Peshkova, V. M. and Savostina, V. M., *Analytical Chemistry of Nickel*, J. Schmorak, Translator, Ann Arbor-Humphrey, Ann Arbor, MI, 1969.

Cobalt

Pyatnitskii, I. V., *Analytical Chemistry of Cobalt*, N. Kaner, Translator, Ann Arbor-Humphrey, Ann Arbor, MI, 1969.

Young, R. S., *The Analytical Chemistry of Cobalt*, Pergamon Press, New York, 1966.

Refractory Metals

Busev, A. I., *Analytical Chemistry of Molybdenum*, J. Schmorak, Translator, Ann Arbor-Humphrey, Ann Arbor, MI, 1969.

Codell, M., *Analytical Chemistry of Titanium Metals and Compounds*, Interscience Publishers, New York, 1959.

Elinson, S. I. and Petrov, K. I., *Analytical Chemistry of Zirconium and Hafnium*, N. Kaner, Translator, Ann Arbor-Humphrey, Ann Arbor, MI, 1965.

Elwell, W. T. and Wood, D. F., *Analysis of the New Metals, Titanium,* *Zirconium, Hafnium, Niobium, Tantalum, Tungsten and Their Alloys*, Pergamon Press, New York, 1966.

Elwell, W. T. and Wood, D. F., *Analytical Chemistry of Molybdenum and Tungsten*, Pergamon Press, New York, 1971.

Gibalo, I. M., *Analytical Chemistry of Niobium and Tantalum*, Ann Arbor-Humphrey, Ann Arbor, MI, 1970.

Moshier, R. W., *Analytical Chemistry of Niobium and Tantalum*, MacMillan-Pergamon, New York, 1964.

Rare Earths

Ryabchikov, D. I. and Ryabukhin, V. A., *Analytical Chemistry of Yttrium and the Lanthanide Elements*, A. Aladjim, Translator, Ann Arbor-Humphrey, Ann Arbor, MI, 1970.

Vickery, R. E., *Analytical Chemistry of the Rare Earths*, Pergamon Press, New York, 1961.

Appendices

Appendix I

A Brief Chronology

NOTE: Texts are date of first publication. Instruments and processes are approximate date of first commercial introduction unless otherwise noted.

METALLURGY	INORGANIC ANALYTICAL CHEMISTRY
14th century BC—Reduction of iron ore	14th century BC—Babylonians use fire assay to test the purity of gold
700 BC—Iron displaces bronze	
14th Century AD—Blast furnace for pig iron	
1530—*De la Pirotechnia* (Vannocio Biringuccio)	
1556—*De re Metallica* (Georg Agricola)	
	1574—*Beschreibung allerfurnemisten mineralischen Ertzt und Bergwercksarten* (Lazarus Ercker)
1600—Wrought iron, cementation process for steel	
1613—Reverberatory furnace	
	1661—*The Sceptical Chymist* (Robert Boyle)
	1681—Phlogiston theory
1709—precoking for ironmaking	
1722—*On the Art of Converting Iron to Steel* (R. A. F. de Réaumur)	
	1729—Bouguer's Law
1734—*Treatise on Copper* (E. Swedenborg)	
1742—Crucible process for steel	
	1768—Lambert's Law
	1774—Joseph Priestley discovers oxygen
1780—Role of carbon in steelmaking discovered	
1784—Puddling process for wrought iron	
1808—Widmanstätten structure discovered in meteorites	1808—*New System of Chemical Philosopy* (John Dalton)
	1811—Avogadro's Theory
	1828—Berzelius: table of atomic weights
	1832—Gay-Lussac titrates silver with chloride
1836—Hot dip galvanizing	
1856—Bessemer (Kelley) process	1856—*Lehrbuch der chemisch-analytischen Titrirmethode* (K. F. Mohr)
	1859—Beer's law
	1862—First issue: *Zeitschrift für Analytische Chemie* (Fresenius)
1863—Sorby: microscopic metallography	
	1871—Mendeleev: periodic table
	1877—synthetic acid/base indicators
1882—Hadfield steel (high manganese)	
1886—Hall/Heroult electrolytic process for aluminum	
	1887—Arrhenius equation
1888—Open hearth (Siemens) process; thermocouple (Le Chatelier)	

METALLURGY	INORGANIC ANALYTICAL CHEMISTRY
1889—Nickel steels	1889—Nerst equation
	1894—*Die wissenschaftlichen Grundlagen der analytischen Chemie* (W. Ostwald)
1898—Tempered high-tungsten tool steel	
1899—Electric arc furnace	
1900—Silicon-iron	
	1903—Conductivity titrations
1904—Vanadium steels	
1905—Monel alloys	
1906—Age hardening of aluminum alloys discovered	
	1909—Sorensen: pH concept
1910—Direct reduction of iron ore (Hoganas process)	
1913—Stainless steel	1913—Moseley: X-ray spectra of the elements
	1914—*Rapid Methods for the Chemical Analysis of Special Steels . . .* (C. M. Johnson)
1915—Nickel-iron high-permeability alloys	
	1920—Glass pH electrodes
1922—Galvannealing process	
	1923—Fluorescent indicators; Debye-Hückel theory; Brønsted theory
	1925—Redox indicators
1926—Type 310 stainless steel	
1927—High-frequency induction furnace; cobalt-iron high-saturation alloys	
1928—Type 304 stainless steel	
	1929—*Applied Inorganic Analysis*, 1st ed. (Hillebrand, Lundell, and Hoffman)
1931—Alnico magnet alloys	1931—*Chemical Analysis of Iron and Steel* (Lundell, Hoffman, and Bright)
1932—Cobalt-base alloys (vitallium)	
1933—High-strength low-alloy steels	
	1934—Ion exchange resins
1935—Electroslag remelting process (developed)	
	1938—Coulometric titrations; *Outlines of Methods of Chemical Analysis* (Lundell and Hoffman)
	1940—UV/visible spectrophotometer; *Fire Assaying* (Shepherd and Dietrich)
	1942—Direct reading spectrophotometer
1943—Precipitation-hardening austenitic stainless steel	
	1944–46—Analytical chemistry of the Manhatten Project (published, 1950)
1945—Vacuum arc remelting furnace	
1949—Sintered aluminum powder	
1950—Type 201 stainless steel; Sendzimer mill	1950—Direct-reading optical emission spectrometer
1951—Titanium alloys	
1952—Basic oxygen process (L-D)	
	1953—*Applied Inorganic Analysis*, 2nd ed. (Hillebrand, Lundell, Bright, and Hoffman)
	1955—X-ray fluorescence spectrometer
1960—Rapid solidification processing; maraging steel; vacuum degassing	1960—Flame atomic absorption spectrophotometer
1962—Basic oxygen process (Stora-Kaldo)	
1963—Continuous casting	

METALLURGY	INORGANIC ANALYTICAL CHEMISTRY
	1964—Ion selective electrodes
	1965—d-c plasma emission spectrometer
	1968—Grimm glow discharge lamp
1970—Electroslag remelting widely used; argon-oxygen decarburization (AOD); rare earth-cobalt magnet alloys	1970—Graphite furnace atomic absorption spectrophotometer
1975—Amorphous metals	1975—ICP emission spectrometer
1978—Metal-matrix composites	
	1979—Dual-beam diode array spectrophotometer
1980—Large-scale ladle refining	1980—Total reflection X-ray fluorescence spectrometer
1982—Single crystal alloys	
	1983—Glow discharge mass spectrometer; single-beam diode array spectrophotometer
1984—Neodymium-iron-boron magnet alloy	1984—ICP-mass spectrometer
1985—Ductile-ordered alloys (intermetallic compounds)	1985—Glow discharge atomic absorption spectrophotometer (solids sampling)
1987—Ion implantation; beam processing; metallurgy of surfaces	1987—Laser ablation-ICP-MS
	1989—Early robot labs for steel control
	1990—Echelle-CID optical emission spectrometer
1992—*Nano-Structured Materials* (journal) begins publication	1992—ICP-OES-MS system

REFERENCES

Beck II, C. M., *Analytical Chemistry*, Vol. 66, No. 4, 1994, pp. 224A–239A.

Beckman, A. O., Gallaway, W. S., Kaye, W., and Ulrich, W. F., *Analytical Chemistry*, Vol. 49, No. 3, pp. 280A–300A.

Cohen, M., *Advancing Materials Research*, P. A. Psaras and H. D. Langford, Eds., National Academy Press, Washington, DC, 1987, pp. 51–110.

Day, R. A. and Underwood, A. L., *Quantitative Analysis*, 2nd ed., Prentice-Hall, Englewood Cliffs, New Jersey, 1967.

Jarnutowski, R., Ferraro, J. R., and Lankin, D. C., *Spectroscopy*, Vol. 7, No. 7, 1992, pp. 22–35.

Johansson, A., *Analytica Chimica Acta*, Vol. 206, 1988, pp. 97–107.

Kallmann, S., *Analytical Chemistry*, Vol. 56, No. 9, 1984, pp. 1020A–1028A.

Kranzberg, M. and Smith, C. S., *Materials Science and Engineering*, Vol. 37, No. 1, 1977, pp. 1–37.

Morrall, F. R., *Wire and Wire Products*, Vol. 1, No. 1, 1971, pp. 52–76.

Smith, C. S., *The Sorby Centenial Symposium on the History of Metallurgy*, Gordon and Breach, New York, 1965.

Wadhams, A. J., *Metals and Alloys*, September 1931, pp. 166–175.

Appendix II

The Chemical Behavior of Analytes

NOTE: Element name and symbol are followed by atomic number, atomic weight, and common aqueous oxidation states with the most stable state underlined. Abbreviations—(s): solution; (p): precipitate; (o): organic; (a): aqueous; RT: room temperature.

Element	Aluminum (Al) 13 26.982 +3	Antimony (Sb) 51 121.757 +3 , +5, −3	Arsenic (As) 33 74.922 +3, +5, −3
Useful precipitations	NaOH: (s) NH_4OH: (p) 8-hydroxyquinoline: (p)	Acid sulfide: (p) Basic sulfide:(s) Accompanies Fe + NH_4OH: (p)	Acid sulfide: (p) Basic sulfide: (s) Accompanies Fe + NH_4OH: (p)
Useful solvent extractions	Ethyl ether/ HCl— from Mo, Fe: (a); 8-hydroxyquinoline-$CHCl_3$/pH 9: (o)	Ethyl acetate/1.5 *M* HCl—Sb(V): (o) TOPO/ MIBK: (o)	
Useful volatilizations/ distillations		SbH_3 (gas at RT) $SbCl_3$ (b.p. approx. 200°C)	AsH_3 (gas at RT) $AsCl_3$ (b.p. 108°C)
Other useful separations/ comments	Amphoteric Mercury cathode: (a)		Highly toxic
Best methods at high concentrations	Volum: Titr. with standard acid after AlF_3 precip. at pH 10 Grav.: 8-hydroxyquinoline	Volum.: Titr. with BrO_3^- Grav.: as Sb_2S_3	Volum.: Titr. with BrO_3^- Grav.: as As metal
Best methods at low concentrations	FAA: 309.3 nm ICP-OES: 369.1 nm (Intf.: Mo) Color: 8-hydroxyquinoline	FAA/GFAA: 217.6 nm ICP-OES: 206.8 nm (Intf.: Cr) Color: Brilliant Green; Rhodamine B	FAA/GFAA: 193.7 nm ICP-OES: 193.7 nm (Intf.: Al) Color: AsH_3 + pyridine + Ag-diethyldithiocarbamate; arsenomolybdate

Element	Barium (Ba) 56 137.327 +2	Beryllium (Be) 4 9.0122 +2	Bismuth (Bi) 83 208.980 +3, (+5)
Useful Precipitations	Sulfate: (p) Chromate: (p)—from Sr Ammonium phosphate (ammoniacal): (p)	NaOH: (s) NH_4OH: (p)	Acid sulfide: (p) Basic sulfide: (p)
Useful Solvent Extractions			Dithizone - $CHCl_3$: (o) TOPO-MIBK: (o)
Useful Volatilizations/ Distillations			
Other Useful Separations/ Comments	Yellow-green flame test Mercury cathode: (a)	Highly toxic Mercury cathode: (a)	
Best Methods at High Concentrations	Volum.: EDTA (ind.: Eriochrome Black T) Grav.: as the sulfate	Grav.: as BeO after NH_4OH precip.; Photoneutron emission	Grav.: as BiOCl or $BiPO_4$
Best Methods at Low Concentrations	FAA: 553.6 nm ICP-OES: 493.4 nm	FAA: 234.9 nm ICP-OES:313.0 nm Color: Aluminon; Fluorimetric: quinalizarin; morin	FAA/GFAA: 223.1 nm (pk. ht. best) ICP-OES: 223.0 nm (Intf.: Cu, Ni) Color: dithizone

Element	Boron (B) 5 10.811 +3	Cadmium (Cd) 48 112.411 +2	Calcium (Ca) 20 40.078 +2
Useful precipitations		Acid sulfide: (p) Basic sulfide: (p) NaOH: (p) NH_4OH: (s)	Oxalate: (p)—from Mg Chromate: (s)—from Ba
Useful solvent extractions	$CHCl_3$—BF_3: (o) (tetraphenyl arsonium chloride; methylene blue)		
Useful volatilizations/ distillations	$B(OCH_3)_3$ (b.p. 68.7°C) BF_3 (b.p. −99°C) BCl_3 (b.p. 12.4° C)		
Other useful separations/ comments	Mercury cathode: (a) Ion exchange (remove other cations and anions) Borates: yellow-green flame test	Highly toxic	Mercury cathode: (a) Yellow-red flame test
Best methods at high concentrations	Volum.: Mannitol complex—titr. released H^+ with standard NaOH. ICP-OES: 249.6 nm (Intf.: Co)	Grav.: as $Cd_2P_2O_7$; as Cd metal (electrolytic) ICP-OES: 226.5 nm	Volum.: EDTA (ind.: Eriochrome Black T) Grav.: as CaC_2O_4
Best methods at low concentrations	ICP-OES: 249.6 nm (Intf.: Co) Color: curcumin (after methyl borate distillation); dianthrimide (direct)	FAA/GFAA: 228.8 nm ICP-OES: 226.5 nm Color: dithizone	FAA: 422.7 nm ICP-OES: 317.9 nm (Intf.: Cr)

Element	Chromium (Cr) 24 51.996 +2, $\underline{+3}$, +6	Cobalt (Co) 27 58.933 $\underline{+2}$, +3	Copper (Cu) 29 63.546 +1, $\underline{+2}$
Useful precipitations	NaOH: Cr(III)(p), Cr(VI)(s) NH_4OH: Cr(III)(p); Cr(VI)(s) Na_2O_2 fusion /H_2O leach: (s) Ag^+,Hg_2^{2+}, Ba^{2+}, Pb^{2+}: (p)—Cr(VI)	ZnO: (s)—from Fe; NaOH:(p) NH_4OH:(s), but Fe and Al coprecip.	Acid sulfide: (p) Basic sulfide: (p) $(NH_4)_2S$: (p) NaOH:(p) NH_4OH: (s)
Useful solvent extractions		Tetraphenylarsonium chloride-$CHCl_3$: (o)	Neocuproine-$CHCl_3$: Cu(I):(o)
Useful volatilizations/ distillations	CrO_2Cl_2 (b.p. 117°C)		
Other useful separations/ comments	Mercury cathode is slow to remove Cr (VI)	Ion Exchange (Cl^-) from Ni, Cu, Fe; Co^{2+}: pink/ Co^{3+}: blue	Ion exchange(Cl^-)— from Ni, Co, Fe
Best methods at high concentrations	Volum.: oxidize with persulfate, titr. with ferrous ammonium sulfate	Volum.: oxidize with excess $K_2Fe(CN)_6$, back titr. with Co^{2+} Grav.: electroplate as metal	Grav.: electrolytic as metal Volum.: iodometric
Best methods at low concentrations	FAA: 357.9 nm ICP-OES: 267.7 nm Color: diphenylcarbazide	FAA: 240.7 (D_2 arc); 242.5 (Zeeman) ICP-OES: 228.6 nm (2nd order) Color: nitroso-R salt, tetraphenyl arsonium chloride	FAA: 324.8 nm ICP-OES: 324.7 nm Color: diethyldithiocarbamate; neocuproine

Element	Gallium (Ga) 31 69.723 +3	Germanium (Ge) 32 72.61 +4	Gold (Au) 79 196.967 +3
Useful precipitations	NH_4OH: (p) NaOH: (s) Cupferron: (p) 8-hydroxyquinoline: (p)	Acid sulfide: (p) Basic sulfide: (s)	$NaNO_2$: (p), as metal from the Pt group Acid sulfide: (p) Basic sulfide: (p)
Useful solvent extractions	Ethyl ether/HCl: Ga(o); Al(a)		Isopropyl ether/dil. HBr: (o) Ethyl ether/HCl: (o)
Useful volatilizations/ distillations		$GeCl_4$ (b.p. 83.1°C)	
Other useful separations/ comments	Metal melts at 29.75°C, boils at 1980°C (widest liquid range)	Highly toxic	Gold salts are strong oxidizing agents ($Au^{3+} + 3e^- \rightarrow Au^o$)
Best methods at high concentrations	Grav.: as Ga_2O_3, after precip. with NH_4OH	Grav.: acid sulfide precip., diss. in NH_4OH, oxidize with H_2O_2, ignite to GeO_2	Fire assay Grav.: as metal. after reduction with oxalic acid, SO_2, $NaNO_2$, or hypophosphorous acid
Best methods at low concentrations	FAA: 287.4 nm ICP-OES: 294.4 nm Color: 8-hydroxyquinoline-$CHCl_3$	FAA: 265.1 nm ICP-OES: 209.4 nm Color: phenylfluorone	FAA: 242.8 nm ICP-OES: 242.8 nm

Element	Hafnium (Hf) 72 178.49 +4	Indium (In) 49 114.818 +3	Iridium (Ir) 77 192.22 $\underline{+3}$, $\underline{+4}$, +6
Useful precipitations	NaOH: (p); NH_4OH: (p); p-Bromomandelic acid: (p); Cupferron: (p); $(NH_4)_2HPO_4$: (p) In all cases Zr accompanies.	NaOH: (p) NH_4OH: (p) Dilute (pH 2-3) acid sulfide: (p) Ammonium oxalate (pH 8): (p)	Acid sulfide: (p) Basic sulfide: (s)
Useful solvent extractions	TOPO-Cyclohexane/HNO_3: (o) Zr accompanies.	Ethyl ether/HCl: (o)	Ethyl ether/HCl: (o)
Useful volatilizations/ distillations			
Other useful separations/ comments	Mercury cathode: (a) Hf and Zr can be separated by ion exchange		$IrCl_4$: dark brown
Best methods at high concentrations	Grav.: as HfO_2 after cupferron precip. and ignition; as HfP_2O_7 after $(NH_4)_2HPO_4$ precip. and ignition (do not overwash).	Grav.: as In_2O_3 after precip. with NH_4OH Volum.: Titr. with $K_2Fe(CN)_6$	Grav.: as metal after precip. with 2-mercaptobenzothiazole followed by reduction in H_2
Best methods at low concentrations	ICP-OES: 273.8 nm (Intf.: Fe, Mo) Color: Pyrocatechol Violet; Xylenol Orange	FAA: 325.6 nm ICP-OES: 451.1 nm Color: dithizone	ICP-OES: 224.3 nm

Element	Iron (Fe) 26 55.847 +2, +3	Lead (Pb) 82 207.2 +2, +4	Magnesium (Mg) 12 24.305 +2
Useful precipitations	NH_4OH: (p) NaOH: (p) Cupferron (as Fe^{3+}): (p)	Acid sulfide: (p) Basic sulfide: (p) Sulfate: (p) Chromate: (p)	$(NH_4)_2HPO_4$: (p) NaOH: (p) 8-Hydroxyquinoline (ammoniacal sol.): (p)
Useful solvent extractions	Cupferron-$CHCl_3$/10% HCl: (o) Ethyl ether/HCl: (o) Acetylacetone-$CHCl_3$ (as Fe^{3+} at pH 1): (o)	Dithizone-$CHCl_3$: (o) TOPO-MIBK: (o)	8-Hydroxyquinoline-$CHCl_3$/ pH 10: (o)
Useful volatilizations/ distillations			
Other useful separations/ comments	Ion exchange (Cl^- system)—from Ni, Co, Cu	Highly toxic	Mercury cathode: (a)
Best methods at high concentrations	Volum.: Reduce with $SnCl_2$, then titr. with $K_2Cr_2O_4$ or Ce (IV)	Grav.: as $PbSO_4$; Electrolytic (as PbO)	Volum.: EDTA (ind.: Eriochrome Black T) Grav.: as $Mg_2P_2O_7$ after precip. with $(NH_4)_2HPO_4$ and ignition.
Best methods at low concentrations	FAA: 248.3 nm ICP-OES: 259.9 nm Color: o-phenanthroline; thiocyanate; 2, 2′-bipyridyl	FAA: 283.3 nm ICP-OES: 220.3 nm (Intf.: Co, Ni, Al) Color: dithizone	FAA: 285.2 nm ICP-OES: 279.0 nm (Intf.: Mn, Cr, Fe)

Element	Manganese (Mn) 25 54.938 +2, +3, +4, +6, +7	Mercury (Hg) 80 200.59 +1, +2	Molybdenum (Mo) 42 95.94 +3, +5, +6
Useful precipitations	Acid sulfide: (s) Basic sulfide: (p) $(NH_4)_2HPO_4$: (p) NaOH: (p)	Acid sulfide: (p) (insol. HNO_3) Basic sulfide: (p)	NH_4OH: (s) NaOH: (s) Acid sulfide: (p) Basic sulfide: (s) α-Benzoinoxime:(p)
Useful solvent extractions			Ethyl ether/HCl: (o)
Useful volatilizations/ distillations		Hg° (b.p. 356.58°C) $HgCl_2$ (b.p. 302°C)	MoO_3 (loss begins at approx. 600°C)
Other useful separations/ comments		Highly toxic Liquid at R.T. Forms amalgams with many metals	Cl^-/F^- System anion exchange—from W, Ti, Nb, Ta, etc.
Best methods at high conc.	Volum.: oxidize with persulfate, titr. with arsenite (visual or potentiometric) Volum.: complex with pyrophosphate, titr. with $KMnO_4$ (potentiometric)	Volum.: Titr. with thiocyanate (Fe^{3+} ind.) Grav.: as HgS after precip. with $(NH_4)_2S$ from basic sol.	Grav.: as MoO_3 after precip with α-Benzoinoxime and ignition Volum.: Pass through Jones reductor, collect in excess std. ferrous ammonium sulfate, titr. excess with $KMnO_4$
Best methods at low concentrations	Color: meta-periodate (as MnO_4^-) FAA: 279.5 nm ICP-OES: 257.6 nm	Cold vapor AA/ FAA/GFAA: 253.7 nm ICP-OES: 435.8 nm	FAA: 313.3 nm ICP-OES: 202.0 nm Color: thiocyanate; toluene-3,4-dithiol

Element	Nickel (Ni) 28 58.693 +2	Niobium (Nb) 41 92.906 (+3), $\underline{+5}$	Osmium (Os) 76 190.23 $\underline{+4}$, +6, +8
Useful precipitations	Dimethylglyoxime: (p) NaOH: (p) NH_4OH: (s) Basic sulfide: (p)— after removal of acid sulfide group	NaOH: (p) NH_4OH: (p) Cupferron: (p)	Acid sulfide: (p) Basic sulfide: (p)
Useful solvent extractions	Dimethylglyoxime-$CHCl_3$: (o)		
Useful volatilizations/ distillations			OsO_4 (b.p. 130°C)
Other useful separations/ comments	Ion Exchange (Cl^- system)— from Fe, Co, Cu	Mercury cathode: (a) Ion exchange (Cl^-/F^- system)— from Mo, Ti, W, Ta, etc.	$OsCl_4$: yellow Highly toxic, especially as oxide vapor
Best methods at high concentrations	Grav.: as dimethylglyoximate Volum.: excess EDTA, back titr. with $Bi(NO_3)_3$	Grav.: as Nb_2O_5 , after precip. with cupferron and ignition	Grav.: as the metal after distillation of OsO_4 and reduction in H_2
Best methods at low concentrations	FAA: 232.0 nm ICP-OES: 231.6 nm (Intf.: Co) Color: Ni-dimethylglyoxime complex (in presence of I_2)	Color: H_2O_2 in conc. H_2SO_4; hydroquinone in conc. H_2SO_4 ICP-OES: 309.4 nm (Intf.: V)	Color: thiourea; ephedrine-HCl ICP-OES: 225.6 nm

Element	Palladium (Pd) 46 106.42 $\underline{+2}$, +4	Phosphorus (P) 15 30.974 +3, $\underline{+5}$, -3	Platinum (Pt) 78 195.08 +2, $\underline{+4}$
Useful precipitations	Dimethylglyoxime: (p)—from weak acid sol. Cupferron: (p)	NaOH: (s) NaOH + Na_2O_2: (s) Accompanies Fe + NH_4OH: (p)	Acid sulfide: (p) Basic sulfide: (s)
Useful solvent extractions	Pd-dimethylglyoximate—$CHCl_3$: (o)	Phosphomolyddate complex— N-butanol: [ox.—yellow: (o); reduced—blue: (a)]	
Useful volatilizations/ distillations		PCl_3 (b.p. 76.1°C)	
Other useful separations/ comments	PdI_2: black precipitate (soluble in NH_4OH + iodide)	Highly toxic volatile compounds Ion exchange (alumina column)	Pt^0 appears as a red colloid if reduced with $SnCl_2$, or as a black precip. if reduced with formaldehyde in basic sol.
Best methods at high concentrations	Grav.: as Pd-dimethylglyoximate from weak acid sol.	Grav.: as $Mg_2P_2O_7$ after precip. with $MgCl_2$ + NH_4OH Volum.: Precip. as ammonium phosphomolybdate, add excess std. NaOH and backtitr. with std. HCl	Grav.: as Pt metal after acid sulfide precip. and ignition to the metal Fire Assay
Best methods at low concentrations	ICP-OES: 229.7 nm FAA: 247.6 nm Color: α-furfuraldoxime; bromide after extraction of phenylthiourea complex	Color: phosphomolybdate; phosphomolybdovanadate ICP-OES: 214.9 nm (Intf.: Cu)	ICP-OES: 214.4 nm FAA: 265.9 nm Color: p - nitrosodimethylaniline

Element	Rhenium (Re) 75 186.207 $\underline{+4}$, +6, $\underline{+7}$	Rhodium (Rh) 45 102.906 $\underline{+3}$, +4	Ruthenium (Ru) 44 101.07 $\underline{+3}$, $\underline{+4}$, +6, +8
Useful precipitations	Nitron: (p) Tetraphenylarsonium chloride: (p) α-Benzoinoxime: (s)— from Mo	Acid sulfide: (p) Basic sulfide: (p)	Acid sulfide: (p) Basic sulfide:(p) Bismuthiol: [Ru(III)] (p)
Useful solvent extractions	Ethyl ether/HCl: (o)		
Useful volatilizations/ distillations	Re_2O_7 (b.p. 362°C)— from Mo		RuO_4 (decomp. 108°C) RuOF (b.p. 184°C)
Other useful separations/ comments	Ion exchange—from Mo Yields yellow-brown precip. with HCl + $SnCl_2$ + KCNS	$RhCl_3$: red Yields yellow color with thiocyanate	Highly toxic volatile compounds $RuCl_3$: dark brown
Best methods at high concentrations	Grav.: as tetraphenylarsonium perrhenate; as nitron perrhenate ICP-OES: 197.3 nm	Grav.: as Rh metal after precip. as the acid sulfide and reduction in H_2 ICP-OES: 233.5 nm	Grav.: as Ru metal after precip. as the acid sulfide and reduction in H_2 ICP-OES: 240.3 nm
Best methods at low concentrations	ICP-OES: 197.3 nm	ICP-OES: 233.5 nm FAA: 343.5 nm Color: sodium hypochlorite	ICP-OES: 240.3 nm FAA: 349.9 nm Color: p-nitrosodimethylanaline; rubeanic acid

Element	Selenium (Se) 34 78.96 $\underline{+4}$, +6, -2	Silicon (Si) 14 28.086 +4	Silver (Ag) 47 107.868 +1
Useful precipitations	Hydrazine sulfate: as the element (p) Accompanies Fe + NH_4OH: (p)	Fuming with $HClO_4$ or H_2SO_4: as silicic acid (p)	NaOH: (p) NH_4OH: (s) Chloride: (p) Acid sulfide: (p) Basic sulfide: (p)
Useful solvent extractions		Silicomolybdate-N-butanol: [ox.: yellow(o); red.: blue (a)]	
Useful volatilizations/ distillations	$SeOCl_2$ (b.p. 175.5°C) H_2Se (gas at R.T.)	SiF_4 (gas at R.T.) H_2SiF_6 (b.p. 300°C)	
Other useful separations/ comments	Highly toxic	Carries down B as it precipitates as SiO_2	Pb^{2+}, Hg_2^{2+}, Tl^+, Bi^{3+}, Sb^{3+} may contaminate AgCl
Best methods at high concentrations	Grav.: as the element, reduced by H_2SO_3, $SnCl_2$, or hydroxylamine-HCl	Grav.: as SiO_2 after dehydration with $HClO_4$ and/ or H_2SO_4	Fire Assay Volum.: titr. with thiocyanate Grav.: as AgCl (protect from light); as metal— electroplate out of oxalate or persulfate sol.
Best methods at low concentrations	ICP-OES: 196.0 nm (Intf.: Al, Co, Fe, Mn, Mg) FAA:/GFAA: 196.0 nm Color: 3, 3′-diaminobenzidine	Color: silicomolybdate FAA: 251.6 nm ICP-OES: 251.6 nm	FAA/GFAA: 328.1 nm ICP-OES: 328.1 nm

Element	Strontium (Sr) 38 87.62 +2	Sulfur (S) 16 32.066 +4, $\underline{+6}$, -2	Tantalum (Ta) 73 180.948 +5
Useful precipitations	Oxalate: (p)—from Ba and Mg NaOH fusion/H_2O leach: (p) Sulfate: (p)	$BaCl_2$: as $BaSO_4$: (p)	Cupferron: (p) NH_4OH: (p) NaOH: (p) Hydrolysis with H_2SO_3 after fuming with $HClO_4$: as hydrous Ta_2O_5: (p)
Useful solvent extractions			
Useful volatilizations/ distillations		H_2S (gas at R.T.)	
Other useful separations/ comments	Mercury cathode: (a) Scarlet red flame test	H_2S is highly toxic Ion exchange (alumina column)	F^-/Cl^- system anion exchange No color with H_2O_2 (unlike Nb in H_2SO_4 and Ti in dilute acid)
Best methods at high concentrations	ICP-OES: 407.8 nm Grav.: as oxalate	Grav.: as $BaSO_4$— first oxidize S with Br_2—reduce Fe before adding $BaCl_2$ Volum.: Ignite in O_2 to SO_2, titr. iodimetrically	Grav.: as Ta_2O_5 after ion exchange separation, cupferron precipitation and ignition
Best methods at low concentrations	FAA: 407.8 nm ICP-OES: 407.8 nm	IR abs: ignite to SO_2 Color: pararosaniline (after ignition to SO_2)	Color: pyrogallol ICP-OES: 240.0 nm (Intf.: Co, Fe)

Element	Tellurium (Te) 52 127.60 $\underline{+4}$, +6, -2	Thallium (Tl) 81 204.383 $\underline{+1}$, +3	Thorium (Th) 90 232.038 +4
Useful precipitations	Hydrazine sulfate or sodium hypophosphite: as the element (p) Accompanies Fe + NH_4OH: (p) Acid sulfide: (p) Basic sulfide: (s)	Chromate: as Tl_2CrO_4: (p); Iodide: as TlI (p); Chloride : as TlCl (p); Weak acid sulfide: (p); Basic sulfide: (p)	NH_4OH: (p) NaOH: (p) Fluoride: (p) Oxalate (pH 3-4): (p) Iodate: (p) $(NH_4)_2HPO_4$: (p)
Useful solvent extractions	TOPO-MIBK: (o)	Ethyl ether/ HCl: (o) TOPO-MIBK: (o)	Cupferron-butyl acetate/ 0.5M H_2SO_4: (o)
Useful volatilizations/ distillations	$TeCl_2$ (b.p. 328°C) H_2Te (gas at R.T.)		
Other useful separations/ comments	Highly toxic; Se can be distilled away from Te (HCl/H_2SO_4)	Highly toxic; Imparts emerald-green color to colorless flame; Fluoresces in NaCl under short λ UV	Highly toxic; H_2O_2: (p) in HNO_3 medium
Best methods at high concentrations	Volum.: titr. with $K_2Cr_2O_7$ (diphenylamine ind.) Grav.: as the element (H_2SO_3 + hydrazine · HCl reduction)	Grav.: as Tl_2CrO_4 from NH_4OH sol. Volum.: Titr. with Ce(IV) ICP-OES: 190.9 nm	Grav.: as ThO_2 after precip. with oxalic acid ICP-OES: 283.7 nm
Best methods at low concentrations	FAA/GFAA: 214.3 nm ICP-OES: 214.3 nm Color: iodine complex	FAA/GFAA: 276.8 nm ICP-OES: 190.9 nm	ICP-OES: 283.7 nm

Element	Tin (Sn) 50 118.710 +2, $\underline{+4}$	Titanium (Ti) 22 47.88 +3, $\underline{+4}$	Tungsten (W) 74 183.84 (+3), $\underline{+6}$
Useful precipitations	Acid sulfide: (p) Basic sulfide: (s) NH_4OH: (p) NaOH: (s) Cupferron: (p)	NH_4OH: (p) NaOH: (p) Cupferron: (p) Na_2CO_3 fusion/ H_2O leach: (p)	NaOH: (s) NH_4OH: (s) Basic sulfide: (s) α-Benzoinoxime (coprecip. with excess Mo only): (p)
Useful solvent extractions	TOPO-MIBK: (o)		
Useful volatilizations/ distillations	$SnCl_4$ (b.p. 114.1°C) SnI_4 (b.p. 364.5°C)		
Other useful separations/ comments	May be electrodeposited from acid oxalate sol.	Ti(III): violet Ti(IV): colorless Phosphate is insoluble	Cinchonine aids precip. of WO_3 by dilute acid hydrolysis
Best methods at high concentrations	Volum.: Titr. with I_2 after reduction with metallic Pb, Ni, Al, or Zn Grav.: as SnO_2 from HNO_3	Grav.: as TiO_2 after ion exchange, NaOH sep. from W, cupferron precip. and ignition Volum.: Jones reductor into excess std. ferric sulfate; back-tir. with $KMnO_4$	Grav.: as WO_3 after ion exchange and precip. with cinchonine (diss. in NaOH and weigh impurities)
Best methods at low concentrations	FAA/GFAA: 286.3 nm ICP-OES: 189.9 nm Color: phenylfluorone	FAA: 364.3 nm ICP-OES: 334.9 nm Color: H_2O_2 in dil. H_2SO_4; diantipyrlmethane; hydroquinone in conc. H_2SO_4	ICP-OES: 207.9 nm (Intf. Al) Color: hydroquinone in conc. H_2SO_4; toluene-3,4-dithiol; thiocyanate

Element	Uranium (U) 92 238.029 +4, $\underline{+6}$	Vanadium (V) 23 50.942 +3, +4, $\underline{+5}$	Zinc (Zn) 30 65.39 +2	Zirconium (Zr) 40 91.224 +4
Useful precipitations	NaOH: (p); NH_4OH: (p)— must be V & CO_2-free; Cupferron: (p); $(NH_4)_2CO_3$: (s) —from Fe, Al & Cr which precip.	Na_2O_2 + NaOH: (s) Cupferron: (p); Accompanies Fe + NH_4OH: (p) NH_4OH: (s) NaOH: (s)	NH_4OH: (s) NaOH: (s) Acid sulfide: (s) Basic sulfide: (p) $(NH_4)_2HPO_4$: (p)	NaOH: (p) NH_4OH: (p) Cupferron: (p) p-Bromomandelic acid: (p) $(NH_4)_2HPO_4$: (p) In all cases Hf accompanies
Useful solvent extractions	Ethyl ether/HNO_3: UO_2^{2+}— (o)		Dithizone-$CHCl_3$	TOPO-Cyclohexane/ HNO_3: (o) Hf accompanies
Useful volatilizations/ distillations				
Other useful separations/comments	Highly toxic U(VI): yellow U(IV): green Forms soluble complex with CO_3^{2-}	Mercury cathode: (a) III: V^{3+} (blue); IV: $V_2O_2^{4+}$ (blue); VO^{2+} (blue); V: VO_2^+ (yellow); VO_3^- (orange)	Amphoteric Whitish flame test	Mercury cathode: (a) Zr and Hf can be separated by ion exchange
Best methods at high concentrations	Grav.: as U_3O_8 after NH_4OH precip. and ignition Volum.: Titr. with $KMnO_4$	Volum.: Oxidize with boiling HNO_3, titr. potentiometrically with ferrous ammonium sulfate	Grav.: as $Zn_2P_2O_7$ after precip. with $(NH_4)_2HPO_4$ and ignition Volum.: Potentiometric titr. with $K_2Fe(CN)_6$	Grav.: as ZrO_2 after cupferron precip. and ignition; as ZrP_2O_7 after $(NH_4)_2HPO_4$ precip. and ignition (do not overwash)
Best methods at low concentrations	ICP-OES: 386.0 nm Fluorimetry: of fused NaF + sample with UV (<300 nm) excitation	FAA: 318.4 nm ICP-OES: 292.4 nm (Intf.: Mo) Color: H_2O_2 (unlike the Ti complex, not bleached by HF)	FAA: 213.9 nm ICP-OES: 213.9 nm (Intf.: Ni, Cu) Color: dithizone Fluorimetry: benzoin complex	ICP-OES: 339.1 nm Color: Pyrocatechol Violet; Xylenol Orange

Appendix IIA

The Alkali Metals

NOTE: The only stable aqueous oxidation state is +1. All can be separated by ion exchange/ ion chromatography. Francium has no stable isotopes.

Element	Useful Precipitations	Useful Solvent Extractions	Flame Test	Flame Emission/ ICP Wavelength	FAA Wavelength	Other Methods
Lithium (Li) 3 6.941			Crimson	460.3 nm	670.8 nm	Fluorimetry: 8-Hydroxyquinoline
Sodium (Na) 11 22.990	Zinc uranyl acetate: (p)		Yellow	330.2 nm (Many intf.)	589.0 nm	
Potassium (K) 19 39.098	ClO_4^-: (p) IO_4^-: (p) $PtCl_6^{2-}$: (p) Tetraphenylborate: (p)	18 - Crown - 6 Ether	Rose/violet	766.5 nm	766.5 nm	X-ray fluorescence: $K\alpha_1 = 3.7412$ Å
Rubidium (Rb) 37 85.468	ClO_4^-: (p) Tetraphenylborate: (p)	18 - Crown - 6 Ether	Rose/violet	420.2 nm	780.0 nm	X-ray fluorescence $K\alpha_1 = 0.9255$ Å
Cesium (Cs) 55 132.905	ClO_4^-: (p) Tartrate: (p) Tetraphenylborate: (p)	21 - Crown - 7 Ether	Red/violet	452.7 nm	852.1 nm	X-ray fluorescence $K\alpha_1 = 0.4003$ Å

Appendix IIB

The Rare Earths

NOTE: This category includes the lanthanides and chemically similar elements. All form precipitates with HF, ammonium oxalate, NH_4OH, NaOH, and Na_2CO_3/H_2O leach. All are left in the aqueous solution on the mercury cathode. All can be separated by ion exchange. All can be determined by X-ray fluorescence. Promethium has been excluded since it has no stable isotopes.

Element	Comments	ICP Wavelength	FAA Wavelength	Other Methods
Scandium (Sc) 21 44.956 +3	Forms complexes more readily than the lanthanides	361.4 nm		
Yttrium (Y) 39 88.906 +3	Properties are half-way between Sc and La	371.0 nm	410.2 nm	
Lanthanum (La) 57 138.906 +3	$I_2 + La(OH)_3$: blue color (no other rare earth exhibits this effect)	398.8 nm		
Cerium (Ce) 58 140.115 $\underline{+3}$, +4	Ce^{3+}: colorless Ce^{4+}: orange-red	418.6 nm (Intf.: Zr)		Volum.: oxidize with persulfate, titr. with ferrous ammonium sulfate (potentiometric)
Praseodymium (Pr) 59 140.908 +3	Pr^{3+}: green	390.8 nm		
Neodymium (Nd) 60 144.24 +3	Nd^{3+}: pale violet	401.2 nm		
Samarium (Sm) 62 150.36 (+2), $\underline{+3}$	Sm^{2+}: red (decomposes in H_2O) Sm^{3+}: yellow	359.3 nm	429.7 nm	
Europium (Eu) 63 151.965 +2, $\underline{+3}$	Eu^{2+}: colorless Eu^{3+}: pale pink	382.0 nm	459.4 nm	Volum.: Jones reductor into excess std. ferric sulfate; back-tir. with $K_2Cr_2O_7$ (Sm and Y *not* reduced and do not interfere)
Gadolinium (Gd) 64 157.25 +3	Gd^{3+}: colorless	342.2 nm		
Terbium (Tb) 65 158.925 +3	Tb^{3+}: pale pink	350.9 nm		
Dysprosium (Dy) 66 162.50 +3	Dy^{3+}: yellow	353.2 nm	421.2 nm	

Element	Comments	ICP Wavelength	FAA Wavelength	Other Methods
Holmium (Ho) 67 164.930 +3	Ho^{3+}: yellow	345.6 nm		
Erbium (Er) 68 167.26 +3	Er^{3+}: pale violet	326.5 nm	400.8 nm	
Thulium (Tm) 69 168.934 +3	Tm^{3+}: green	313.1 nm	371.8 nm	
Ytterbium (Yb) 70 173.04 (+2), $\underline{+3}$	Yb^{2+}: only with applied potential (-1.5V) Yb^{3+}: yellow	328.9 nm	398.8 nm	
Lutetium (Lu) 71 174.967 +3	Lu^{3+}: colorless	261.5 nm		

Subject Index

About the Author

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ISBN 0-8031-2066-4