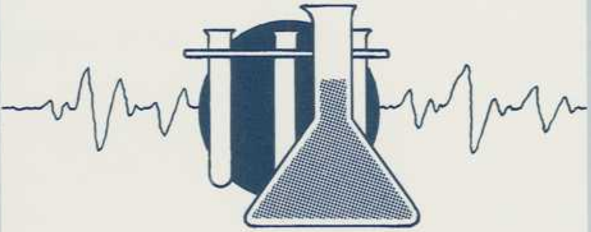
CHEMICAL ANALYSIS OF METALS



Francis T. Coyle, editor

ASTM

STP 944

CHEMICAL ANALYSIS OF METALS

A symposium sponsored by
ASTM Committee E-3 on
Chemical Analysis of Metals
Philadelphia, PA, 19 June 1985

ASTM SPECIAL TECHNICAL PUBLICATION 944
Francis T. Coyle, Cabot Corporation, editor

ASTM Publication Code Number (PCN)
04-944000-01

1916 Race Street, Philadelphia, PA 19103

Library of Congress Cataloging-in-Publication Data

Chemical analysis of metals.

(ASTM special technical publication; 944)
"ASTM publication code number (PCN) 04-944000-01."
Includes bibliographies and index.
1. Metals—Analysis—Congresses. 2. Alloys—
Analysis—Congresses. I. Coyle, Francis T. II. American
Society for Testing and Materials. Committee E-3 on
Chemical Analysis of Metals. III. Series.
QD132.C44 1987 620.1′6 86-32130
ISBN 0-8031-0942-3

Library of Congress Catalog Card Number: 86-32130

Printed in Baltimore, MD
Feb. 1987

Foreword

The symposium, Chemical Analysis of Metals, was presented at Philadelphia, PA, 19 June 1985. The symposium was sponsored by ASTM Committee E-3 on Chemical Analysis of Metals. Francis T. Coyle, Cabot Corporation, served as chairman of the symposium and is editor of the resulting publication.

Related ASTM Publications

Impediments to Analysis, STP 708 (1980), 04-708000-24

Flameless Atomic Absorption Analysis: An Update, STP 618 (1977), 04-618000-39

Metals and Alloys in the Unified Numbering System, Fourth Edition, DS 56c (1986), 05-056003-01

A Note of Appreciation to Reviewers

The quality of the papers that appear in this publication reflects not only the obvious efforts of the authors but also the unheralded, though essential, work of the reviewers. On behalf of ASTM we acknowledge with appreciation their dedication to high professional standards and their sacrifice of time and effort.

ASTM Committee on Publications

ASTM Editorial Staff

Contents

Overview

For years ASTM Committee E-3 on Chemical Analysis of Metals has held symposia relating to the analysis of metals and alloys, which produced special technical publications. Committee E-3 is concerned with the standardization of referee methods relating to chemical analysis of metals and alloys for compliance with compositional specifications. The symposium "Chemical Analysis of Metals" was held in concurrence with the celebration of the 50th anniversary of Committee E-3 and the 25th anniversary of Committee E-16 on the Sampling and Analysis of Metal-Bearing Ores and Related Materials. In constructing the program, suggestions were sought from knowledgeable people engaged in the use and development of standards.

ASTM Committee E-3 has subcommittees, two that deal with the analysis of ferrous and nonferrous materials, thus this symposium provides information relative to the analysis of these materials. For the last 50 years, a great deal of time and effort has been spent developing referee methods for use by producers and users of metals and alloys as well as by commercial, governmental, and educational laboratories. The subject material was organized with a view to expounding upon the state of the art, development and application to future needs. E-3 standard methods are based upon chemical dissolution of the samples followed by detection and measurement of the elements of interest. Pertinent papers on these subjects were selected and reviewed for this volume.

The paper entitled "Rapid Dissolution of Steel Industry Materials for Chemical Analysis" provides information of value to chemists involved in the analysis of these materials. This covers selection of proper acids and fusion media in order that the selected method of analyses can give acceptable results. After proper dissolution, measurements can be made by atomic absorption spectroscopy, photometry, redoximetric, or complexometric titrations. Examples are given which include data on accuracy and precision.

"Novel Sample Preparation Techniques for Chemical Analyses—Microwave and Pressure Dissolution" further addresses the importance of sample dissolution with respect to performing high volume analyses with speed, reliability, and safety. Classical old techniques and new techniques are discussed, and examples achieved through their use are presented.

"The Application of Ion Exchange to the Determination of Impurities in Aluminum and Aluminum Alloys" is a vivid example of work that has led to a new standard, which is incorporated in the revision of aluminum analytical methods. Separation of aluminum has considerably lowered the detection limits for residual metallic impurities.

Classical volumetric analysis is widely used in the laboratory. The presentation on the "Applications of Automatic Titration Instruments in the Specialty Metals Industry" offers valuable hints on how the use of automatic titrators has led to improved precision and performance. The details involving analyses of specialty metals for major levels of various elements such as chromium, vanadium, boron, and cobalt are presented.

The ongoing transition of elemental analyses is demonstrated by the authors in their paper entitled "The Use of Modern Atomic Spectroscopy in an Industrial Laboratory." One laboratory's experience with the DC plasma Echelle Grating Spectrometer is followed through various stages of usage until it is now the mainstay of their analytical methodology.

An interesting excursion through the analytical chemistry of beryllium is portrayed under the title of "General Analytical Chemistry of Beryllium." The reader may follow the evolution of methods from the classical of the past to modern day instrumental techniques. Volumetric, spectrophotometric, gravimetric, and fluorometric methods have largely been replaced by atomic absorption, plasma emission methods. The chemistry of beryllium and its similarity to that of other elements is demonstrated. The evolution of analytical techniques and the descriptions of the methods are of value to all chemists, since this evolution is taking place with respect to elemental analyses of all metals and alloys.

The needs of modern industry have led to automation in almost every aspect of manufacturing. This volume addresses the utilization of laboratory automation in the paper entitled "Microprocessor-Based Determinator Design and the Impact of Future Trends in the Area of Computer-Controlled Automation of Analytical Chemistry Methods." Some examples are discussed at length.

Analytical laboratory information management as used in a metals laboratory is presented under the title "Analytical Laboratory Information Management System (ALIMS)." A computerized system used to control laboratory sample information from log-in to completion is detailed. Instruments controlled by the system include inductively coupled plasma, atomic absorption spectroscopy, optical emission spectroscopy (ICP, AAS, OES) balances, Leeco Diagnostics (LECO) analyzers, spectrophotometers, and automatic titrators.

The utilization of inductively coupled plasma emission spectrometry has progressed at a rapid pace. The author of "Quality Assurance in Metals Analysis Using Inductively Coupled Plasma" describes methods of assessing the quality of analytical results.

"Interdependence of Chemical and Instrumental Methods of Analysis" provides information relating to many aspects of classical and chemical determinations used separately or together. Examples are given in the analysis of precious and base metals.

In summary, this publication has been organized to provide analytical chemists with information relating to all phases of metals analysis starting with the dissolution of samples. The use of various analytical techniques is described followed by examples in the ferrous and nonferrous industries. The evolution of methods and development of standards is based upon the free dissemination to the chemist of information of this type. The contributors to this volume have presented practical working chemists with information that can be utilized further, improved upon, and thus lead to ongoing progress in the analysis of metals. Further work will lead to more standard methods, better quality control, automation, and improved analytical information as required by producers, users, governmental, academic, and accreditation agencies.

Francis T. Coyle

Cabot Corporation, Country Line Rd., Boyertown, PA 19512; symposium chairman and editor.

Om P. Bhargava[1]

Rapid Dissolution of Steel Industry Materials for Chemical Analysis

---

REFERENCE: Bhargava, O. P., "**Rapid Dissolution of Steel Industry Materials for Chemical Analysis,**" *Chemical Analysis of Metals, ASTM STP 944,* Francis T. Coyle, Ed., American Society for Testing and Materials, Philadelphia, 1987, pp. 5-16.

ABSTRACT: This paper describes a rapid, simple technique for solubilizing a wide range of materials such as ores, sinters, slags, ferro-alloys, and other reagents and additives used in integrated steel making operations including environmental dusts and particulate matter. The procedure involves fusion of the specimen with sodium peroxide, or with a sodium peroxide-sodium carbonate mixture in a zirconium or virtreous carbon crucible. Treatment of the fused melt with water and acid yields a clear solution. It avoids the tedious operations involved in solubilizing residues left by other dissolution techniques. Losses of normally volatile elements, such as arsenic, phosphorus, lead, and zinc, do not occur. Solutions obtained by this procedure may be analyzed by a wide range of methods (for example, atomic absorption spectroscopy, photometry, redoximetric, or complexometric titrations or gravimetry) for such elements as aluminum, arsenic, calcium, chromium, copper, iron, magnesium, phosphorus, manganese, lead, titanium, vanadium, and zinc, at concentrations from trace to major. Numerous examples of methods developed employing the dissolution technique are cited, with data on accuracy and precision, to demonstrate the wide range of usefulness of the technique. Combined with automated instrumental methods such as DC and inductively couple plasma spectrometers for solution analysis, this procedure offers an attractive alternative to purely physical methods of analysis, which are often subject to matric interferences.

KEY WORDS: analysis, steels, slags, sinter, iron ore, ferro-alloys, sludge, environmental, industrial hygiene, gravimetry, redoximetric, complexometric, photometric, atomic absorption, fusion, solution, aluminum, arsenic, calcium, chromium, copper, iron, lead, magnesium, manganese, phosphorus, silicon, titanium, vanadium, zinc

Integrated steel production begins with mining operations and moves through an intricate progression of processes in coke ovens, blast furnaces, steelmaking, continuous casting or ingot teeming, conditioning, rolling, annealing, coating operations, and various environmental control facilities. It

---

[1] Supervisor, Corporate Analytical Chemistry, Stelco Inc., P.O. Box 2030, Hamilton, Ontario L8N 3T1, Canada.

involves many diverse materials, such as ores, sinter, limestone, coal, coke, ferro-alloys, process materials, reagents, steelmaking additives as well as various dusts and residues of environmental significance. Some physical methods of analysis are applicable to solids with or without prior initial preparation, such as polishing or briquetting, but the physical form of the specimen does not always lend itself to such techniques, hence dissolution of the specimen, usually into an aqueous medium, is necessary before the determination of elements by more traditional aqueous chemical procedures or instrumental methods such as atomic absorption spectroscopy, DC or IC plasma.

With the wide variety of materials with which the steel chemist is confronted, it is not surprising that a diversity of sample dissolution procedures has evolved, usually based on attack by acidic media chosen in the light of the material to be solubilized and the nature of the subsequent analytical steps. Sometimes this step itself can be time-consuming. Regrettably also, in many instances, some portion of the specimen remains undissolved after the preliminary attack. For completeness, it is not uncommon to filter this out, ignite it, fuse with a suitable flux then dissolve and add this to the initial solution.

Except in cases where the residue can be discarded without affecting the result, there seemed little to be gained from the time and effort expended with such an initial acid attack.

A time-saving procedure that can be applied to almost all materials submitted for aqueous chemical analysis is based upon fusing the entire specimen initially, either with sodium peroxide alone or with a peroxide-sodium carbonate mixed flux, followed by dissolution of the cooled melt in an acid chosen to be compatible with the subsequent analytical procedure.

This basic dissolution technique is effective for a wide range of materials, including iron ore, sinter, ferro-alloys, calcium silicon, stool dressing, slags [*1*], sludge, baghouse and flue dusts, and atmospheric particulates. The solutions of these specimens are suitable for the determination of many elements, such as aluminum, arsenic, calcium, chromium, copper, iron, magnesium, manganese, phosphorus, lead, silicon, titanium, vanadium, and zinc, using a variety of chemical analytical techniques. The following sections illustrate the versatility of this specimen dissolution technique.

Gravimetry

Determination of silicon in ferro-phosphorus by gravimetry is carried out as follows: the specimen (0.3 g) is fused with a mixed flux of 3.5-g sodium peroxide and 0.5-g sodium carbonate in a zirconium crucible. The melt is leached with water and 30-mL hydrochloric acid (HCl) is added. After boiling for 2 to 3 min, the specimen is completely dissolved. The entire operation of fusion and dissolution is complete within 5 min. Perchloric acid is added and after dehydration using the usual hydrogen fluoride-sulfuric acid (HF-H_2SO_4) treatment, pure silica is determined gravimetrically.

Similarly the ASTM Test Method for Silica in Iron Ores and Manganese Ores (E 247 82) for the determination of silica in iron ores and manganese ores by gravimetry incorporates the sodium peroxide fusion in a zirconium crucible.

Redoximetry

Determination of total iron in iron ores, sinters, concentrates, and so forth is accomplished as follows. The specimen (0.3 g) is fused in a zirconium crucible with sodium peroxide (2 g). After leaching, the melt is dissolved in HCl. After boiling for 2 to 3 min, the ferric iron can be reduced by either stannous chloride and mercuric chloride addition [*2*] or by passing through a silver reductor [*3*] (a method free from mercury pollution and vanadium interference) and is then determined redoximetrically with dichromate using diphenylamine indicator. The technique is used in ASTM Test Method for Iron in Iron Ores by the Silver Reduction Trimetric Method (E 1081). This rapid dissolution enables the determination of total iron in ores in three specimens in $^1/_2$ h with results matching the referee method.

The results for International Organization for Standardization, British Chemical Standards, and National Bureau of Standards (ISO, BCS, and NBS) reference standards in Table 1 show that excellent results are obtained on specimens whose compositions vary widely. This dissolution technique is also used for the redoximetric determination of iron in iron ores in ASTM Test Method for Total Iron Ores by the Pollution Free Titrimetric Method (E 1028) using stannous chloride, titanous chloride, and perchloric acid.

Complexometry

This technique was applied to the determination of aluminum in iron ore, sinter [*4*], and so forth in the range of 0.25 to 5.0% aluminum. The specimen

TABLE 1—*Accuracy of total iron determination.*

Ore Specimen	Total Iron, % ISO or Certified	Total Iron, % Determined $\bar{x}$
Sweden-2	64.84	64.84_5
Sweden-7	61.65	61.58_5
Sinter, British BCS 303	35.93	35.83_5
Canadian	65,22	65.15
Minette	31.82	31.75
Philippine iron sand	60.57	60.58
Krivoy rog	47.32	47.31_5
Marcona	62.66	62.56_5
Nimba BCS 175/2	66.1	66.03
Sibley NBS 27e	66.58	66.59_5

(0.1 to 0.3 g) is fused with the mixed flux sodium carbonate (0.5 g) and sodium peroxide (2 g) in a zirconium crucible. After leaching with water the melt is completely solubilized by HCl and aluminum separated as ammonium hydroxide (R_2O_3) precipitates. The R_2O_3 hydroxides are dissolved in HCl. Elements such as iron, titanium, and zirconium, are separated from aluminum by solvent extraction with cupferron and chloroform. After removal of the traces of organic matter from the aqueous phase an excess of ethylenediaminetetraacetate (EDTA) is added and titrated with zinc solution using xylenol orange indicator. Addition of ammonium fluoride releases the EDTA bound to aluminum, which is then titrated with zinc and the percent of aluminum is calculated. The results of our laboratory demonstrate excellent precision and compare well with those of the average values reported in an ISO round-robin test of the method shown in Table 2. A detailed description of this method is given in ASTM Test Method for Aluminum in Iron Ores by Complexometric Titration (E 738).

Photometry

A method for the determination of phosphorus in iron ore, sinters, and so forth, in the range 0.002 to 0.7% phosphorus, was successfully developed [5]. Specimen (0.3 g) is fused with the mixed flux of sodium carbonate (0.5 g) and sodium peroxide (2 g) in a vitreous carbon crucible. The melt is leached with water and solubilized by addition of perchloric acid. The phospho-molybdenum blue complex is formed by the addition of ammonium molybdate-hydrazine sulfate solution, and absorbance is measured at 725 nm. The method is rapid and much simpler than previous methods. Two iron ore specimens were submitted from The South African National Institute of Metallurgy for cooperative tests to establish them as reference materials. Specimens A and B are duplicate bottles of the same material. Precision of the phosphorus results are shown in Table 3.

The accuracy of the method is demonstrated in Table 4. The agreement between the BCS values and those found is quite satisfactory. The method has been further simplified [*6*] by dissolving the melt in hydrochloric acid and

TABLE 2—*Precision of aluminum determination.*

Specimen	ISO[a], %	Determined, %
BCS 303	3.513	3.50, 3.51, 3.49
Minette	2.343	2.35, 2.36, 2.35
Philippine Iron Sand	1.447	1.42, 1.43, 1.44
Krivoj rog	0.665	0.67, 0.67, 0.67
Marcona	0.367	0.36, 0.36, 0.36
BCS 377	1.761	1.77, 1.78, 1.77

[a] $\bar{x}$ ISO round robin.

TABLE 3—*Precision of phosphorus determination.*[a]

Specimen	n	$\bar{x}$	σ
SRM 1A	5	0.043	0.001
SRM 1B	5	0.041	0.001
SRM 2A	5	0.043	0.001
SRM 2B	5	0.044	0.001

[a] n = number of replicates. $\bar{x}$ = mean (percent). σ = standard deviation.

TABLE 4—*Accuracy of phosphorus determination.*

	% Phosphorus	
Specimen	Certified	Determined
BCS 302	0.71	0.73
BCS 303	0.54	0.51, 0.52
BCS 378	0.037	0.039, 0.038
BCS 175/2	0.047	0.048, 0.048

avoiding perchloric acid. This version has been accepted as an ASTM Test Method for Phosphorus in Iron Ores by the Phospho-Molybdenum-Blue Photometric Methods (E 1070) to replace ASTM E 278.

Another photometric example is the determination of titanium [5] in iron ores, and so forth, 0.01 to 0.6% titanium. The specimen (0.5 g) is fused with sodium peroxide (4 g) in a zirconium crucible. The melt is leached with water and dissolved in HCl. After reducing the iron with ascorbic acid and suitable buffering, the titanium-chromotropic complex is developed and measured at 470 nm. The precision of the results on the South African standard reference material (SRM) iron ores is shown in Table 5.

The comparison of results with the certified values of standard reference iron ores and those found by this rapid method is shown in Table 6.

The determination of vanadium [5] in various specimens in the range 0.001

TABLE 5—*Precision of titanium determination.*[a]

Specimen	n	$\bar{x}$	σ
SRM 1A	5	0.033	0.001
SRM 1B	5	0.034	0.001
SRM 2A	5	0.492	0.008
SRM 2B	5	0.479	0.006

[a] n = number of replicates. $\bar{x}$ = mean (percent). σ = standard deviation.

TABLE 6—*Accuracy of titanium determination.*

Specimen	% Titanium	
	Certified	Determined
BCS 302	0.216	0.226. 0.224
BCS 303	0.179	0.187, 0.183
BCS 378	0.070	0.060, 0.070
BCS 175/2	0.057	0.058, 0.056
BCS 377	0.114	0.117, 0.115
Philippine iron sand	3.84	3.91, 3.92

to 0.1% is another application. The specimen (0.5 g) is fused with sodium peroxide (2 g) in a zirconium crucible. The melt is leached with water and then dissolved in sulfuric acid. In an aliquot portion vanadium is oxidized to quinquevalent state with potassium permanganate. The complex of vanadium (V) is formed with N-benzoylphenylhydroxylamine (BPHA) after HCl addition and extracted with chloroform. The absorbance of the complex is measured at 530 nm. The precision of the results on the South African SRM iron ores is shown in Table 7.

Reference standard iron ores with certified values for vanadium could not be found, hence a comparison could not be made.

Determination of arsenic [5] in iron ore, and so forth, in the range 0.0002 to 0.1% arsenic, is considered next. The specimen (0.5 g or 0.05 g) is fused with sodium peroxide (3 g or 1 g) in a zirconium crucible. The melt after leaching with water is dissolved in dilute sulfuric acid. The pentavalent arsenic is reduced to trivalent state in the presence of potassium iodide and stannous chloride.

Zinc is added to liberate arsine, which is absorbed in a solution of silver diethyldithiocarbamate in ephedrine-chloroform solvent (this is found less objectionable than the pyridine solvent used normally). Absorbance of the complex is measured at 540 nm. Table 8 compares the expected values in the ISO iron ore specimens with those found with this rapid procedure.

TABLE 7—*Precision of vanadium determination.*

Specimen	n	$\bar{x}$	σ
SRM[a] 1A	5	0.005	0.001
SRM 1B	5	0.005	0.001
SRM 2A	5	0.050	0.001
SRM 2B	5	0.054	0.001

[a] SRM = standard reference material. n = number of replicates. $\bar{x}$ = mean (percent). σ = standard deviation.

Automated Analysis

Having discussed the application of the rapid dissolution technique to the photometric determination of some elements in a manual mode, further application of this technique as applied to automated analysis will now be illustrated.

The steps in the rapid dissolution of sinter for the automated analysis of major sinter components [7] are as follows. The sinter specimen (0.1 g) is mixed with sodium carbonate (0.5 g) and sodium peroxide (2 g) and fused in a vitreous carbon crucible. The melt is leached with water followed by the addition of 25 mL of (3 + 2) HCl. The solution after boiling somewhat is transferred to a 1 L volumetric flask containing 40 mL of 8% volume/volume (v/v) sulfuric acid and 500 mL of water. This solution is made up to volume with water and is ready for the determination of alumina, silica, calcium oxide, magnesia, and total iron (55 to 66% iron) on the auto analyzer. Calibration of the auto analyzer is established by running accurately analyzed internal reference standards as well as NBS, BCS, ISO standard reference sinters and iron ores.

Vitreous carbon crucibles are expensive but up to 18 fusions can be carried out before a crucible must be discarded. This cost is justified because the interference of zirconium in the determination of calcium is eliminated, which permits photometric determination of all elements of interest in a single specimen solution. If calcium results are not required, zirconium crucibles can be used. For example, iron and silica can be determined by auto analyzer for routine quality control at mine sites, either in place of or as a backup to the much more expensive X-ray spectrometric procedures. Because this work has been presented previously [7], the details of the photometric systems for the determination of sinter components on the auto analyzer, will not be described.

Tables 9 through 13 show the results for alumina, silica, calcium oxide, magnesia, and total iron, respectively.

The second illustration of an auto analyzer procedure is the composite automated determination of major blast-furnace slag components. However, for this application the blast-furnace slag specimen (0.100 g) is sintered with 2-g sodium peroxide in a platinum crucible at 380°C for 1/2 h instead of fusing at a higher temperature.

TABLE 8—*Precision of arsenic determination (ISO iron ores).*

Specimen	Expected, %	Determined, %
76-22	0.0008	0.0006, 0.0005
76-16	0.002	0.0016, 0.0015
76-23	0.02	0.025, 0.025
76-24	0.055	0.063, 0.062

TABLE 9—*Alumina results in sinter.*[a]

Specimen	n	s	% Al_2O_3 $\bar{x}$	% Al_2O_3 Assigned
April 25/71	7	0.027	0.51	0.45
March 18/69	7	0.022	0.68	0.60
May 28/69	7	0.035	0.73	0.70
June 20/64	7	0.029	0.91	0.91
Dec. 11/57	7	0.026	1.12	1.04
Nimba BCS ore	4	0.026	1.05	1.08

n = number of replicates. s = standard deviation. $\bar{x}$ = mean (percent).

TABLE 10—*Silica results in sinter.*[a]

Specimen	n	s	% SiO_2 $\bar{x}$	% SiO_2 Assigned
April 25/71	5	0.023	4.24	4.20
May 28/69	5	0.033	5.06	5.10
March 18/69	5	0.014	5.20	5.20
Jan. 20/64	2	0.030	6.65	6.68
Dec. 11/57	5	0.030	11.43	11.38

[a] n = number of replicates. s = standard deviation. $\bar{x}$ = mean (percent).

TABLE 11—*Calcium oxide results in sinter.*[a]

Specimen	n	s	% CaO $\bar{x}$	% CaO Assigned
Jan. 20/64	7	0.07	6.30	6.17
May 28/69	7	0.08	9.79	9.90
Dec. 11/57	7	0.13	10.95	10.90
March 18/69	7	0.12	11.18	11.26
April 25/71	7	0.08	12.90	12.83

[a] n = number of replicates. s = standard deviation. $\bar{x}$ = mean (percent).

This treatment is followed by the addition of 0.5-g ferrous ammonium sulfate to the hot sinter in the crucible, which is subsequently placed in a hot 600-mL tall-form beaker. Immediate treatment with 50 mL of hot 0.36 *N* HCl and heating results in complete dissolution in 15 s. The solution is then boiled for 30 s. Stabilization of the monomeric silicic acid species is completed by

TABLE 12—*Magnesia results in sinter.*

			% MgO	
Specimen	n	s	$\bar{x}$	Assigned
Jan. 20/64	16	0.08	2.60	2.6
Dec. 11/57	16	0.15	4.42	4.3
April 25/71	16	0.05	5.71	5.7
May 28/69	16	0.08	7.04	7.4
March 18/69	16	0.12	8.06	8.1

[a] n = number of replicates. s = standard deviation. $\bar{x}$ = mean (percent).

TABLE 13—*Total iron results in sinter.*[a]

			% Fe	
Specimen	n	s	$\bar{x}$	Assigned
Dec. 11/57	4	0.07	50.0	50.2
March 18/69	3	0.11	52.1	52.2
May 28/69	3	0.22	54.1	53.7
April 25/71	3	0.19	54.1	53.9
Jan. 20/64	4	0.13	58.7	58.7

[a] n = number of replicates. s = standard deviation. $\bar{x}$ = mean (percent).

immediate addition of 300-mL water containing 40 mL of 8% v/v H_2SO_4. The crucible is then removed and washed, and the contents diluted to 1 L in a volumetric flask. This solution is now ready for the determination of silica (SiO_2, 40%), alumina (Al_2O_3, 10%), calcium oxide (CaO, 40%), and magnesium oxide (MgO, 15%) on the auto analyzer, as colored complexes of molybdenum blue, chromazurol, glyoxylhydroxyanil, and Titan yellow, respectively. These determinations have also been reported [*1*] previously. This scheme should be applicable to the analysis of cement, and so forth.

Table 14 shows results for SiO_2 determination in slag specimens used for internal monitoring and instrumental (X-ray fluorescence) standardization. Comparison is made with the values determined gravimetrically by an umpire method.

The assigned values for alumina obtained using complexometric titrations in conjunction with xylenol orange as the metallorochromic indicator are compared in Table 15 with those obtained by the auto analyzer system. Table 16 shows the results for calcium oxide in slags. The precision is equal or better than that obtained by umpire methods. Results for magnesium oxide determination are shown in Table 17. The agreement is quite acceptable.

TABLE 14—*Precision of silica determination.*[a]

Specimen	Certified, %	n	$\bar{x}$	σ
D-589	35.3	10	35.4	0.3
C-264	33.9	10	34.0	0.4
B-264	34.9	10	34.9	0.3
C-682	36.8	10	36.9	0.3
C-710	39.8	10	39.8	0.4

[a] n = number of replicates. $\bar{x}$ = mean (percent). σ = standard deviation.

TABLE 15—*Precision of alumina determination.*[a]

Specimen	Certified, %	n	$\bar{x}$	σ
D-589	9.0	10	9.0	0.04
C-265	9.8	9	9.8	0.05
B-264	8.8	8	8.7	0.10
C-682	9.3	9	9.3	0.05

[a] n = number of replicates. $\bar{x}$ = mean (percent). σ = standard deviation.

TABLE 16—*Precision of lime determination.*[a]

Specimen	Certified, %	n	$\bar{x}$	σ
D-589	38.5	7	38.6	0.2
C-264	41.9	7	41.8	0.3
B-264	38.4	7	38.4	0.3
C-682	39.2	7	39.2	0.2
C-710	35.7	7	35.8	0.1

[a] n = number of replicates. $\bar{x}$ = mean (percent). σ = standard deviation.

TABLE 17—*Precision of magnesia determination.*[a]

Specimen	Certified, %	n	$\bar{x}$	σ
D-589	14.1	5	14.4	0.3
C-264	11.9	5	12.1	0.3
B-264	15.4	5	15.2	0.3
C-682	12.6	5	12.7	0.2
C-710	11.6	5	11.4	0.2

[a] n = number of replicates. $\bar{x}$ = mean (percent). σ = standard deviation.

TABLE 18—*Parameters for the analysis of major baghouse dust components by atomic absorption.*

Baghouse dust	30% Fe	5% Pb	10% Zn	3% Mn
Resonance line, nm	372.0	283.3	213.9	279.5
Dilution, ppm	100	100	10	100

Atomic Absorption Spectrophotometry AAS

A variety of matrices, such as baghouse dust, stool dressing, sludges, and bonderite can be fused (0.1 g specimen) with sodium peroxide (1 g) in a zirconium crucible. After leaching with water and addition of hydrochloric acid, elements, such as zinc, lead, copper, manganese and iron are determined by AAS after appropriate dilution using air (9 L/min) and acetylene (1.5 L/min) flame. Parameters for the analysis of baghouse dust major components by atomic absorption are as shown in Table 18.

Ferro Alloys Analysis

For the past few years the steelmaking operations have shown a need for strict control of elements such as aluminum and titanium in ferro-alloys and other steelmaking additives. The determination of aluminum and titanium in silicon manganese and ferro manganese in the range of 0.01 to 0.8% aluminum and 0.01 to 0.6% titanium, is accomplished as follows: Specimen (0.2 g) is fused with sodium peroxide (2 g) in a zirconium crucible, and the melt leached with water. After addition of HCl and boiling, the solution is diluted to 100 mL and aspirated on the AAS, using a nitrous-oxide-acetylene flame.

The determination of aluminum and titanium in calcium silicon, ferro silicon, and calsibar is accomplished as above except that sodium carbonate (0.5 g) is added to the flux in order to control the somewhat fiery reaction with sodium peroxide (1.5 g). Resonance line aluminum 309.4 nm and titanium 364.3 nm are used for determining aluminum and titanium, respectively.

Environmental and Industrial Hygiene Analyses

Environmental and industrial hygiene considerations require monitoring of lead and zinc in various materials. Lead (0.01%) and zinc (0.02%) concentrations in stool dressing are determined by fusing the specimen (0.1 g) with 1 g sodium monoxide (Na_2O_2) in zirconium crucible. The melt is leached with water. After addition of HCl and boiling, the solution is made up to 100 mL for analysis by atomic absorption spectroscopy using background correction. Stool dressing has a wide range of composition. Iron varies from 3 to 40%; aluminum from 15 to 80%, zinc from 0.2 to 20%, silicon from 1 to 5%, and elements, such as titanium, nickel, chromium, and calcium, from 0.1 to 0.5%.

Dewatered and dried sludges from blast-furnace spiral heat exchangers are fused and treated in the same way as stool dressing material. Background corrections are necessary for copper, lead, and zinc, in the range 0.04 to 0.1% copper, 0.05 to 0.4% lead, and 0.1 to 4% zinc. The sludge consists of some 65% iron oxide (Fe_2O_3), 15% SiO_2, 2% Al_2O_3, 2% CaO, 1% MgO, and about 5% carbon. It is important to note that with this fusion technique, losses of normally volatile elements, such as arsenic, lead, phosphorus and zinc, do not occur.

Conclusion

In our experience we have found this rapid dissolution to be very useful and provides an important technique that gives a complete solution for analysis of the various materials in the steel industry. Combined with automated instrumental methods such as DC or inductively coupled plasma for solution analysis, this procedure offers an attractive alternative to physical methods of analysis, which often are subject to matrix interferences.

Acknowledgment

Acknowledgment is made to Stelco Inc. for permission to publish this contribution.

References

[*1*] Bhargava, O. P. and Hines, W. G., *American Laboratory,* Dec. 1977.
[*2*] Bhargava, O. P., *Analyst,* Vol. 101, 1976, p. 125.
[*3*] Bhargava, O. P., *Talanta,* Vol. 25, 1978, p. 357.
[*4*] Bhargava, O. P., *Talanta,* Vol. 26, 1979, p. 146; also ISO/DIS 6830.
[*5*] Bhargava, O. P., Gmitro, M., and Hines, W. G., *Talanta,* Vol. 27, 1980, p. 263.
[*6*] Bhargava, O. P. and Gmitro, M., *Talanta,* Vol. 31, 1984, p. 301.
[*7*] Bhargava, O. P. and Hines, W. G., *Analytical Chemistry,* Vol. 48, 1976, p. 1701.

H. Jerome Seim[1]

The Application of Ion Exchange to the Determination of Impurities in Aluminum and Aluminum Alloys

---

REFERENCE: Seim, H. J., "**The Application of Ion Exchange to the Determination of Impurities in Aluminum and Aluminum Alloys,**" *Chemical Analysis of Metals, ASTM STP 944*, Francis T. Coyle, Ed., American Society for Testing and Materials, Philadelphia, 1987, pp. 17-30.

ABSTRACT: Methods are described for the determination of low percentages of gallium and lead in aluminum alloys using anion exchange chromatography and atomic absorption spectrophotometry. Limits of quantitation can be lowered by at least an order of magnitude over methods without preconcentration. With minor modifications, the method for gallium can be applied to the determination of trace levels of iron, zinc, and cadmium. The lower limits of measurement using 1-g samples are 0.001% for both gallium and lead. Using larger sample weights, the limits for both elements can be lowered to at least 0.0005%.

KEY WORDS: aluminum alloys, analyzing, gallium, lead (metal), iron, zinc, anion exchange, hydrochloric acid, atomic absorption

With the advent of new and more sensitive instrumental techniques over the past two decades, the application of separation techniques, such as solvent extraction, ion exchange, or coprecipitation, has lost considerable favor in the chemical analysis of metals. However, there are numerous instances where these instrumental techniques by themselves lack sufficient sensitivity to make specific low-level determinations that are requested of the analyst. Specific examples for aluminum alloys are gallium, lead, bismuth, and tin. These elements exhibit low sensitivity by the most commonly used instrumental techniques of atomic absorption and plasma spectroscopy. These techniques are also limited in that solution concentrations greater than 1 g of aluminum per 100 mL are not too practical.

---

[1] Research associate, Kaiser Aluminum and Chemical Corporation, Center for Technology, P.O. Box 877, Pleasanton, CA 94566.

This paper will describe how anion exchange can be successfully applied to answer some of these requests. Aluminum is an ideal element for using strongly basic anion resins in the chloride form since it is not adsorbed from any concentration of hydrochloric acid. Other common alloying elements that behave similarly include magnesium, chromium(III), nickel, beryllium, the alkali metals, and the alkaline earth metals. Manganese, titanium, and iron(II) are only slightly adsorbed from hydrochloric acid (HCl) solutions approaching 12 *M*. Alloying elements that are adsorbed and can be separated and concentrated from aluminum include bismuth, cadmium, cobalt, copper, iron(III), gallium, lead, tin, vanadium, zinc, and zirconium. Several of these elements exhibit sufficient sensitivity by atomic absorption or plasma spectroscopy so that preconcentration is seldom required.

The technique has been applied to the analysis of a variety of metallic materials including nickel (Ref *1* and ASTM Method for Chemical Analysis of Carbon Steel, Low-Alloy Steel, Silicon Electrical Steel, Ingot Iron, and Wrought Iron [E 350]), manganese [*2*], iron [*3,4*], and the rare earth metals [*5*]. Modifications of the technique have also been applied to the determination of cobalt, nickel, and lead in ASTM Method for the Chemical Analysis of Carbon Steel (E 350) and ASTM Method for Chemical Analysis of Cast Iron (E 351). However, it has received very limited application to aluminum alloys. There is one method in ASTM Method for Chemical Analysis of Aluminum and Aluminum Base Alloys (E 34) in which major amounts of zinc are determined by titration with disodium (ethylenedinitrilo)-tetraacetate (EDTA) after separation by anion exchange. This method is an adaptation of an International Standards Organization (ISO) procedure.

Experimental Procedure

Apparatus

Absorbances were measured with an Instrumentation Laboratory IL 351 Atomic Absorption Spectrophotometer, equipped with a 5-cm nitrous oxide-acetylene burner for gallium determinations and a 10-cm air-acetylene burner for lead determinations. The instrument was equipped with an impact bead nebulizer.

Anion Exchange Columns

Glass columns, provided with a coarse-fitted disk, stopcock, and reagent reservoir, are approximately 20 mm in diameter and 300 mm in length. A self-leveling column design previously described by the author [*5,6*] is shown in Fig. 1. This column works best with 50 to 100 mesh resin because it is easier to control and maintain flow rates.

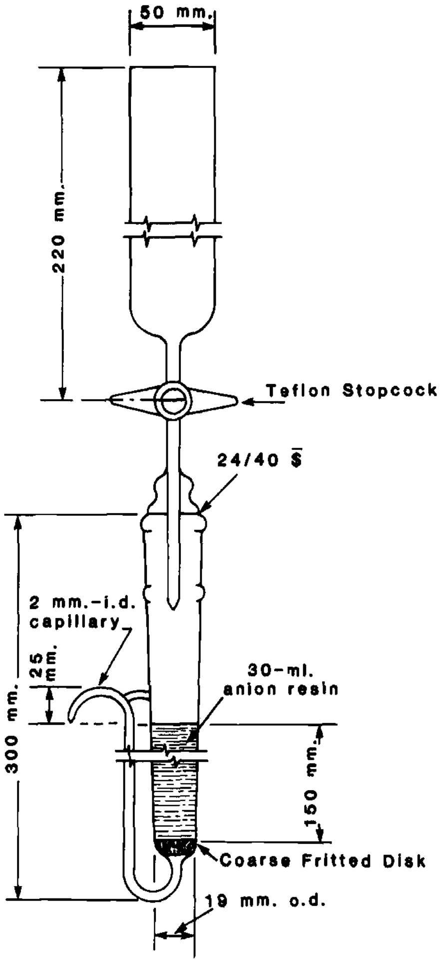


FIG. 1—*Self-leveling ion exchange column.*

Reagents

Standards

Standard solutions (1000 μg/mL) were prepared from gallium and lead (purity: 99.9% minimum) by dissolving in HCl and nitric acid (HNO_3), respectively. Standard solutions (100 μg/mL) were prepared by a one to ten dilution of the high standards.

For the gallium determination, prepare a series of calibration solutions in 100-mL volumetric flasks containing 5 to 50 μg/mL of gallium, 5 mL of potassium chloride (KCl) solution, and 10 mL of 5 *M* HCl. For the lead determination, prepare a similar series in 100-mL volumetric flasks containing 5 to 20 μg/mL of lead and 10 mL of 5 *M* HCl. Use 0.5 *M* HCl as the reference solution.

Hydrochloric Acid, Reagent Grade

Dilute acid concentrations are expressed in molarity for the ion exchange steps to emphasize the need for careful dilution of the concentrated acid, but standardization is not required. The following dilute acids are required: 6 *M* (510-mL HCl/L), 5 *M* (425-mL HCl/L), 4 *M* (340-mL HCl/L), and 1.75 *M* (146-mL HCl/L). The 0.5 *M* HCl is prepared by diluting 125 mL of 4 *M* HCl to 1 L.

Potassium, Chloride Solution, Reagent Grade

A solution containing 40 mg/mL of potassium was prepared by dissolving 76.27 g of KCl in water and diluting to 1 L.

Ion Exchange Resin

Use a strongly basic anion exchange resin of the polystyrene-quaternary ammonium type, chloride form, having a cross linkage of 8% and a 50 to 100 nominal mesh size. Dowex 1-X8 and Bio-Rad AG 1-X8 have been found satisfactory.

Procedures

Preparation of Column

Wash the resin with successive portions of water, decanting to remove "fines" until a clear supernatant solution is obtained. Stir the resin slurry and transfer a sufficient amount of the suspension to the glass column to obtain a resin bed approximately 150 mm high after settling. Using a 19-mm-outside diameter (OD) column, this is about 30 mL of wet resin. Wash the column with 150 mL of 0.5 *M* HCl, followed by 200 mL of water using a flow rate of 3 to 5 mL/min. When not in use, the resin bed in the column should always be covered with water.

Determination of Gallium

Transfer a 1.0-g sample (containing 0.001 to 0.05% gallium), weighed to the nearest milligram, to a 250-mL beaker. Add 10 mL of water and, in small increments, 30 mL of HCl (1 + 1). When the reaction subsides, add 2 mL of

30% hydrogen peroxide (H_2O_2) and boil for 5 min. Filter through a 1.2-μm membrane filter, wash with hot water, and reserve the filtrate. If a black silicon residue is present, transfer the filter and residue to a platinum crucible and carefully ignite at 500 to 600°C until the carbon is removed. After cooling, add 5 mL of hydrofluoric (HF) solution, followed by the dropwise addition of HNO_3 (1 + 1) until a clear solution is obtained. Evaporate to dryness and dissolve the residue in 1 mL of HCl (1 + 1) and a minimum amount of water. Transfer the solution to the reserved filtrate.

Evaporate the filtrate, using a ribbed cover glass, to a volume of about 10 mL or until heavy crystallization occurs. Add 40 mL of 6 *M* HCl and warm to dissolve the salts.

Condition the anion exchange resin by passing 50 mL of 6 *M* HCl through the column at a flow rate of 3 to 5 mL/min. Transfer the cooled test solution to the reservoir of the column and rinse the beaker with small portions of 6 *M* HCl. Pass the solution through the column at a flow rate of 3 to 5 mL/min. Wash the column reservoir three times with 10-mL portions of 6 *M* HCl. Allow each wash to drain before adding the next.

Wash the column with 200 mL of 4 *M* HCl, maintaining the same flow rate. This step separates all the aluminum and those metals not adsorbed by anion exchange, plus most of the copper, if present. Discard the eluate and washes.

Elute the gallium with 150 mL of 0.5 *M* HCl at a flow rate of 3 to 5 mL/min, collecting the eluate in a 250-mL beaker. Cover with a ribbed cover glass and evaporate just to dryness, but do not bake. Dissolve the residue in 1.0 mL of 5 *M* HCl and 2 to 3 mL of water with gentle heating. Cool, add 0.5 mL of KCl solution, and transfer to a 10-mL volumetric flask. Complete the analysis for gallium by comparing the absorbances with those of the appropriate calibration solutions using atomic absorption spectrophotometry.

To prepare for the next determination, wash the column with 200 mL of hot water (boiling) using a flow rate of 5 to 7 mL/min to elute any zinc. Under these conditions, the resin bed will maintain a temperature of about 50°C. If high zinc alloys, such as the 7000 series, have been analyzed, wash with a second 200-mL portion of hot water.

Determination of Lead

Transfer a 1.0-g sample (containing 0.001 to 0.02% lead), weighed to the nearest milligram, to a 250-mL beaker. Add 10 mL of water and, in small increments, 20 mL of 6 *M* HCl. When the reaction subsides, add 2 mL of 30% H_2O_2 and boil for 5 min. Filter through a 1.2-μm membrane filter, wash with hot water, and reserve the filtrate. If a black silicon residue is present, treat the filter and residue as described in the gallium determination. Adjust the volume of the filtrate to 50 mL.

Condition the anion exchange resin by passing 50 mL of 1.75 *M* HCl through the column at a flow rate of 3 to 5 mL/min. Transfer the test solution to the column reservoir and rinse the beaker with small portions of 1.75 M HCl. Pass the solution through the column at a flow rate of 3 to 5 mL/min. Wash the reservoir three times with 15-mL portions of 1.75 M HCl. Allow each wash to drain before adding the next. Discard the eluate.

Elute the lead with 50 mL of 0.5 M HCl, followed by 100 mL of hot water, collecting the eluate in a 250-mL beaker. Cover with a ribbed cover glass and evaporate just to dryness, but do not bake. Dissolve the residue in 1.0 mL of 5 M HCl and 2 to 3 mL of water with gentle heating. Cool and transfer the solution to a 10-mL volumetric flask. Complete the analysis for lead by comparing the absorbances with those of the appropriate calibration solutions using atomic absorption spectrophotometry.

To prepare for the next determination, wash the column with an additional 200 mL of hot water to elute any residual zinc.

Results and Discussion

Resin Behavior

The adsorption behavior of a metal ion in an ion exchange column can be predicted from its volume distribution coefficient D_v

$$D_v = \frac{C_r}{C_s} \tag{1}$$

where

C_r = milliequivalents per millilitre (meq/mL) of the metal ion in the resin and

C_s = meq/mL in the solution.

The most extensive investigation of the anion exchange behavior of the elements in HCl was performed at the Oak Ridge National Laboratory by Kraus and Nelson [7]. Examples of the relationship between Log D_v and the molarity of HCl for elements pertinent to the present study are shown in Fig. 2.

Gallium

Early experiments in our laboratory on the determination of gallium in aluminum alloys used an adsorption step from 6 M HCl to separate the gallium from the aluminum. Elution was performed using 0.8 M HNO_3. Under these conditions, all of the copper, iron, and zinc were eluted with the gallium. Atomic absorption measurements on synthetic solutions showed that iron and zinc had no effect on the gallium response, while copper exhibited an apparent slight enhancement. Based on 1-g samples and the concentration of the

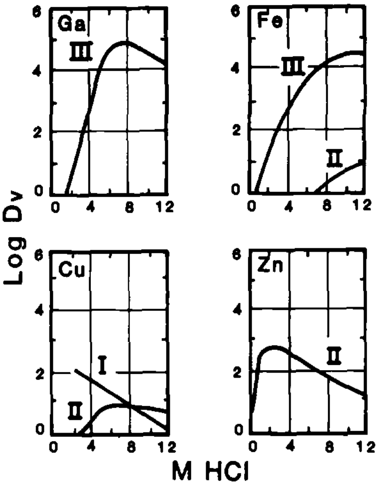


FIG. 2—*Adsorption of gallium, iron, copper, and zinc on strong base ion exchange resin from HCl solutions* [7].

gallium eluate to 10 mL, the extent of this enhancement for various percentages of copper is illustrated in Table 1. From these data, it appears as if the maximum enhancement approaches a maximum of 4%. However, a similar set of tests were performed by W. E. Pilgrim of Reynolds,[2] also shown in Table 1, that exhibited no enhancement.

Nevertheless, it was decided to change the eluting acid to varying concentrations of HCl to learn if a chromatographic separation of gallium from both

TABLE 1—*Effect of copper on the determination of gallium by atomic absorption (based on 1 g of aluminum and a final volume of 10 mL).*

	Gallium Found, %	
Copper, %	Kaiser	Reynolds
0.00	0.0200[a]	0.0158[a]
0.10	0.0203	. . .
0.25	0.0205	. . .
0.50	0.0204	0.0158
0.75	0.0205	. . .
1.00	0.0206	0.0157
2.00	0.0208	0.0155
4.00	0.0208	0.0156

[a] Gallium added, %.

---

[2] Pilgrim, W. E., Reynolds Metals Co., personal communication, 2 July 1981.

the copper and zinc was feasible. Examination of Fig. 2 predicts that elution with 4 *M* HCl should separate most of the copper from the gallium, zinc, and iron. Figure 2 also predicts that the elution with 0.5 *M* HCl should separate the gallium from the zinc and that no separation from iron(III) is possible.

The first series of tests were run on 1-g samples of National Bureau of Standards (NBS) 85b (3.99% copper and 0.019% gallium) using small self-leveling columns. These columns have an OD of 16 mm, a bed depth of 90 mm, and hold approximately 12 mL of resin. The sample solutions were passed through the column in 50 mL of 6 *M* HCl. After washing with small portions of 6 *M* HCl, the copper was eluted with 100 mL of 4 *M* HCl, the gallium with 100 mL of 0.5 *M* HCl, and the zinc with 100 mL of hot water. Flow rates were 3 to 5 mL/min. The gallium fraction was evaporated to dryness and made up to 10 mL in 0.5 *M* HCl for determination by atomic absorption. Results obtained on nine samples of NBS 85b gave an average of 0.0200% gallium, a range of 0.0180 to 0.0215%, with a relative standard deviation (RSD) of 6.5%.

However, when three 1-g samples of NBS 85b were spiked with 70 mg of zinc (which is equivalent to 7.0% zinc), about 5% of the total zinc was eluted with the gallium fraction. In order for a method to be acceptable in ASTM E 34, it must be applicable to alloy compositions given in the scope that includes alloys containing up to 20% copper and 10% zinc. It was believed that the resin capacity would become overloaded when used for such highly alloyed materials, and that larger columns would be necessary. However, the small columns would be applicable for most aluminum alloys.

All remaining experimental work was performed using columns containing 30-mL resin as illustrated in Fig. 1. Eight 1.0-g samples of NBS 85b were analyzed using a procedure similar to that described for the small columns. Exceptions were that the copper was eluted with 200 mL of 4 *M* HCl, the gallium with 150 mL of 0.5 *M* HCl, and the zinc with 200 mL of hot water. Results obtained on NBS 85b and other standard reference materials (SRMs) are summarized in Table 2.

TABLE 2—*Results for gallium on standard reference materials using 30 mL of resin.*

SRM	n	$\bar{X}$, % Ga	σ	RSD, %	Certified, % Ga
NBS 85b	8	0.0205	0.00052	2.5	0.019
BCS 181/2	2	0.0124	0.00007	0.6	(0.01)[a,b]
NBS 87a	3	0.020	0.0007	3.5	0.02
NBS 859	2	0.0212	. . .	. . .	. . .[a]

NOTE: n = number of samples, $\bar{X}$ = sample mean, σ = standard deviation, and RSD = the relative standard deviation.

[a] Not certified.

[b] Reported for information only.

Four of the NBS 85b samples were spiked with 70 mg of zinc, and essentially 100% of the zinc was recovered using a second 200-mL elution with hot water. Two of the samples were spiked with 160 mg of copper to give the equivalent of 20% copper, and the procedure gave a 96% separation of the copper from the gallium fraction.

Precision and Bias

Eight laboratories cooperated in the interlaboratory testing of the gallium method. The samples used were NBS 85b and an Alcoa spectrographic standard certified at 0.005% gallium. Each of the samples was analyzed on three separate days. Repeatability R_1 and reproducibility R_2 were calculated by analysis of variance (ASTM Practices for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals [E 173]) using $M = 1$. The data obtained are summarized in Table 3. Using ASTM guidelines, the lower limit of the method's scope can be established at 0.001% gallium.

No information on the accuracy of the method is available. The accuracy may be judged, however, by comparing the accepted reference values with the corresponding arithmetic average obtained by interlaboratory testing.

Use of an Ionization Suppressant

One of the testing laboratories, Ledoux and Co., modified the procedure by using KCl as an ionization suppressant for gallium. E. W. Hobart[3] reported that he observed an increase in response of about 20%. He also observed a slight enhancement caused by the presence of residual copper, but that this was eliminated using KCl. These observations have been confirmed in our laboratory. Suspecting that the conflicting observations might be the result of different nebulizers, W. E. Pilgrim[4] repeated his study of copper enhancement using both flow spoiler and impact bead nebulizers. He still observed no enhancement with either, but did obtain nearly twice the sensitivity with the

TABLE 3—*Interlaboratory test results of gallium method.*

Test Specimen	Gallium Found, %	Repeatability (R_1, E 173, $M = 1$)	Reproducibility (R_2, E 173, $M = 1$)
Alcoa Standard GA-2-A, 1075 Alloy, (0.005% Ga)	0.0053	0.00049	0.00050
NBS 85b 2024 alloy (0.019% Ga)	0.0204	0.00108	0.00258

---

[3] Hobart, E. W., Ledoux and Co., personal communication, 13 Feb. 1985.

[4] Pilgrim, W. E., Reynolds Metals Co., personal communication, 18 April 1985.

impact bead nebulizer. Nevertheless, because of its apparent advantages, the use of KCl as an ionization suppressant has been incorporated into the revised method. It is my belief that copper acts as a mild ionization suppressant with some instruments and that excess potassium swamps out its effect. It should be emphasized, however, that an ionization suppressant was not used in the interlaboratory test program reported in Table 3.

Lead

The anion exchange separation of lead offers a somewhat different problem because of its low D_v, which reaches a maximum of about 20 between 1.0 and 2.5 *M* HCl, as shown in Fig. 3. It also exhibits no adsorption at HCl concentrations above 6 *M*. Because of the narrow range of lead adsorption, the total chloride concentration becomes very important, as shown in Fig. 4 [*7*]. Although the data shown are for zinc, Kraus et al. [*8*] reported similar behavior for iron, cobalt, and gallium in lithium chloride (LiCl) solutions. In 12 *M* LiCl, the distribution coefficients are more than 100 times greater than in 12 *M* HCl. No additional data have been reported for aluminum chloride ($AlCl_3$) solutions, but it is assumed that its behavior will not be significantly different. One gram of aluminum as $AlCl_3$ in 50 mL of solution has a chloride ion concentration of about 2.2 *M*. If one assumes no loss of chloride during the dissolution of the sample, the simplest way to control the chloride ion concentration is to control the amount of HCl used. For example, if one dissolves a 1-g sample of aluminum alloy in 20 mL of 6 *M* HCl and dilutes to 50 mL, the chloride ion concentration will be 2.4 *M* and no additional acid is needed.

Another factor that must be considered is the volume of solution used. Because of the low D_v, lead is slowly moving down the column during the ion exchange process, and the total volume of solutions used must be kept to a minimum. Therefore, transfer and washings are performed with a minimum volume of 1.75 *M* HCl.

Lead, like zinc, is best eluted with hot water. However, the column still contains appreciable iron after the adsorption step, and the lead is eluted first

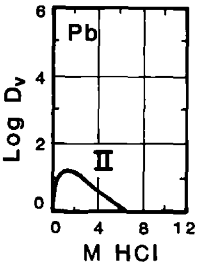


FIG. 3—*Adsorption of lead by anion exchange from HCl solutions* [7].

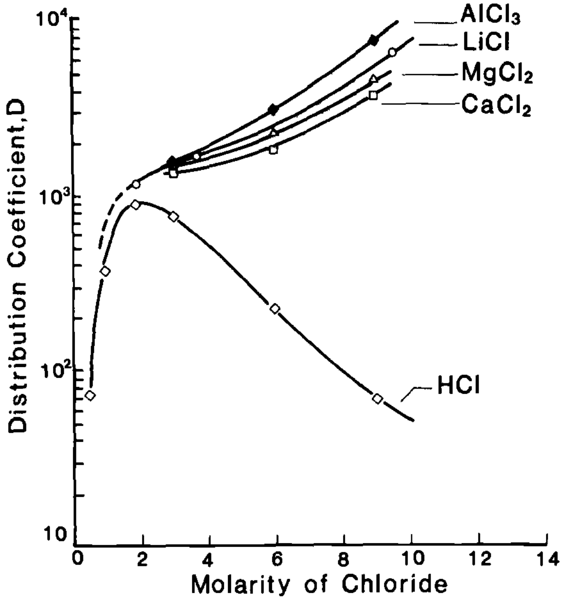


FIG. 4—*Adsorption of Zn(II) from various chloride solutions* [7].

by 50 mL of 0.5 *M* HCl, followed by 100 mL of hot water to prevent precipitation of iron in the resin. Elution with 150 mL of 0.1 *M* HCl gives incomplete recovery of lead.

Preliminary tests of the method were performed using the 30-mL columns on NBS 85b, which is certified at 0.021% lead. The results obtained are summarized in Table 4, and it can be seen that the method gives excellent precision. NBS 85b was also used in the interlaboratory testing of the direct atomic absorption method for lead in ASTM E 34, and the average result obtained was 0.021% lead.

Further testing of the method was done on samples containing lead having percentages at or below the scope of the atomic absorption method, which is 0.01% lead. The only NBS sample that is certified for lead at this level is NBS

TABLE 4—*Comparison of results for lead on NBS 85b (0.021% Pb).*

Method	n	$\bar{X}$, % Pb	Range, % Pb	σ	RSD, %
Proposed	7	0.0215	0.0208 to 0.0218	0.00035	1.6
Certification[a]	8	0.021	0.016 to 0.027	0.0035	16.8

NOTE: n = number of samples, $\bar{X}$ = random variable, σ = standard deviation, and RSD = relative standard deviation.

[a] Electrolytic and dithizone methods.

855, which is a 356 casting alloy. The results obtained are shown in Table 5, and the improvement in precision over the direct atomic absorption method is quite evident.

Finally, a recovery experiment was performed by spiking NBS 859, a 7075 type alloy that has not been certified for lead. Samples were analyzed as is and after adding the equivalent of 0.020% lead. The results shown in Table 6 indicate that the recovery is quite satisfactory.

Application of Larger Sample Weights

In order to learn whether the ion exchange technique might be applicable to the analysis of relatively pure aluminum, a limited number of experiments were conducted using sample weights greater than 1 g. From Fig. 4, it is evident that increasing concentrations of $AlCl_3$ change the distribution coefficients compared to those obtained in HCl solutions.

Early experiments were conducted on the determination of lead to learn if $AlCl_3$ would increase the D_v as it does for zinc and whether its adsorption curve would be shifted toward higher molarities of chloride. These experiments were conducted with 5 g of aluminum in 100 mL of solution, which contributes a chloride concentration of 5.5 *M*. Total chloride concentration was adjusted by varying the amount of excess HCl. When the total chloride was 7.5 *M*, the recovery of lead was about 50% and when it was 6.0 *M*, the recovery was about 80%. These results indicate that $AlCl_3$ does shift the ad-

TABLE 5—*Comparison of results for lead on NBS 855 (0.015 ± 0.005%).*

Method	n	$\bar{X}$, % Pb	Range, % Pb	σ	RSD, %
Proposed	3	0.0107	0.0106 to 0.0107	0.00006	0.6
Certification[a]	4	0.0143	0.010 to 0.02	0.0051	35.4

NOTE: n = number of samples, $\bar{X}$ = sample mean, σ = standard deviation, and RSD = relative standard deviation.

[a] Direct atomic absorption.

TABLE 6—*Test of lead recovery by spiking NBS 859[a] (7075 alloy).*

n	% Pb Added	$\bar{X}$, % Pb	RSD, %	% Recovered
3	none	0.00164	1.1	. . .
3	0.020	0.0214	2.1	99.0

NOTE: n = number of samples, $\bar{X}$ = sample mean, and RSD = relative standard deviation.

[a] Not certified.

sorption curve for lead since lead is not adsorbed from 6 *M* HCl alone, but the increased adsorption is insufficient for analytical purposes.

Dilution of a solution containing 5 g of aluminum to 250 mL with a total chloride concentration of 2.4 *M* also gave a lead recovery of only 80%. This is attributed to the increased volume passing through the column and the relatively low D_v for lead. It has been determined that the maximum sample size that can be analyzed and obtain good recovery of lead is 2.5 g of aluminum in 125 mL of solution having a total chloride concentration of 2.4 *M*.

The application of larger sample sizes to the determination of gallium is not nearly as critical as for lead since its D_v is 10 000 in 12 *M* HCl. Experiments were conducted using 5-g samples of 4-9's aluminum dissolved in 100 mL of 6 *M* HCl. These solutions were spiked with the equivalent of 4.0% copper and 0.2% iron to aid in the visual observation of the ion exchange process. They were run as is and with the addition of the equivalent of 0.001 and 0.005% gallium. The solutions were adjusted to a volume of 100 mL having a total chloride concentration of 6 *M* and ion exchanged. The balance of the procedure was identical to that used for 1-g samples.

The results of these tests, summarized in Table 7, show that one can determine gallium at concentrations below 10 μg/g using 5-g samples. Although one would like to obtain greater recoveries, it is postulated that this might be accomplished by modifying the column size or the elution procedure.

The procedure using 5 g of aluminum in which the chloride concentration as $AlCl_3$ is 5.5 *M* behaves dramatically different from the procedure using 1-g samples in which the chloride concentration as $AlCl_3$ is 2.2 *M*. When using 5-g samples, not only the iron, but also the copper, is held as a tight band at the top of the resin bed. When the reservoir and resin are washed with small portions of 6 *M* HCl, the copper can be observed to move down the resin. In the procedure using 1-g samples, the copper can be observed to move down the resin during the adsorption step, and a small amount is actually eluted with the aluminum fraction. These observations verify that the distribution coefficient for copper is increasing with increased concentrations of $AlCl_3$. Further research is warranted on this system.

TABLE 7—*Test of gallium recovery by spiking 5-g samples of 4-9's aluminum.*

	μg Ga/g Al			
n	Added	$\bar{X}$ Found	RSD, %	% Recovered
2	none	1.7	5.8	. . .
3	10.0	10.8	3.3	92.6
6	50.0	48.6	3.4	94.0

NOTE: *n* = number of samples, $\bar{X}$ = sample mean, and RSD = relative standard deviation.

Summary and Conclusions

Methods have been developed to analyze aluminum alloys using anion exchange chromatography and atomic absorption spectrophotometry to determine gallium as low as 0.002% and lead, 0.001%. The limit of measurement for both elements can be lowered to at least 0.0005% by increasing the sample size and making slight modifications in the procedures.

Although the gallium procedure is rather lengthy in elapsed time, it does not require excessive operator time, and multiple columns can be operated with no difficulty. The lead procedure is considerably shorter.

Using the gallium procedure, trace levels of zinc and cadmium can be determined by concentration of the hot water eluate. Iron can be determined in the gallium fraction if precautions are taken during the evaporation steps to avoid loss of ferric chloride by volatilization. The determination of copper is not recommended since a quantitative separation is not easily obtained in the chloride system.

Certain trace impurities can also be separated from HCl and $AlCl_3$ solutions in the preparation of high-purity reference solutions.

Acknowledgments

I wish to thank A. BeLue and G. M. Calkins for making most of the atomic absorption measurements. Special thanks are also offered to W. E. Pilgrim of Reynolds Metals and E. W. Hobart of Ledoux and Co. for their many helpful suggestions.

References

[*1*] Kirk, M., Perry, E. G., and Arritt, J. M., *Analytica Chimica Acta*, Vol. 80, 1975, pp. 168-169.

[*2*] Korkisch, J., Steffan, I., and Nonaka, J., *Analytica Chimica Acta*, Vol. 109, 1979, pp. 181-185.

[*3*] Shevchuk, I. A., Dovzhenko, N. P., and Kravtsova, Z. N., "Atomic-Absorption Determination of Lead and Bismuth in Steels Using Ion-Exchange Chromatography," *Ukrainskii Khimicheskii Zhurnal (Russian Edition)*, Vol. 47, No. 7, 1981, pp. 773-776.

[*4*] Janousek, I., "Determination of Lead, Bismuth, Zinc, and Cadmium in Technical Iron and Ferromanganese by Atomic Absorption Spectrometry," *Hutnicke Listy*, No. 1, 1974, pp. 53-54.

[*5*] Seim, H. J., Johnson, J. L., Stever, K. R., and Heady, H. H., "Ion Exchange Separation and Instrumental Analysis of Impurities in Rare Earth Metals," U.S. Bureau of Mines Report of Investigations, No. 6097, Reno, NV, 1962.

[*6*] Seim, H. J., Morris, R. J., and Frew, D., *Analytical Chemistry*, Vol. 29, 1957, pp. 443-446.

[*7*] Kraus, K. A. and Nelson, F., "Metal Separations by Anion Exchange," *Symposium on Ion-Exchange and Chromatography in Analytical Chemistry, STP 195*, American Society for Testing and Materials, Philadelphia, 1956, pp. 27-57.

[*8*] Kraus, K. A., Nelson, F., Clough, F. B., and Carlston, R. C., *Journal of the American Chemical Society*, Vol. 77, 1955, p. 1391.

Thomas R. Dulski[1]

Applications of Automatic Titration Instruments in the Specialty Metals Industry

---

REFERENCE: Dulski, T. R., "**Applications of Automatic Titration Instruments in the Specialty Metals Industry,**" *Chemical Analysis of Metals, ASTM STP 944,* Francis T. Coyle, Ed., American Society for Testing and Materials, Philadelphia, 1987, pp. 31-44.

ABSTRACT: Classical volumetric analysis remains an essential service in the modern specialty alloy industry, but now a new generation of automatic titrators can remove some of the tedium and operator-skill factors associated with the technique. Carpenter Technology's recent experience with two commercial instruments is described. The new titrators allow high-speed closed-loop electronic control of potentiometric redox or acid-base titrations in any of several fixed-endpoint or endpoint-seeking modes. Major modification of the basic chemistry of manual titration procedures is usually not required to adapt them to the automatic equipment, although sometimes minor changes are necessary. Applications for the determination of major levels of chromium, vanadium, boron, and cobalt in highly alloyed materials have demonstrated that, when properly configured, these instruments can routinely meet or exceed the performance data for the equivalent manual method in skilled hands.

KEY WORDS: volumetric analysis, titrimetry, specialty alloys, automated analysis, classical chemical analysis, evaluation

Automatic titration equipment has been around for a long time, first as custom-designed configurations to solve particular problems at particular laboratories, and later as general-purpose commercial instruments, which have enjoyed bouts of popularity since their introduction to the marketplace three decades ago [*1-3*]. Early systems were of two types: "dead-stop" buret valves that terminated titrant delivery at a predetermined potentiometric or photometric signal level, and recording titrators that plotted classical step-function titration curves for graphical interpolation of the endpoint. Difficul-

---

[1] Senior chemist, Carpenter Technology Corporation, P.O. Box 662, Research and Development Center, Reading, PA 19603.

ties with the "dead-stop" systems were evident from the start: crude direct-response circuitry frequently led to endpoint overshoot, and time savings were minimal since an operator was required to read and record the buret volume, calculate the results, and often even refill and "rezero" the buret. The recording titrators were potentially more accurate but required near-perfect synchrony between the movement of a strip chart drive and the movement of a piston-driven buret, a goal that was difficult to achieve. In addition, the graphical treatment of the true endpoint proved tedious and led to the incorporation of differential circuitry that allowed the first derivative of the solution potential to be plotted. Endpoint determination then was reduced to counting chart divisions.

Despite a slow but steady evolution of features, automatic titration systems remained more of a laboratory curiosity than a workhorse because they tended to be difficult to set up, finicky to maintain, and offered, at best, only minor efficiency advantages over manual titration methods. Recent advances in digital circuit design and microprocessor technology, however, have changed this picture dramatically. Today, commercially available automatic titration systems can prove to be practical, timesaving, and highly accurate analytical tools. This paper describes our laboratory's experience with this new technology.

Procedure

In 1982 CarTech's Research and Development Center acquired a Fisher Scientific Titrimeter II AEP Automatic Titration System. This is a modular system consisting of an electrometer, a digital buret, a "titrate-demand" module, a recorder, a sample holder, and a programmable calculator. The electrometer is essentially a research grade analog pH/millivolt meter. The digital buret is a piston-driven syringe that dispenses titrant in 0.002-mL increments and displays the dispensed volume to the nearest 0.01 mL. The entire syringe assembly is designed for quick and simple replacement, facilitating changes in titrants and buret capacity. The "titrate demand" module is the central controller for the system; it processes information from the electrometer and feeds back control to the digital buret to achieve an operator-selected endpoint condition. In "fixed endpoint mode" this endpoint condition is an exact electrometer set point, a pH value, for example; while in "automatic endpoint-seeking mode," the endpoint condition is a defined rate of change in the value of the volume-based first derivative of the electrometer output (dE/dV) where E is the electrode potential and V is the volume signal. The recorder is a standard millivolt-range model with paper advance driven by either time or volume signals; its primary utility is in the method development phase when parameters are being optimized. The sample holder is a magnetic stirrer and utility stand for holding the sample beaker, reference, and indicating electrodes, titrant delivery tip, and any needed accessories.

The programmable calculator is the Hewlett-Packard HP-97S, which is linked to the rest of the system through an interface module. Programs stored on magnetic cards handle all or most of the calculations, and a permanent record tape of results is generated.

Today at our laboratory, this system is in routine daily use for the potentiometric determination of chromium by the peroxydisulfate (persulfate) oxidation/ferrous ammonium sulfate reduction method, the potentiometric determination of vanadium by the nitric acid oxidation/ferrous ammonium sulfate reduction method, and the determination of major levels of boron by the ion exchange/mannitol-acid/base titration method.

By 1984 it became clear that the new generation of automatic titrators could be an enormous time and cost saving for volumetric work without any sacrifice in analytical accuracy or precision. Indeed, instrument usage for routine analysis became so high that it began to present scheduling problems and to impede the development of new automated methods. In the fall of 1984 the R&D Center acquired a second, more advanced unit, the Fisher Scientific Computer-Aided Titrimeter (or CAT).

Unlike the first system, the CAT is unitized and "user-friendly." Two Z80 microprocessors interactively control titrations and calculate results. Extensive read-only memory (ROM) areas are devoted to "Help" messages and default method parameters while user-definable memory provides space for up to 25 "customized" methods. A thermal printer is used to document sample identity, method parameters, and results; it also provides graphical presentation of the titration in a variety of formats, when required. Two light emitting diode (LED) "windows" are used to guide a menu-driven dialogue: one to ask questions and the other to display the operator's keypad-selected response. In addition to the "fixed endpoint" and first derivative endpoint-seeking modes of the first instrument, several unique options are available to aid in special situations, such as when reaction kinetics are slow or electrode response is sluggish.

A method for the determination of cobalt has been developed for the CAT. It is based on the oxidation of cobaltous ion with excess ferricyanide in ammoniacal citrate solution and back-titration with cobaltous nitrate.

Experimental Work

Chromium

The adaption of the classical potentiometric determination of chromium to automatic control involved some initial problems that were solved by minor modifications of the chemistry. The classical approach is based on oxidation of chromium to the (+VI) oxidation state by boiling the dissolved sample with ammonium persulfate and silver nitrate. A measured excess of ferrous ammonium sulfate reduces the chromium, and the excess reductant is determined by potentiometric titration with potassium dichromate solution or, alternately, by visual titration with potassium permanganate solution. The basic method is generally applicable over the range 0.1 to 100% chromium and has been in use for nearly 100 years [*4,5*].

It was believed possible to eliminate the back-titration in the automated version of the method by titrating to a dead stop with ferrous ammonium sulfate solution. As with the potassium dichromate back-titration, a small correction for vanadium in the sample would be required. A platinum indicating electrode and a saturated calomel reference electrode were used, and the system was configured in endpoint-seeking mode, since it was known that the absolute endpoint potential varied somewhat with the ionic background of the sample. In this mode the system continuously calculates and monitors the value of (dE/dV), while controlling the rate of titrant addition by reference to the time-based derivative (dE/dt) where E is the electrode potential and t is the time signal. The value of the (dE/dt) function is an operator-selected parameter that the system attempts to meet, but not exceed; the value of the (dE/dV) function, on the other hand, reflects only the reaction chemistry, and its maximum value occurs at the true endpoint.

The shape of the (dE/dV) titration curve for chromium before the endpoint deflection was found to be markedly affected by the ionic matrix of the sample. Iron-base and nickel-base alloy samples, for example, differ greatly in the extent to which the endpoint approach is bowed; similar differences occur between stainless and low alloy samples. Such effects become significant when the (dE/dV) function is drifting in a negative direction at the moment of endpoint takeoff.

Figure 1 illustrates the drift problem and the solution that was found. If the stainless standard (National Bureau of Standards [NBS] SRM367—AISI 446) in Fig. 1A had been used to establish a titer, then the low alloy standard (NBS SRM106a—Nitroalloy G) will show erroneously high results caused by endpoint overshoot. The fact that this occurs despite the use of the (dE/dV) function, which is supposed to be isolated from titration rate effects, suggests that some sort of data handling problem may be involved. The problem was solved by adopting a technique already employed in some versions of the procedure, (for example, ASTM Methods for Chemical Analysis of Carbon Steel, Low-Alloy Steel, Silicon Electrical Steel, Ingot Iron, and Wrought Iron [E 350]), namely, adding phosphoric acid and reducing the amount of sulfuric acid in all samples. The phosphoric acid complexed iron in the samples and also adjusted the formal potential of the endpoint. Reducing the amount of sulfuric acid kept the total acidity in the optimal range. The Fig. 1B curves are the result of these changes. Note that the (dE/dV) function is now drifting in a positive direction at the moment of endpoint deflection for both samples. An SRM367 titer will now yield the correct result for SRM106a.

An added advantage to the modified chromium procedure is that when dissolved samples must be taken to fumes (to destroy carbides, for example) the

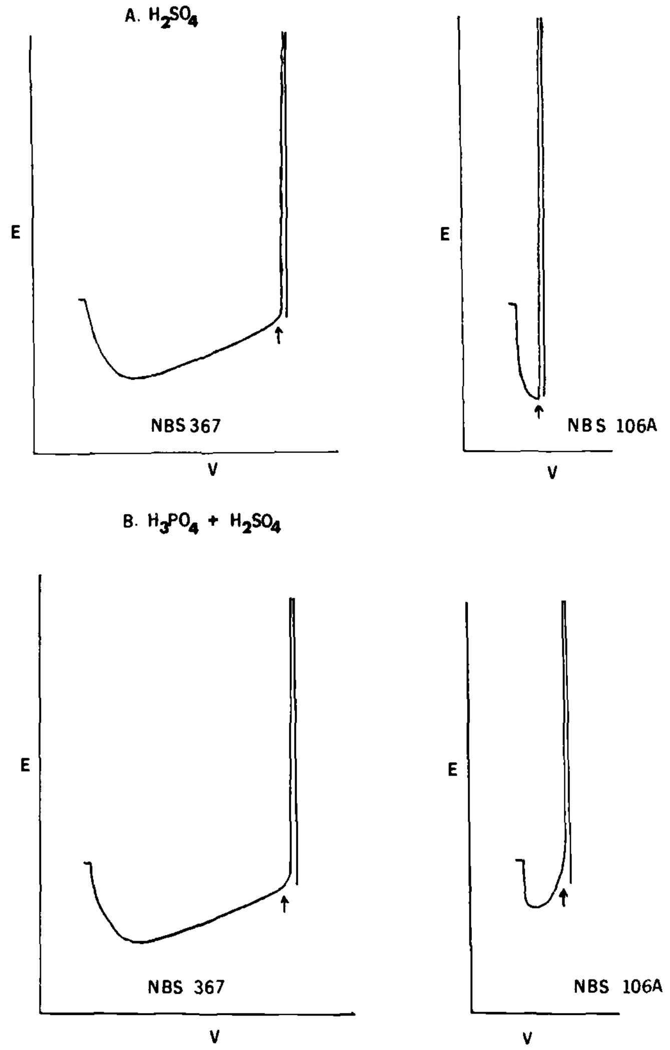


FIG. 1—*Effect of acids on titration curves for chromium (*E *represents the electrode potential and* V *represents the volume signal, that is, the volume of titrant dispensed).*

presence of phosphoric acid will hold hydrolyzable elements such as tungsten, niobium, and tantalum in solution. The danger of sample loss caused by spattering is thus greatly reduced.

Table 1 lists some automated chromium results derived from primary standards, and Table 2 summarizes the precision obtained. The pooled data show a standard deviation (1-sigma) of ±0.02% over a data set that covers the range 1 to 24% chromium. Table 3 illustrates the statistical treatment used to obtain an estimate of precision for all the methods investigated in this paper.

TABLE 1—*Chromium results from primary standards.*

Standard	Alloy Type	Certified % Cr[a]	Found % Cr
NBS 139a	AISI 8640 low alloy	0.486	0.490, 0.503
NBS 163	low alloy—Nitroalloy G	0.982	0.992, 1.00, 1.00
NBS 106a	low alloy—Nitroalloy G	1.15	1.16, 1.16, 1.16, 1.16
NBS 106b	Nitralloy G low alloy	1.18	1.20, 1.21, 1.20, 1.21
NBS 36b	low alloy	(2.17)	2.19, 2.19
NBS 134a	8Mo/2W/1V high speed	3.67	3.70, 3.70
NBS 153a	M34 high speed	3.72	3.98, 3.90
NBS 132b	M2 high speed	4.38	4.39, 4.38
NBS 135	medium alloy	5.15	5.14
NBS 73c	420 stainless	12.82	12.84, 12.82, 12.83, 12.86, 12.82, 12.84, 12.81
NBS 344	PH-type stainless	14.95	15.05, 15.02
NBS 345	17-4 PH stainless	16.04	16.07, 16.07, 16.10, 16.07, 16.05, 16.01
NBS 121c	321 stainless	(17.58)	17.61, 17.65, 17.60
NBS 160b	317 stainless	(18.4_5)	18.41, 18.38, 18.50
NBS 101f	304L stainless	18.49	18.54, 18.59, 18.50
NBS 349	Waspaloy	(19.50)	19.48
NBS 169	Nichrome-type	20.26	20.23, 20.23, 20.25, 20.24, 20.26, 20.28, 20.22, 20.27
NBS 367	446 stainless	24.19	24.24, 24.19, 24.26, 24.23, 24.21
NBS 64a[b]	high carbon ferrochromium	66.01	66.03
NBS 196	low carbon ferrochromium	(70.87)	71.03, 71.06

[a] Values in parentheses are provisional.
[b] Fused in $Na_2O_2 + Na_2CO_3$.

TABLE 2—*Summary of precision data for chromium.*

Standard	Certified % Cr	Replicates	Average % Cr Found	1-sigma	RSD, %
NBS 106a	1.15	4	1.16	0	0
NBS 106b	1.18	4	1.20	±0.006	0.50
NBS 73c	12.82	7	12.83	±0.017	0.13
NBS 345	16.04	6	16.06	±0.030	0.19
NBS 169	20.26	8	20.25	±0.021	0.10
NBS 367	24.19	5	24.23	±0.027	0.11

NOTE: pooled variance = 0.000 467, pooled standard deviation = ±0.022, and total number of degrees of freedom = 27. RSD = relative standard deviation.

Vanadium

The automation of the classical potentiometric vanadium method also presented problems; in this case, however, they were anticipated. The classical method used involves boiling the dissolved sample with nitric acid to oxidize vanadium to the (+V) oxidation state, reduction with a measured excess of ferrous ammonium sulfate, and a potentiometric back-titration [*6*]. A plati-

TABLE 3—*Summary of statistical treatment for Tables 2, 5, 7, and 10.*

$$\text{1-sigma} = \pm\sqrt{\frac{\Sigma d^2}{(n-1)}}$$

$$\text{RSD} = \frac{(\text{1-sigma}) \times 100}{\text{average value found}}$$

$$\text{Pooled variance} = \frac{\Sigma(\Sigma d^2)}{\Sigma(n-1)}$$

$$\text{Pooled standard deviation} = \pm\sqrt{(\text{pooled variance})}$$

$$\text{Total number of degrees of freedom} = \Sigma(n-1)$$

NOTE: d = deviation of a result from the average and n = number of replicates in a data subset.

num indicating electrode and a saturated calomel reference electrode were used. Again a dead-stop ferrous ammonium sulfate titration was substituted in the automated version, and phosphoric acid was added.

The presence of tungsten levels in excess of 2% was found to depress vanadium results, both with and without the use of phosphoric acid. Without phosphoric acid, tungsten precipitated as tungstic acid, evidently entraining some vanadium (+III). With phosphoric acid, the soluble phosphotungstate complex apparently changed the endpoint characteristics enough to produce a premature deflection and, again, low vanadium results. The tungsten problem was solved by adopting a set of strategies, based on the estimated tungsten concentration: at less than 2% tungsten samples are fumed in phosphoric and sulfuric acids before vanadium oxidation; at 2 to 6% tungsten, samples are fumed in perchloric acid,[2] cooled, diluted, reduced with sulfurous acid and sulfuric acid, boiled and cooled; all prior to vanadium oxidation; at levels above 6% tungsten, samples are treated the same as for 2 to 6%, except that a high tungsten standard sample, treated in the same manner, is always used to establish the titer.

When manganese is present at levels above 5%, it produces a positive error on low vanadium results caused apparently by the oxidation of some small portion of the manganese by the nitric acid. In this case a sodium hydroxide separation is used to remove the manganese interference.

Table 4 contains some vanadium results obtained with the automatic titrator, and Table 5 presents the precision estimate that they yielded. The pooled data show a standard deviation (1-sigma) of ±0.02% over a data set that covers the range 0.2 to 2% vanadium.

---

[2] Vanadium (+V) is evidently not entrained in the tungsten, which precipitates.

TABLE 4—*Vanadium results from primary and secondary standards.*

Standard	Alloy Type	Certified % V[a]	Found % V
NBS 73c	420 stainless	0.030	0.027
NBS 346	valve steel	0.058	0.061
NBS 30e	low alloy	0.149	0.146, 0.148
NBS 30f	SAE 6150 low alloy	(0.18)	0.18, 0.17, 0.18, 0.18
NBS 348	A286 high temp.	(0.25)	0.23, 0.25, 0.24
NBS 50a	H26 hot work	0.970	0.96
NBS 50b	H26 hot work	1.02	1.06
CSH13[b]	H13 hot work	1.02	1.02, 1.01, 1.03, 1.01, 1.01, 1.02, 1.04, 1.03, 0.99, 1.02, 1.02, 1.02, 1.01
CSM1[b]	M1 high speed	1.05	1.04, 1.05, 1.06, 1.07, 1.02
IS00629[b]	IN100 high temp.	(1.13)	1.15
NBS 50c	H26 hot work	1.16	1.15
NBS 134a	8Mo/2W/1V high speed	1.25	1.29, 1.28
ISO1165[b]	Hy Sat 48 (Co-base)	(1.79)	1.75
CSM2[b]	M2 high speed	1.81	1.77, 1.83, 1.81, 1.80
NBS 132b	M2 high speed	1.83	1.83, 1.82
CSM10[b]	M10 high speed	1.99	1.98, 2.01, 1.99, 1.96
NBS 153a	M34 high speed	2.06	2.06, 2.05, 2.06, 2.06

[a] Values in parentheses are provisional.

[b] Carpenter Technology intra-company standard.

TABLE 5—*Summary of precision data for vanadium.*

Standard	Certified % V	Replicates	Average % V Found	1-sigma	RSD, %
NBS 30f	(0.18)	4	0.18	±0.005	2.82
CSH13	1.02	13	1.02	±0.012	1.21
CSM1	1.05	5	1.05	±0.019	1.84
CSM2	1.81	4	1.80	±0.025	1.39
CSM10	1.99	4	1.98	±0.021	1.05
NBS 153a	2.06	4	2.06	±0.005	0.24

NOTE: pooled variance = 0.000 246, pooled standard deviation = ±0.016, and total number of degrees of freedom = 28.

Boron

For many years our laboratory has used the mannitol-acid/base titration for boron following a mixed-bed ion exchange separation to remove interferences [7]. The sample is dissolved using controlled-acid conditions under reflux in boron-free glassware. It is then passed through a resin bed that retains both sample matrix ions and excess free acid. The eluent is boiled to expel carbon dioxide and cooled. Each sample is then carefully adjusted to pH 7.00 while nitrogen is sparged through the solution. Mannitol is added to form the borate complex and release a stoichiometric amount of hydrogen ions. While maintaining the nitrogen flow, the sample is titrated with standard sodium hydroxide solution to return it again to precisely pH 7.00. In skilled hands, using a high precision, research-grade pH meter, the manual version of this method can achieve a level of accuracy sufficient to statistically justify the reporting of three decimal places at and around the 1% boron level.

Adaption of the procedure to the automatic titration system was comparatively straightforward. The sample holder was modified with a glass frit diffuser for the introduction of nitrogen. A universal pH electrode and saturated calomel reference electrode were used, and the system was configured to seek pH 7.00 in fixed endpoint mode. Both pH adjustments are under automatic control, although, of course, only the volume readings for the endpoint after the mannitol addition generate boron results.

Although our manual titration work had traditionally been based on normality, it was decided to try a titer approach with the automatic system to eliminate the need to periodically restandardize the sodium hydroxide titrant and to compensate for systematic errors. Since primary alloy standards are unavailable in the concentration range of interest (0.5 to 2.0% boron), two alternatives were studied and found to yield equally acceptable results. One technique involves spiking a boron-free alloy with a standard boron solution prepared from NBS SRM951 boric acid (or equivalent purity reagent). The other technique utilizes a very well-established secondary standard as the titer sample. Both forms of titer compensate for the small positive error caused by silicic acid from the sample matrix. As a weak acid, silicic acid is not retained by the resin column and is titrated with the boron. In the manual normality approach this necessitates a special correction.

Table 6 summarizes some results obtained using secondary standards and prepared synthetics as "unknowns," and Table 7 summarizes the precision obtained. The pooled data show a standard deviation (1-sigma) of ±0.004% over a data set that covers the range 0.4 to 2% boron.

Cobalt

Cobalt is a difficult element to determine with high precision at high concentration levels. One classic approach that has not been widely accepted is the ferricyanide potentiometric titration [*8*]. The chemistry relies on the high stability of cobalt's (+II) oxidation state in the absence of complexing ligands. Even after fuming with perchloric acid only the divalent species is present in the cold, water-diluted solution. This species can be oxidized with excess standard potassium ferricyanide solution in an ammoniacal citrate medium and the excess reagent back-titrated potentiometrically with standard cobalt (II) nitrate solution.

The method has not gained wide acceptance because many matrix elements interfere. These problems were investigated using the computer-assisted titrator, and suitable solutions were found.

TABLE 6—*Boron results from secondary standards.*

Standard[a]	Certified % B	Found % B
IS00335	0.084[b]	0.084
CS18N	0.390[b]	0.392, 0.395, 0.395, 0.384, 0.382, 0.390, 0.391, 0.384, 0.387, 0.384, 0.384, 0.381
CSZ9E	0.960[b]	0.960, 0.958, 0.960, 0.962, 0.964, 0.964, 0.964, 0.958, 0.964, 0.962, 0.958, 0.958, 0.964, 0.962, 0.960, 0.962, 0.960, 0.960, 0.960, 0.958, 0.964, 0.960, 0.960, 0.961, 0.959, 0.961, 0.963, 0.960
607N	1.06[b]	1.063, 1.060, 1.054
586E	1.08[b]	1.077, 1.068, 1.070
633N	1.20[b]	1.194, 1.194, 1.183, 1.184
CS80E	2.00_3[b]	2.001, 2.001, 2.007, 2.010, 2.005, 2.005, 2.007, 2.009, 1.998, 1.997, 1.991
Synthetic A	(0.800)[c]	0.810
Synthetic B	(1.000)[c]	1.002, 1.007
Synthetic C	(1.200)[c]	1.211
Synthetic D	(1.400)[c]	1.408
Synthetic E	(2.000)[c]	2.000

[a] All standards are Carpenter Technology T-304 stainless alloy standards.
[b] Value established by manual/normality titration.
[c] Amount added to boron-free T-304 stainless alloy.

TABLE 7—*Summary of precision data for boron.*

Standard	Certified % B	Replicates	Average % B Found	1-sigma	RSD, %
CS18N	0.390	12	0.387	±0.0050	1.286
CSZ9E	0.960	28	0.961	±0.0021	0.219
607N	1.06	3	1.059	±0.0046	0.433
586E	1.08	3	1.072	±0.0047	0.441
633N	1.20	4	1.189	±0.0061	0.511
CS80E	2.00_3	11	2.003	±0.0058	0.290

NOTE: pooled variance = 0.000 016 93, pooled standard deviation = ±0.004 11, and total number of degrees of freedom = 55.

First, there are a number of cations that undergo precipitation reactions with either ferricyanide, or its reaction product, ferrocyanide, or both. Fortunately the copper (+II) precipitate, like the cobalt (+II) compound, is completely soluble in the ammonium hydroxide medium and does not form. Iron (III) ferrocyanide (the familiar precipitate known as Prussian blue) is prevented from forming by the addition of citrate ion, which keeps iron as a soluble complex. Certain other precipitates are produced by elements that are rarely found in more than trace amounts in cobalt alloys: cadmium, lead, silver, tin, and zinc. Nickel, however, remains a problem despite the reported solubility of its ferrocyanide in ammonium hydroxide. When nickel is present, a fine white precipitate is visible in the solution and the titration produces poor results for cobalt. Evidently, some sort of complex competition between nickel and cobalt for the two hexacyanoligands is involved.

Most of the masking agents that were tried in an attempt to prevent the nickel precipitation failed because they disrupted the redox oxidation of cobalt. The solution lay in the use of a controlled amount of disodium ethylenediaminetetraacetate (EDTA). The EDTA complexes both nickel and cobalt, but the cobalt-EDTA complex still undergoes the same oxidation by ferricyanide as the uncomplexed cation [*9*]. This stratagem works for samples containing up to 20% nickel; above that level, such a high concentration of EDTA is required to prevent nickel precipitation that the redox equilibrium begins to be affected.

The second interference involves the redox chemistry directly. Manganese was found to consume ferricyanide stoichiometrically in the identical molar ratio as cobalt. Table 8 summarizes these studies that were based on synthetics prepared from high purity metals. Correction for manganese then reduces to a simple subtraction of that element's concentration, as determined by atomic absorption, colorimetry, or titration.

One other interference was discovered; molybdenum when present at concentrations above 5% leads to an erroneously low cobalt result. Evidently, when present in this amount, molybdenum irreversibly complexes some cobalt (possibly by the formation of a heteropoly salt) [*9*].

Samples with more than 20% nickel or more than 5% molybdenum can still be analyzed for cobalt by this technique by first isolating the cobalt by ion exchange [*10*]. On a strongly basic, chloride-form, anion exchange resin, manganese and nickel (as well as chromium, vanadium, and aluminum) are eluted with 9 *M* hydrochloric acid (HCl). When cobalt is eluted with 4 *M* HCl, it is assumed to be unaccompanied by any other interferences, and the eluate can be wet-ashed with nitric and perchloric acids (to destroy organics from the resin) and titrated.[3] The separation adds some time to the procedure, but

TABLE 8—*Effect of manganese on cobalt titration using synthetic solutions.*

	Added				
Synthetic	% Mn	% Fe	% Co	Apparent % Co	Corrected % Co
I	0.50	49.50	50.00	50.40	49.90
II	1.00	49.00	50.00	50.91	49.91
III	5.00	45.00	50.00	55.01	50.01
IV	10.00	40.00	50.00	59.98	49.98

[3] In practice the best results were obtained when disodium EDTA was added to even the ion-exchange separated samples just before ferricyanide addition. It is possible that copper, which accompanies the cobalt in the 4 *M* HCl fraction, may perturb the endpoint somewhat in the absence of EDTA.

it eliminates the need for the manganese correction, as well as eliminating the effects of high concentrations of nickel and molybdenum.

Table 9 shows the data obtained from both versions of the method and Table 10 summarizes the precision. The EDTA-masking approach shows a pooled standard deviation (1-sigma) of ±0.10% over the concentration range 21 to 49% cobalt, while the ion-exchange separation approach shows a pooled standard deviation (1-sigma) of ±0.06% over the concentration range 12 to 17% cobalt.

TABLE 9—*Cobalt results from primary and secondary standards.*

Standard	Alloy Type	Certified % Co[a]	Separation	Found % Co
NBS 153a	Mod M34 high speed	8.47	yes	8.47, 8.46, 8.55
NBS 1206-2	Rene 41	11.55	yes	11.49, 11.58, 11.59, 11.56
NBS 1207-1	Waspaloy	13.05	yes	13.01, 13.15, 13.11
271-2A[b]	CTX-1	(13.71)	yes	13.60
NBS 349	Waspaloy	13.95	yes	13.88, 13.86, 13.93, 13.98, 13.97, 13.96, 13.96, 13.99
187-1A[b]	CTX-3	(14.93)	yes	15.04
980-2X[b]	CTX-3	(15.06)	yes	15.02, 14.93, 14.74, 14.88
HA-903[c]	Inco 903	(15.09)	yes	15.11, 15.15, 15.15, 15.14
196-1A[b]	CTX-3	(15.15)	yes	15.09
IS00630[b]	IN 100	(15.66)	yes	15.71, 15.64, 15.66, 15.75
IS00304[b]	Astroloy	(17.26)	yes	17.44, 17.46, 17.53, 17.49
IS00117[b]	AISI 661	(19.79)	no	19.73, 19.76, 19.65, 19.76
NBS 1187	AMS 5376A	20.80	no	20.72, 20.68, 20.65, 20.95, 20.91
NBS 1187	AMS 5376A	20.80	yes	20.92
ALN25[d]	Alnico VB	(23.88)	no	24.06, 24.18, 24.15, 24.18, 24.09
NBS 168	IN 155	41.20	no	41.33, 41.22, 41.21, 41.26, 41.21
NBS 168	IN 155	41.20	yes	41.18
NBS 167	IN 155	42.90	no	42.84, 42.79, 42.74, 42.94, 43.11
NBS 167	IN 155	42.90	yes	42.92
IS01165[b]	Hiperco 50	(49.42)	no	49.35, 49.46, 49.16, 49.33, 49.30

[a] Values in parentheses are provisional.
[b] Carpenter Technology intra-company standard
[c] Sample courtesy Huntington Alloys.
[d] Sample courtesy Crucible Materials Corporation.

TABLE 10—*Summary of precision data for cobalt.*

Standard	Certified % Co	Separation	Replicates	Average % Co Found	1-sigma	RSD, %
NBS 1206-2	11.55	yes	4	11.56	±0.045	0.39
NBS 349	13.95	yes	8	13.94	±0.048	0.34
980-2X	(15.06)	yes	4	14.89	±0.12	0.79
HA-903	(15.09)	yes	4	15.14	±0.019	0.13
IS00630	(15.66)	yes	4	15.69	±0.050	0.32
IS00304	(17.26)	yes	4	17.48	±0.039	0.22
IS00117	(19.79)	no	4	19.72	±0.052	0.26
NBS 1187	20.80	no	5	20.78	±0.14	0.66
ALN25	(23.88)	no	5	24.13	±0.054	0.23
NBS 168	41.20	no	5	41.25	±0.051	0.12
NBS 167	42.90	no	5	42.88	±0.15	0.34
IS01165	(49.42)	no	5	49.32	±0.11	0.22

	Separation	No Separation	Overall
Pooled variance	0.00 347	0.009 97	0.006 79
Pooled standard deviation	±0.059	±0.100	±0.082
Total number of degrees of freedom	22	23	45

Conclusions

When development work with the new generation of automatic titrators was initiated, four criteria for the new methods were applied: (1) they should be faster than the equivalent manual determinations; (2) they should be free from the need for special skills and from "operator-sensitive" factors; (3) they should be applicable over a wide concentration range; and (4) 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 methods in skilled hands. Based on the work with chromium, vanadium, boron, and cobalt, these criteria have been satisfied.

Future work at our laboratory is expected to extend the array of elements determined by automatic potentiometric titration to further exploit the advantages of this new technology. Methods for manganese, iron, and nickel, which likewise meet the four performance criteria, appear to be achievable goals.

Acknowledgments

I wish to thank R. R. Bixler, M. A. Noll, and F. J. Stoltz for their help in generating the chromium, vanadium, and boron data. I also wish to thank Carpenter Technology Corporation for permission to publish this work.

References

[*1*] Shaffer Jr., P. A., Briglio, A., Jr., and Brockman, J. A., Jr., *Analytical Chemistry,* Vol. 20, 1948, p. 1008.

[*2*] DeLoach, W. S., Eiland, J. L., and Harmon, J. G., *Journal of Chemical Education,* Vol. 26, 1949, p. 609.

[*3*] Hawes, R. C., Strickler, A.; and Petterson, T. H., *Electrical Manufacturing,* Vol. 47, 1951, p. 76.

[*4*] Walters, H. E., *Journal of the American Chemical Society,* Vol. 27, 1905, p. 1550.

[*5*] Kelley, G. L. and Conant, J. B., *Journal of Industrial Engineering Chemistry,* Vol. 8, 1916, p. 719.

[*6*] Kelley, G. L., Wiley, J. A., Bohn, R. T., and Wright, W. C., *Journal of Industrial Engineering Chemistry,* Vol. 11, 1919, p. 632.

[*7*] Martin, J. R. and Hayes, J. R., *Analytical Chemistry,* Vol. 24, 1952, p. 182.

[*8*] Dickens, P. and Maassen, G., *Archive für das Eisenhüttenwesen,* Vol. 9, 1936, p. 487.

[*9*] Cotton, F. A. and Wilkinson, G., *Advanced Inorganic Chemistry,* 3rd ed., Wiley, New York, 1972, pp. 677 and 953.

[*10*] Lewis, L. L. and Straub, W. A., *Analytical Chemistry,* Vol. 32, 1960, p. 96.

Gerald J. DeMenna[1] *and William J. Edison*[2]

Novel Sample Preparation Techniques for Chemical Analysis—Microwave and Pressure Dissolution

---

REFERENCE: DeMenna, G. J. and Edison, W. J., **"Novel Sample Preparation Techniques for Chemical Analysis—Microwave and Pressure Dissolution,"** *Chemical Analysis of Metals, ASTM STP 944*, F. T. Coyle, Ed., American Society for Testing and Materials, Philadelphia, 1987, pp. 45–59.

ABSTRACT: As the capabilities of an analytical laboratory expand to meet the increasing demand for tighter specifications and lower detectability, one must be cautious not to let the chemistries involved be a limitation to the analysis. This becomes particularly true when sophisticated, multi-element analytical capability in an instrument allows over 800 elemental determinations per hour, and the typically labor-intensive preparation of the samples prevents utilizing such capability. Classical preparation techniques involve multiple steps and introduce contamination and error into the analysis. Some procedures involve costly equipment or slow dissolution times, which further reduce the laboratories throughput. There are many techniques: some very old that have been forgotten through lack of use and others that are so unconventionally new that analysts usually do not consider them, which are applicable to the preparation of many types of samples. This report reviews a selection of the techniques themselves and the results obtained from the analysis of several types of samples.

KEY WORDS: dissolution, chemical attack, fusion, microwave, pressure bomb, ultrasonic, oxidation, ashing, analytical spectroscopy, sample introduction, inorganic chemistry, flux, acid digestion

The improvements in analytical technology are rapidly changing the requirements of the inorganic analytical laboratory. Environmental laboratories must achieve lower detection limits, food and agriculture testing requires higher precision on essential mineral determinations, industrial metal manu-

---

[1] Regional laboratory manager, Beckman Instruments, Inc., 594 Dial Ave., Piscataway, NJ 08854.
[2] Chief chemist, Chem-Chek Consulting, P.O. Box 350, South Bound Brook, NJ 08880.

facturers need to determine an alloy's composition from minor percentages to trace parts per million, and the ever-popular independent testing laboratory has to be able to perform all such analyses to stay in business. Since the fundamentals of classical quantitative analysis back in the late 1800s developed [*1*], almost all methods for determining the composition of a sample require the complete or quantitative dissolution of the sample specimen. Titrimetry, gravimetry, colorimetry, electrochemical measurements including polarography and coulometry, and the "modern" instrumental procedures of atomic absorption spectrophotometry and plasma emission spectroscopy, all utilize a solution of the material to be analyzed [*2,3*]. This rule holds true to all kinds of sampled materials, regardless of their complexity or their resistance to chemical attack.

Any sample's composition is slightly changed as the form of the sample is changed. Grinding and pulverizing introduce contaminants and loose moisture or other volatiles. Dry ashing a sample may change the crystal habit of a molecule, rendering it passive to any attacking medium. Chemical treatments introduce a multitude of complex reaction mechanisms that may cause volatilization, crystallization, precipitation, oxidation, reduction, and chelation, just to name a few [*4,5*]. Some preparation methodologies employ mineral acids, individually or mixed, to "open out" the sample and present a stable, soluble solution for analysis. Many inorganic compounds are easily volatile under the appropriate conditions, primarily fluorides (silicon, boron, germanium, phosphorus, arsenic, and antimony), chlorides (arsenic, selenium, antimony, ruthenium, osmium, rhenium, chromium, tin, and thallium), and oxide complexes when heated solutions are taken to fuming in an open vessel (arsenic, antimony, selenium, tellurium, tin, molybdenum, rhenium, and lead) [*5-7*].

Reaction vessels and equipment recommended for most decomposition procedures are either expensive or contaminating, and the procedures are typically tedious if they are to be precise, or are fairly rapid, but prone to errors [*8,9*]. Most industry would benefit from a combination of these two extremes, and this paper shall present a variety of relatively under-utilized procedures and chemistries to economically expedite the attack and dissolution of a sample without sacrificing precision or risking contamination. The material contained herein represents a small sampling of the tremendous library of information existing on sample preparation technology, and the listed references will help open up other techniques for the dissolution of a sample.

Note

The contents of this article present equipment and chemicals that are potentially hazardous, even when used as directed. The material is presented as an educational aid to analytical chemists in many fields in the hope of simplifying and expediting their job duties. It is the sole responsibility of the reader to follow any and all safety precautions pertaining to the equipment(s) of chemical(s) being utilized.

The authors, G. DeMenna and B. Edison; their affiliations, Beckman Instruments and Chem-Chek Consulting, respectively and ASTM assume no liability whatsoever for any material, financial, or personal loss incurred from damages arising from the implementation of equipment, chemicals, or procedures listed herein.

Equipment

The normal compliment of laboratory equipment was used for this work: calibrated glassware and balances, polytetrafluoroethylene (PTFE) polymer and polyethylene vessels (4-oz [113-g] bottles and 400-mL beakers), ACS reagent grade minerals acids (or one of the spectrographically analyzed, purified grades), preparatory reagents (as described in the text), and an instrument to do the analyses [*3,4*]. The work represented here was performed on a SpectraSpan Model V, simultaneous direct-current plasma with an Echelle spectrometer (SpectraMetrics/Beckman). The analytical emission wavelengths used are listed in the appropriate procedures. Special preparatory equipment or apparatus is also detailed in the specific procedure pertaining to the equipment.

Procedures

Crucibles and Fusions

High-temperature procedures are quite common for the analysis of geologicals, biologicals (primarily organic-based), structural metals (ferrous and nonferrous), catalyst and ceramic materials, and precious metal-bearing substances. Materials high in carbon or refractory compounds require ignition to elevated temperatures, either alone or with a fluxing agent, to oxidize the carbon and decompose the refractory component. The popular crucible materials are quartz (or vycor), graphite and platinum, with zirconium and nickel finding increased use because of their relatively low cost and moderate durability. The ignitions are usually done in a muffle furnace with some calibrated temperature controller assembly. Periodically, fusions are performed over an open gas burner to allow visual observation of the melt.

Platinum-ware is the ideal high-temperature material because of its stability and low volatility at white heat (>1100°C), its resistance to most chemicals, and its general overall inertness. One precaution is to make sure some oxidizing material is present to prevent the absorption of reduced metal species (iron, copper, lead, cobalt, cadmium, mercury, silver, gold, and so forth) into the platinum walls. The major drawback to routine use of platinum equipment is its volatile and usually high cost [*1,8,10*]. At the time of this initial investigation (1981), a 35-mL platinum crucible with lid cost $1150.00. There is an alternative to pure (refiner's grade) platinum; produced by a precious metal manufacturer, the only one at the time of this writing. It is called a ZGS-Pt TRI-M crucible, and consists of a palladium core upon which a composite of zirconia-grain stabilized platinum is permanently layered. Such a mixture gives the temperature and chemical stability of pure platinum (since palladium has a similar thermal modulus to platinum), with the lower cost of palladium, which comprises half the weight. The cost for a 35-mL crucible with lid was $485.00, over a 50% reduction in cost. The ZGS material is advertised to be superior to pure platinum in its chemical resistance and volatility, but there is some initial contamination as shown below.

The first evaluation consisted of a series of chemical "attacks" on a crucible of each material to see if their chemical resistances were comparable. Initial treatment was boiling for 16 h in concentrated hydrochloric acid (HCl) in a PTFE beaker, followed by five fusions with 5 g of a mixed lithium borates-lithium carbonate mixture, which were dissolved in 4% nitric acid (HNO_3). The final step was boiling for 16 h in a mixture of 1 to 1 nitric acid-hydrogen fluoride (HNO_3-HF) acids in a PTFE beaker. All solutions were analyzed by DCP/AES to give a total "contaminant value." The treated crucibles were then ignited to white heat at 1100 to 1175°C for 1 h to indicate any volatility losses. A blank of the reagents used in this investigation was analyzed separately. The sum total of their impurities was less than 40 μg (or 1 ppm), and their contribution was ignored in making the relative comparison between the two crucibles. The results of these findings are listed in Table 1.

Fusion fluxes and sintering agents are frequently used for attacking geological materials, silicate, phosphate, and other rocks, and allowing almost all components to be stable in a single solution. Common fluxing materials include the basic media—sodium and lithium borates (meta- and tetra-borate), their carbonates, sodium peroxide—and acidic media—potassium pyro- and per-sulfates, sodium silicate, alkali fluorides [*6,9,11-13*]. While fusion prep-

TABLE 1—*Crucible analysis (values are micrograms/crucible, 1 ppm = 40 µg).*

Element	Wavelength, Å	ZGS/TRI-M, µg	Refiner's Pt, µg
Ag	3280	124	193
Au	2675	52	109
Cu	3247	49	27
Fe	2599	213	331
Pd	3404	875	540
Rh	3692	178	307
Si	2516	85	56
Zr	3391	459	<20

NOTE: Volatility loss after ignition: ZGS/TRI-M = 6.9 mg and Refiner's Pt = 8.3 mg.

arations are useful, they do require high heat and can be hazardous under certain circumstances, particularly when employing an oxidizing agent in a mixture, such as potassium nitrate (KNO_3) with sodium carbonate (Na_2CO_3). Presented in this section are some new or previously unused fusion media to minimize time and hazard, yet preserve the quality of the analysis.

Aqua regia is commonly used as a strong oxidizing acid for wet digestions, particularly for precious metals. The 3:1 mixture of HCl : HNO_3 generate free chlorine in a high Cl^- solution, with a boiling range of 120°C [4,14]. There is an old precious metal ore assay method that uses solid *aqua regia* to attack the sample. It consists of a mixture of ammonium nitrate and ammonium chloride, from ratios of 3:1 to 1:3, mixed 5 parts to 1 part of sample [1,6]. The mixture is heated in either graphite or vycor, preferably on a hot plate or over a small gas flame in a fume hood. A muffle set at 250°C can be used but allow for fairly dense fumes initially. The melt is leeched out in water, or preferably a dilute stabilizing solution of HCl (for transition and precious metals), tartrate (for heavy metals and hydride-forming elements), hydrogen peroxide (for complexing titanium, vanadium, and molybdenum and some refractory species), or fluoride (for the hydrolytic and refractory metals) [6,7,9,15]. This procedure is indicated for many types of ore samples, ashing residues; pyrite, arsenide and metalliod compounds; Cu-Zn-Pb-Sn bearing materials and unsintered ceramics. The reaction is too violent for use on unoxidized transition metals and alloys, though it works quite well on aluminum and its alloys. Since ammonium salts are quite clean spectroscopically, there is virtually no contamination, and the cost per preparation is very low. Silicaceous residues are unattacked and removed by filtration.

A National Bureau of Standards Reference Material SRM-330 copper ore and a U.S. Geological Survey (USGS) standard precious metal ore were prepared and analyzed by DCP/AES. The results of the analysis and correlation with certified values are listed in Table 2.

Sodium peroxide is an extremely powerful oxidizing agent and is quite vigorous, if not hazardous, in its reactions. Lithium metaborate is an excellent basic flux to solubilize and complex silicate materials, but has little oxidizing

TABLE 2—Aqua regia *fusion results (values are μg/g in sample, unless noted and [K] = known, certified value; [M] = measured data).*

Element	Wavelength	[K]	SRM-330 [M]	USGS [M]
Cu	5105 Å	0.84%	0.83	297.0 ppm
Cd	2265	(1.6)	1.72	0.39
Zn	2062	. . .	91.5	65.4
Ag	3280	1.37	1.33	4.92
Au	2675	0.09	0.08	0.88
Re	3461	0.30	0.27	<0.1
Te	2385	. . .	16.4	2.05
Pt	2659	(0.8)	0.79	3.43

potential [*5,6*]. A flux of these substances, mixed in ratios of 1:4 to 4:1, combine the best features of both. Such a mixture will fuse with less spitting and violence than pure sodium per oxide (Na_2O_2), but have the stabilizing activity of $LiBO_2$, and the overall precision of the analysis should improve. An unforeseen advantage of this method is the economic use of sodium peroxide (Na_2O_2), which is in short supply and costly. This mixture is applicable to the dissolution of geological or catalyst materials containing precious metals, rare earths, or unoxidized base metals. A spent cracking catalyst (containing reduced precious metals) and a USGS standard rock, IZ, were prepared and analyzed. The method recommends a 6:1 flux to sample ratio, and fusion at 900°C for high metaborate mixes, and 650°C for high peroxide blends; all times range 10 to 15 min. The melts were leeched and dissolved in 4% HCl. The data from spectrometric analysis are presented in Table 3.

Pressure Vessel Dissolutions

When a sample matrix contains components that are volatile or unreactive under normal conditions, then a "pressurized" dissolution method is recommended. Such procedures consist of heating the sample and dissolution media in an unsealed vessel, within a pressurized chamber (auto-claving), or heating in a sealed reaction vessel (bomb). Bomb equipment is capable of generating higher pressures (6895 kPa [1000 psi]) and temperatures (375°C) than auto-claving (345 kPa [50 psi], 225°C) [*6,11,12,16*]. For materials con-

TABLE 3—*$LiBO_2/Na_2O_2$ mixed flux results (values are μg/g in sample, unless noted and standard deviations calculated on triplicate preparations).*

Element	[K]	Na_2O_2 Alone	Na_2O_2 + 2 $LiBO_2$
	SPENT CRACKING CATALYST, EXXON CORP., LINDEN, NJ		
Al	17.53%	17.4 ± 0.22%	17.6 ± 0.24%
Si	23.19%	23.0 ± 0.31%	23.3 ± 0.28%
Re	1090	1093 ± 18.5	1086 ± 16.2
Pt	1295	1303 ± 14.5	1291 ± 10.1
Pd	82	82.4 ± 0.9	81.9 ± 1.2
Ru	165	160 ± 2.9	163 ± 2.3
V	498	492 ± 13.0	496 ± 11.5
Ni	230	227 ± 11.8	231 ± 7.8
	USGS STANDARD IZ, RUTGERS UNIVERSITY, NEW BRUNSWICK, NJ		
SiO_2	54.93%	55.02 ± 0.58%	54.86 ± 0.63%
Al_2O_3	16.45%	16.52 ± 0.19%	16.48 ± 0.22%
MnO	1245	1178 ± 39.7	1289 ± 30.2
Fe_2O_3	7.65%	7.53 ± 0.87%	7.69 ± 0.37%
Cr_2O_3	205	193 ± 7.9	209 ± 2.8
CeO_2	78.5	74.4 ± 4.8	80.7 ± 1.9
Nd_2O_3	35.0	33.9 ± 2.1	35.0 ± 1.4
Dy_2O_3	(4.5)	4.11 ± 0.23	4.33 ± 0.16

taining potentially volatile species, such as arsenic, antimony, titanium, tin, gallium, germanium, molybdenum, and chromium in HCl; silicon, boron, phosphorus, sulfur, and germanium in HF; inter-metallic compounds such as carbides and nitrides; ceramics and refractory compounds; and materials in general where little or no oxidation is required, are easily prepared by pressure bomb attack. This section will evaluate bomb dissolutions and the various procedures that can be employed.

The typical bomb digestion vessel (manufactured by Parr Mfg. Co.), consists of a thick PTFE container nestled in a heavy stainless or nickel-steel jacket with a snug-fitting screw cap. The capacity ranges from 15 to 75 mL, and costs about $300.00 for a 35-mL capacity bomb; which precludes their common use as a bulk preparatory device [*9,11*]. An alternative to individual steel bombs is several individual bottles placed in a bulk pressure chamber, similar to auto-claving except that the bottles are tightly sealed. A small 3-q (2.8-L), PTFE-lined, household pressure cooker, which retails for $15.00; and a dozen 2-oz (65-mL) PTFE bottles (their cost about $100.00) can provide the analyst with capabilities equivalent to $3600.00 worth of Parr bombs for under the cost of a single bomb. This system can generate internal temperatures over 250°C and pressures in excess of 276 kPa (40 psi) quite safely. The only restriction is the use of nonoxidizing media, which would otherwise produce rapid and intense pressures, and lead to disasterous conditions [*5,15*].

Almost any nonoxidizing acid or attacking media can be used for sample preparations: HCl, HF, phosphoric acid (H_3PO_4), diluted sulfuric acid (H_2SO_4), alkaline/chelate mixtures (employing ethylenediaminetetaacetate [EDTA] nitrilotriacetic acid [NTA], tartrate, or citrate), or coordinating ligands (SCN(-), CN(-), ammonia [NH_3], ethylenediamine or BF_4(-)) [*5,6,15*]. The pressure cooker used for this work was a Presto brand PC-3 model with black PTFE lining and an aluminum lid. The modifications required to achieve satisfactory operating conditions were to spray the aluminum lid with Vykem-brand plastic spray (for protection in case of a blowout), and fixing a 50-g weight on the cooker's normal counter-weight. This provides an internal pressure of 345 kPa (50 psi), with the rubber safety plug rated at 448 kPa (65 psi), and the lid rated at 827 kPa (120 psi) rupture pressure; so with normal precautions there is no immediate hazard.

The evaluation of this technique was based upon the preparation and analysis of two kinds of samples: an antimony-tantalate sintered ceramic, which has both volatile and refractory components, and a complex arseno-apatite mineral. The SbTa-O ceramic was treated in triplicate, by three different procedures. The results and precisions are shown in Table 4.

1. 1 g of powdered sample (<200 mesh) was mixed with 25-mL 1:1:1 HCl/HF/H_2SO_4 and heated at 150°C in an open 250-mL PTFE beaker for 8 h for complete dissolution. Acid mixture was added periodically to maintain a 25-mL volume.

TABLE 4—Presto Bomb *catalyst dissolution (values are µg/g in sample unless noted).*

Element	[K]nown	PREP #1, Open Beaker	% RSD	PREP #2, Parr Bomb	PREP #3, Presto Bomb
Sb	33.15%	31.7 ± 2.4%	8.3	33.0 ± 0.4%	32.8 ± 0.3%
Ta	49.00%	47.8 ± 2.0%	4.4	48.7 ± 0.2%	48.9 ± 0.4%
As	328	76 ± 29	41	326 ± 3.2	318 ± 4.4
Nb	122	108 ± 3.3	3.7	116 ± 1.4	120 ± 1.1
Al	265	241 ± 6.2	9.5	276 ± 2.4	259 ± 2.3
Cu	23	18.7 ± 0.4	22	21.7 ± 0.2	22.8 ± 0.2
Si	650	140 ± 90	>50	656 ± 7.7	645 ± 7.9
Sn	180	51.2 ± 27	>50	178 ± 1.7	183 ± 1.5
Ti	45	38.4 ± 5.9	15.4	44.0 ± 0.5	43.5 ± 0.7
Mg	95	84.9 ± 5.4	8.6	88.2 ± 0.9	93.1 ± 0.8
Pb	410	381 ± 16	7.8	411 ± 6.2	406 ± 3.9

2. 1 g of powdered sample was mixed with 15 mL of acid mixture and heated in an oven at 300°C for 2 h in a Parr steel bomb with a 40-mL PTFE vessel.

3. 1 g of powdered sample and 15 mL of acid mixture were placed in a 2-oz (56-g) PTFE bottle and "steamed" at 250°C for 2 h in a Presto bottle bomb.

The apatite mineral, powdered to <200 mesh, was prepared as a single preparation by three separate methods. The data and correlation between the methods is listed in Table 5.

1. A 0.5-g sample and 20-mL concentrated H_2SO_4 were heated at 250 to 275°C (to fumes) in a 400-mL PTFE beaker for 4 h to complete solution. 10-mL additional acid was added to maintain volume.

2. A 0.5-g sample was fused with 4-g mixed lithium metaborate-tetraborate, 1:1, in a ZGS/TRI-M crucible for 25 min, with an additional 2 h for complete solution in 4% HNO_3.

3. A 0.5-g sample, 7-g $LiOH \cdot H_2O$, 1-g H_4EDTA, 1-g tartaric acid and 1-mL HBF_4 were placed in a 2-oz (57-g) PTFE bottle and "steamed" at 250°C for 2 h [*16*].

Comparative X-ray diffraction data are not available at this time.

TABLE 5—Presto Bomb *mineral preparation (values are μg/g in sample unless noted).*

Element	[K]nown	#1, open	#2, fusion	#3, bomb
Fe	30.71%	30.29%	30.77%	30.69%
As	21.85%	21.48%	21.89%	21.77%
Ca	8.23%	8.29%	8.17%	8.20%
Zn	5.15%	4.90%	5.13%	5.10%
P	2.25%	2.07%	2.30%	2.32%
Si	1480	1382	1459	1467
Cr	480	468	483	479
Al	175	154	77	172
Cu	125	89	122	118
Ag	75	63	70	68
Pb	57	59	48[a]	63

[a] Loss of Pb as PbO through volatilization may have occurred here.

Reflux/Flask Condenser Cap

Some samples are easily attacked but contain components that are volatile under the normal conditions of dissolution. Boron forms boric acid, which is steam-distillable in dilute acid; fluoride causes variable amounts of boron, silicon, and phosphorus to be lost from solution, and chloride forms easily distilled salts with arsenic, antimony, chromium, gallium, germanium, mercury, selenium, tin, titanium, and vanadium under certain conditions [*2-4,13,15*]. Such problems can be compensated for by the use of expensive ground-glass joint labware and distillation/condenser apparatus. Or, a rather small piece of Pyrex, shaped like a horn, can be placed in the neck of an erlenmeyer flask to trap and condense vapors coming from a heated preparation. This piece of equipment is called a reflux cap and is manufactured solely by G. F. Smith of Columbus, OH. They are available in various sizes to fit standard erlenmeyer flask necks. The extension that extends above the neck serves as the "expansion chamber" and cooling condenser; which receives steam and vapors from a small hole at the tip of the insert.

A sample of National Bureau of Standards SRM-1573, certified tomato leaves, were by treatment with *Aqua Regia* in an open erlenmeyer, and one with a reflux cap. Each preparation was run in triplicate, and the precision and correlation data shown in Table 6.

Microwave Oven Digestions

As the need for increased analytical throughput in most production laboratories exists, so will the need for reproducible "mass preparatory" techniques. The "Presto-bomb" satisfies part of that need and so does the increasingly popular microwave oven. This simple kitchen device allows direct heating of the sample itself, where the microwave energy is conducted

TABLE 6—*Reflux cap digestion (values are µg/g unless noted).*

Element	[K]nown	Open Flask	Reflux Cap
Ca	3.00%	3.04 ± 0.04%	3.06 ± 0.06%
P	0.34%	0.32 ± 0.01%	0.34 ± 0.005%
Zn	62	58.5 ± 2.1	60.9 ± 1.1
B	30	(7 to 18)	29.1 ± 0.33
Pb	6.3	5.3 ± 0.27	6.1 ± 0.10
Cr	4.5	4.3 ± 0.15	4.4 ± 0.07
As	0.27	nd	0.30 ± 0.04

NOTE: The boron was invariably lost with heating, and the arsenic was completely volatilized below the DCP limit of detection.

through the aqueous media, allowing a very rapid and efficient attack on many types of sample matrices [*11,16*]. In addition to the nonoxidizing dissolution media employed in bomb digestions, microwave procedures can also utilize attacks with mildly oxidizing mixtures. Such methodology can be used to prepare a wide variety of organic and inorganic substances for chemical analysis: rocks and minerals, ceramics, and oxides (including refractories), metallurgical, environmental, biological, and physiological [*2,5*]. The internal temperature of a digestion will vary with the molecular characteristics of the sample and the dissolution media being used but will range from 100°C to over 350°C in spots. Pressures within a sealed PTFE bottle can also build up safely to 345 kPa (50 psi), which is sufficient to attack even inert refractory compounds.

At the time of this writing, there is one manufacturer of a "laboratory-grade" microwave oven. It has a 600-W power level, the standard sized cavity is lined with plastic, it comes with a chemically resistant carousel, and it has a vent hole in the rear of the housing. This company also supplies a unique vessel and manifold system, made of PTFE, to house the dissolution reaction, maintain a constant pressure, and vent any over-pressure safely to the vent. Its cost is about $3500.00 for a typical system. A standard household microwave oven with a 1000-W power level and a carousel, can be purchased almost anywhere for under $300.00. With a little effort, some polyethylene sheet (from Bel-Art or Nalgene) can be cut to fit the inner surfaces of the chamber and glued in place with clear silicone seal from the hardware store. The oven's schematic will give the optimum location for a small 3/4-in. (2-cm) vent hole to be drilled, usually through the back panel, through which a section of tygon tubing is inserted and hooked up to some vacuum attachment to draw a negative pressure in the oven. The door, which is usually bare metal, and the sealing gasket, can be sprayed with one of a variety of plastic-coating sprays to provide an inert surface in case a bottle ruptures and evolves acid vapors. This work was done on a Sharp 1000-W carousel microwave oven, using Vykem spray (Fisher Scientific Co.) to coat the door. The total cost for the completed system was $340.00. The reaction vessels were the 2-oz (57-g) PTFE bottles used in the Presto-bomb evaluations, and there has been no failures in them to date.

The first study evaluated the dissolution of some National Bureau of Standard certified materials and a USGS standard, a refractory basalt rock (USGS/BHVO-1), a high alkali clay (SRM-97a), and a dried tomato leave sample (SRM-1573). The preparation, which was done in duplicate, consisted of 1-g powdered sample, 5-mL concentrated H_2SO_4, 3-mL concentrated HCl, and 1.5-mL concentrated HF, placed in a 2-oz (57-g) PTFE bottle, which was then tightly capped with the use of a crescent wrench, and irradiated at TV DINNER (800 W) for 2-min cycles, with a 1-min equilibration period, until the solution appeared complete, typically 10 min for biological and agricultural samples, and 15 to 18 min for geological matrices. Contrary to some limited references on microwave digestions, the necks of the bottles should not be wrapped with any material (PTFE tape, parafilm) that may cause the cap to bond to the bottle permanently. The acid mixture listed above has been found to be universally suitable for most oxidized samples (no massive metal present) and is even suitable for mineral analysis by adding 0.3-g *m*-benzene-disulfonic acid to the reaction [*1,4,13*]. The *m*-benzene-disulfonate salts are extremely stable and soluble, stemming from its high pKa and its moderate chelating abilities for divalent ions. Such a mixture would allow a sample substance containing high-silicon and high-alkaline earths to be dissolved in a single stable solution; a feat that previously required a fusion with an appropriate flux [*9,18*]. The results of DCP analysis of the prepared samples is listed in Table 7.

The plating bath industry has been utilizing fluoroborate (BF_4^-) salts for years to prepare stable solutions of various elements. The anion is small, clean, inexpensive, and forms coordinated ligands with many metals and semi-metals [*8,13*]. The concentrated acid (45% W/W) can be used in pressure bombs, microwave dissolutions, or simply open vessel digestions. Since the prepared acid contains virtually no free fluoride, glassware can safely be used, up to 125°C, where it dissociates back to F^- and HBF_3OH, trifluorohydroboric acid [*18*]. It is a "universal" attacking medium where many types of elements are present in a sample, and the analyst would like a single reagent to use for preparation; many minerals, natural (zeolite) and synthetic catalysts, cements and high alkali materials (since there is no fluoride precipitation), and basic metal ores (oxides) are simply prepared this way [*6*]. The procedure for preparing high purity fluoroboric acid is found in most chemistry texts [*7,10*].

The samples submitted were sludges, slimes, and slags from various stages in a solder (Sn/Pb/Zn/Ag) smelting foundry. The substances were in a highly oxidized state, and contained a variety of element types. The preparation consists of placing 0.5-g powdered sample and 15-mL fluoroboric acid in a 2-oz (57-g) polyethylene bottle and heating for 2 cycles of 2 min each on THAW

TABLE 7—Microwave Plasma *dissolutions (values are µg/g in sample unless noted and results are average of duplicate preparations).*

Element	Wavelength	[K]nown	BHVO-1	[M]
K	7698 Å	0.46%		0.48%
Rb	7800	10.0		11.5
Ca	3179	8.18%		8.22%
Sr	4077	440		452
Al	3944	7.35%		7.29%
Zr	3391	177		185
La	3988	16.7		15.5
Ti	3234	1.63%		1.66%
Fe	2599	8.51%		8.47%
Cr	2677	290		284

	[K] SRM-1573a	[M]	[K] SRM-97a	[M]
K	4.46%	4.51%	0.42%	0.44%
Rb	16.5	17.9	...	3.2
Ca	3.00%	3.17%	0.079%	0.081%
Sr	44.9	46.8	0.15	0.14
Al	0.12%	0.10%	20.54%	20.15%
Zr	...	1.4	465	453
La	0.9	1.1	...	17.1
Ti	...	3.9	1.14%	1.16%
Fe	690	675	0.32%	0.31%
Cr	4.5	4.3	...	41.4

(450 W), then 3 cycles of 3 min each on ROAST (700 W), after which, a clear solution resulted. The data obtained from DCP/AES analyses are presented in Table 8.

Ultrasonic Bath Treatment

While ultrasonic energy has been used for nebulization of a sample before introduction in a plasma emission source [*2,12,15*], there are no references of its use in attacking and dissolving the sample. Until now, a standard 400-W laboratory ultrasonic bath can be used to facilitate the dissolution of a sample under relatively mild conditions. A sample, mixed with an appropriate attacking medium (such as those described previously) is placed in a plastic bottle, which is suspended in the ultrasonic bath and sonicated at 10-min intervals. The bottles are checked periodically and vented as necessary. The action of the ultrasonic energy serves to increase the "intimacy" between the acid and sample surface, thus allowing a more efficient attack under milder conditions, minimizing potential loss of volatile species. An extra benefit arises from the action of the ultrasonic energy to superficially disrupt the patterned arrangement of atoms in crystalline materials, such as minerals and rock samples; allowing dissolution to occur without the need of fusion or pres-

TABLE 8—*Microwave-fluoroborate digestion (values are weight % unless noted).*

Element	Bottom Sludge	Vat Slime	Top Slag
Pb	47.1	8.75	17.8
Sn	2.08	13.3	59.4
Ca	166 μg/g	0.89	9.18
Cu	3.47	63.8	7.62
Zn	0.69	5.41	2.87
Sb	16.0	2.92	498 μg/g
Cd	4.38	855 μg/g	2.23
Bi	1.55	0.49	627 μg/g

NOTE: Samples were diluted with DI water after treatment. No hydrolysis was observed after two days.

sure digestion. Two materials were prepared by this method and analyzed by DCP/AES. One was a fluorescent zinc sulfide (ZnS) or sphaelerite, the other a National Bureau of Standards certified citrus leave material. The procedure involved sonication of 1 g of powdered sample with 2 mL each HCl, HF, and H_2SO_4 in a plastic bottle. A 300-W Branson ultrasonic bath, unheated, was used for the dissolution. Three cycles of 10 min were needed to completely dissolve the material. The results of analysis and correlation to certified values are shown in Table 9.

Conclusion

After reviewing the preponderance on numbers presented herein, it is evident that there exists a multitude of alternative preparation methods that can provide equally satisfactory results. The cheaper ZGS/TRI-M crucibles, the use of "solid" *aqua regia* for precious metal and ore dissolutions, mixing two good fusion fluxes to combine the best of both worlds, low pressure digestion

TABLE 9—*Ultrasonic bath preparations (values are μg/g in sample, unless noted and [K] = known, certified value; [M] = measured data).*

Element	USGS ZnS		SRM 1572	
	[K]	[M]	[K]	[M]
Zn	66.0%	65.8%	30	31.5
P	518	511	0.10%	0.11%
Fe	2.63%	2.59%	90	93
Mn	0.85%	0.83%	20	21
Mg	0.33%	0.32%	0.60%	0.53%
Cu	219	240	20	23
K	48	55	1.80%	1.61%
Cr	69	67	(2)	1.3
Pb	392	385	25	4.0[a]

[a] Loss of lead in this preparation was not investigated by replicate analysis.

bombs as a "mass preparatory" apparatus all have great potential as routine techniques. The data here show excellent correlation to values from "typical" preparations at a fraction of the time and cost. The chemistry is satisfactory as shown by the good reproducibility of replicate preparations: the use of liquid fusions, an alkali material (LiOH), and a series of organic chelating/complexing agents to draw the sample into solution. In this instance, EDTA stabilizes the alkaline earths and light transition elements; the tartrate binds the heavy metals and semi-metals while the alkaline pH dissolves the acidic-oxide elements: boron, silicon, germanium, phosphorus, arsenic, antimony, selenium, sulfur, molybdenum, tungsten, and vanadium. These procedures are directly transferable to microwave preparations, where direct heating serves the same purpose as pressure to facilitate the chemical attack. The results seen here are excellent in terms of their precision *and* accuracy when evaluated in the light of their bulk preparatory capabilities.

Discussion

When considering a new or improved method for implementation in your analytical environment, do not shirk away from the unusual or untried. The difficulties encountered in most analytical laboratories stem not from the inability of the chemist to know his or her analytical techniques but from a lack of knowledge of simple descriptive inorganic chemistry. No analytical procedure will work if the sample cannot be quantitatively and reproducible dissolved in a form suitable for analysis. If there is a way to solubilize lead with tartaric acid, use it in an existing preparation method. If alkaline EDTA is the only way to maintain silicon and calcium in the same solution without using a fusion, then consider the cost and time savings over "classical" techniques. It was by accident that a technician found that fusing a beryl sample (a Be-Al silicate) with sodium hexafluorosilicate quantitatively solubilized the beryllium as BeF_4^{-2}, while leaving the main interfering elements precipitated as silica (SiO_2) and cryolite (Na_3AlF_6). Fluoroboric acid cannot be bought in pure form but can be easily and safely made in the laboratory and is an ideal dissolution agent for many samples. Again, this can be combined with the use of supplemental stabilizing agents. Almost no one uses iodine anymore, but a methanolic iodine solution will oxidize and dissolve most ferrous and nonferrous metals, leaving any molecular compounds (oxides, carbides, nitrides, and intermetallic species) unattacked. Iodic acid with a little HF rapidly dissolves steels, including high Cb and tantalum alloys.

Fire assay is the only technique that is method intensive and is respected enough that it will always remain so. The authors are both analytical chemists by profession, but have been grass-roots, descriptive inorganic chemists since their first Gilbert Chem-Craft kits. There are thousands of good texts dealing with descriptive and reaction chemistry of the periodic table of elements and should be consulted for some background before trying to attack a new or unknown sample. Though there are only 106 actual elements, inorganic reaction chemistry can be as complex as that of the millions of organic compounds that exist. This leaves plenty of room for new developments and ideas in the field of sample preparation technology, and hopefully this paper will give a good start!

Acknowledgments

The authors wish to thank Thomas A. Edison, whose practical application of the Scientific Method inspired most of the developments shown here; Warren V. Miller, a mentor, former employer and superb synthetic inorganic chemist; Michael Carr of Rutgers University Geology Dept., for the rock samples; SpectraMetrics/Beckman, for maintaining the D.C. Plasma equipment; Karen R. Centrella, a nonferrous person that has good hearing; and Francis Coyle of KBI/Cabot, for his quality organization of the ASTM symposium for which this work was completed.

References

[*1*] Fresenius, C. R., *A System of Instruction in Quantitative Chemical Analysis,* John Wiley and Sons, New York, 1881, pp. 130-190, 227-353, 480-596.

[*2*] Van Loon, J. C., *Selected Methods of Trace Metal Analysis: Biological and Environmental Samples,* John Wiley Interscience, Toronto, Canada, 1985, pp. 6-13, 53-112, 170, 278.

[*3*] Staff, I. C. S., *Quantitative Analysis,* International Textbook Co., Vol. 1-4, 1930.

[*4*] Skoog, D. and West, D., *Fundamentals of Analytical Chemistry,* Holt, Rinehart and Winston, New York, 1963, pp. 128-149, 192-199, 725-760.

[*5*] Minczewski, J., Chwastowska, J., and Dybcznyski, R., *Separation and Preconcentration Methods in Inorganic Trace Analysis,* Ellis Harwood Ltd., Halsted Press, Chicester, England, 1983, pp. 9-34, 37-92, 316-353.

[*6*] Bock, R., *A Handbook of Decomposition Methods in Analytical Chemistry,* International Textbook Co. Ltd., London, 1979.

[*7*] *Handbook of Chemistry and Physics,* CRC Publishing Co., Ohio, 1959.

[*8*] Treadwell, F. P. and Hall, W. T., *Analytical Chemistry,* 9th ed., Vol. II, MIT Press, 1932.

[*9*] Jeffery, P. and Hutchison, D., *Chemical Methods of Rock Analysis,* 3rd ed., Pergamon Press, Oxford, England, 1981, pp. 18-58, 377.

[*10*] Phillips, C. S. and Williams, R. J., *Inorganic Chemistry, II-Metals,* Oxford Press, New York, 1966.

[*11*] Johnson, W. and Maxwell, J., *Rock and Mineral Analysis,* John Wiley and Sons, Toronto, Canada, 1981, pp. 92-121, 237-247, 263, 280.

[*12*] Beamish, F. E. and Van Loon, J. C., *Analysis of Noble Metals,* Academic Press, New York, 1966, pp. 30-76, 215-310.

[*13*] Burns, D., Townshend, A., and Carter, A., *Inorganic Reaction Chemistry—Reactions of the Elements and Their Compounds,* Ellis Harwood Ltd., Halsted Press, Chichester, England, 1981, Parts A and B.

[*14*] Vas, R. (producer), *Thomas Alva Edison—The Wizard Who Spat on the Floor,* NOVA/WGBH Educational Foundation, Boston, MA, 1980, show transcript.

[*15*] DeMenna, G. J. and Miller, W. V., *Preparation of Standards for Plasma Emission Spectroscopy,* Vol. 25, Issue 3, The Spex Speaker, Spex Industries, Metuchen, NJ, Sept. 1980.

[*16*] DeMenna, G. J., *Journal of the Fluorescent Mineral Society,* Vol. 13, 1985, pp. 35-40.

[*17*] *The Scientific American Cyclopedia of Receipts,* Notes and Queries, Munn and Co., New York, 1891.

[*18*] Sidgwick, N. V., *The Chemical Elements and Their Compounds,* Vols. 1 and 2, Oxford University Press, London, 1950.

Arnold Savolainen,[1] *Hank Griffin,*[1] *and George Olear*[1]

The Use of Modern Atomic Spectroscopy in Industrial Analysis

REFERENCE: Savolainen, A., Griffin, H., and Olear, G., "**The Use of Modern Atomic Spectroscopy in Industrial Analysis,**" *Chemical Analysis of Metals, ASTM STP 944,* American Society for Testing and Materials, Philadelphia, 1987, pp. 60-73.

ABSTRACT: Industrial laboratories are being forced to develop faster, more accurate and precise but less expensive analytical methods. This paper describes one laboratory's learning process over the past 20 years. The changes that occurred by changing from wet chemistry and arc/spark emission spectroscopy to atomic absorption spectrometry to manual and then automated plasma spectroscopy are described. The rationale of choosing a particular plasma spectrometer is explained along with how to automate specimen introduction, computerize data collection, and display results of a running analysis. An algorithm used to improve results is also described.

A number of different methods that were developed for the new methodology are described. These methods cover a wide range of topics such as plating bath analysis, steel analysis, precious metals analysis, comparisons to fire assaying, analysis of impurities in titanium dioxide (TiO_2), and solders. Along with these methods are some time studies that demonstrate the economic rational for buying this type of instrumentation.

KEY WORDS: industrial analysis, atomic spectroscopy, analytical capabilities, atomic absorption spectroscopy, interferences, plasma emission spectroscopy, plasma sources, echelle grating spectrometers, automatic analyses, multielement analyses, computerization, precision, accuracy, data handling

As technologies advance and process controls become tighter, industrial analytical laboratories are required to provide more information at less cost. This generally means relying on instrumental methods of analysis. Our laboratory analyzes all types of ferrous and nonferrous metals including precious metals for major, minor, and impurity elements. Developments in the field of atomic spectroscopy during the last 20 years have greatly improved the productivity of our laboratory. This paper describes our rationale in choosing analytical capabilities in the field of atomic spectroscopy.

---

[1] Supervisor of chemistry laboratory, senior chemist, and senior chemist, respectively, Texas Instruments, Inc., 34 Forest St., MS 10-16, Attleboro, MA 02703.

Atomic Absorption Spectroscopy

Twenty years ago, we relied on arc/spark emission spectroscopy and wet chemistry for all our metals analysis. These methods were not quantitative enough for trace analyses, and major component analyses took such a long time that the lab needed approximately twice as many technicians than it presently needs.

In 1969 we bought an atomic absorption spectrophotometer (AAS) because we determined that it could easily replace much of our previous methodology for trace, minor, and major component analyses of metallic elements. We used AAS for five years and converted most metal analyses to this instrument. During this time, we found that, although AAS is an extremely useful technique, it does have some drawbacks. Chemical interferences can be a problem requiring closely matched specimens and standards. Fuel mixtures for the various kinds of flames should be closely controlled or they can lead to interferences. Calibration curves generally do not cover wide concentration ranges. High solid content solutions cannot be easily introduced into the flame because they clog the burner. This constitutes a safety hazard as well as completely changing the calibration.

This list of potential problems with AAS is not meant to condemn the technique; in fact, we find AAS to be a quantitative and precise analytical technique. What it points out is that when using AAS, like any instrumental technique, one should be aware of both the capabilities and limitations. The capabilities are usually spelled out in detail in instructions from the manufacturer. One learns the limitations through experience.

We also discovered that instrumental techniques are useful only after the proper chemistry has been worked out for a particular analysis. Everyone in the lab, chemists and technicians alike, learned more chemistry developing AAS analyses than they ever had learned running wet chemical analyses. It is very important to remember that the chemistry involved in the specimen and standard preparation is more important than the actual instrumental analysis.

Plasma Emission Spectroscopy

In 1974, we had overextended the capacity of the AAS and were looking for a second instrument. During the late 1960s and early 1970s, a new family of instruments became available, plasma emission spectrometers [*1,2*]. It quickly became apparent that they would compliment our AAS capabilities because they could be used to do analyses that could not be done by AAS, that is, phosphorous, low levels of silicon, boron, refractories [*3*], and so forth. Generally, they also had much larger linear working ranges, which meant that we would have to make far fewer dilutions, and there were fewer of the previously described interferences.

In 1974, the only commercially available plasma spectrometer was the direct current plasma (DCP) spectrometer. In 1975, inductively coupled plasma (ICP) spectrometers also became available. Which type of plasma emission spectrometer should one buy? The main area of concern with instrument manufacturers, as well as in the literature, was whether one plasma source was better than another. Plasmas are nothing more than excitation sources. The two that were commercially available, inductively coupled and direct current plasmas, can both be used to cause all the elements and many molecular species to emit radiation, which by itself is useless. The analytical usefulness of this radiation is related to the monochrometer or polychrometer. The plasma sources both have advantages and disadvantages, but neither one is the ultimate excitation source.

In our case, the most important parameter was resolution. In the analysis of metals, because of the large number of emission lines, spectral overlap was the most important factor. When we considered the resolution of an echelle monochrometer, approximately 0.01 nm in the ultraviolet region, versus the resolution of conventional monochrometers, approximately 0.03 nm in the ultraviolet region [*4*], it became apparent that the resolution of the monochrometer would be the determining factor in the type of plasma emission spectrometer we would buy. Since the echelle grating came with the DC plasma as a complete spectrometer, this is what we bought.

When we got our first DC plasma echelle grating spectrometer (DCPES), we were faced with several analytical problems. Following are some of the methods we developed to solve these problems.

One of our first methods was the analysis of phosphorous in electroless nickel plating baths. We were using an ammonium phosphomolybdate gravimetric procedure in accordance with ASTM Method for Chemical Analysis of Steel, Cast Iron, Open-Hearth Iron, and Wrought Iron (E 30), which required 4 to 5 h for one set of specimens, but we needed a method that was much faster and just as accurate. We found that the baths could be analyzed directly by DCPES using standards of phosphorous in water. The agreement with the gravimetric method by DCPES (Table 1) was excellent, and the anal-

TABLE 1—*Phosphorus in nickel plating baths.*

DCPES			
213.6 nm	214.9 nm	253.5 nm	Gravimetric
0.20	0.19	0.20	0.21
0.13	0.13	0.14	0.14
0.20	0.21	0.20	0.22
0.21	0.22	0.21	0.22
0.06	0.07	0.07	0.07
0.06	0.05	0.05	0.05

ysis time was only 0.5 h/set of specimens. This saved us over 100 h/year, or at a rate of $20/h, we saved about 10% of the cost of the instrument on this one job in the first year.

Automated Analyses

In 1976, we found that the capacity of both the DCPES and the AAS was not sufficient. The problem is typical of most analytical labs: give the customer a little and he wants a lot. In this case, we were being asked to analyze multiple elements in each specimen. An example of this was the analysis of impurities in fine silver. Previously we determined the concentration of two impurities (copper and lead) by arc emission spectrography but were now determining 13 impurities by DCPES. At just that time, the multielement DCPES [5] was introduced. This was a brand new spectrometer with an echelle polychrometer that allows one to simultaneously analyze for up to 20 elements at a time. It also contains a new three-legged DC plasma with the stability and limited spacial resolution in the plasma necessary for multielement analyses.

While waiting for the delivery of our multielement spectrometer, we were also doing some development work. The multielement analyses would be very fast but, having a technician sit in front of the instrument to feed in specimens and push buttons, would be very counter-productive. Their time could be better spent in preparing more specimens, interpreting results from previous analyses, and so forth. With this in mind, we developed an automatic sampling system for the spectrometer [*6*]. It consisted of a turntable connected to the spectrometer by an interface that works on a timing system. The turntable automatically positioned standards and specimens for introduction to the spectrometer. The interface automatically activated the instrument analysis cycles.

As long as the specimens and standards were placed in the turntable in the correct order, the spectrometer would run automatically for hours at a time. In addition, the system restandardized the spectrometer with both high and low standards at regular intervals. The time saved using this system is truly impressive. A 4-h run on the spectrometer required less than ½ h of actual operator's time. Within three months of the time our multielement DCPES arrived, it was running automatically.

Multielement Analysis

Development of multielement analytical methods is a complicated undertaking. The chemistry of dissolving a number of elements in the same solution is complex. This also applies to preparation of the standards. For accurate analysis, a very important parameter is the choice of emission lines. When choosing the proper emission lines, a complete study of interferences must be undertaken.

There are five main types of interferences: transport, chemical, background, spectral, and enhancement or depression [7]. The first two can be overcome by proper specimen and standard preparation. The last three can be identified by scanning the spectral area of analytical importance. The ability to scan was not offered as an option with this instrument so we developed a scanning device using a simple drive wheel on the horizontal grating dial. Figure 1 shows various scans in a very difficult matrix, titanium dioxide. Scans need to be done while aspirating (1) water, (2) the aqueous analyte, (3) titanium dioxide (TiO_2) solution, and (4) TiO_2 plus analyte solution. The first set of scans, for yttrium, shows what would be a nonresolved spectral interference with any other commercial spectrometer. The two emission lines of yttrium and titanium in the 437.5-nm region are separated by only 0.011 nm; however, while there is some spectral overlap, they are sufficiently resolved by the echelle grating so that the yttrium emission line is a useful analytical line in this matrix. One would have to understand that when using this yttrium line in a titanium matrix that titanium would present a background for the yttrium. As long as the background is understood, it can be compensated for and, therefore, will not be a problem.

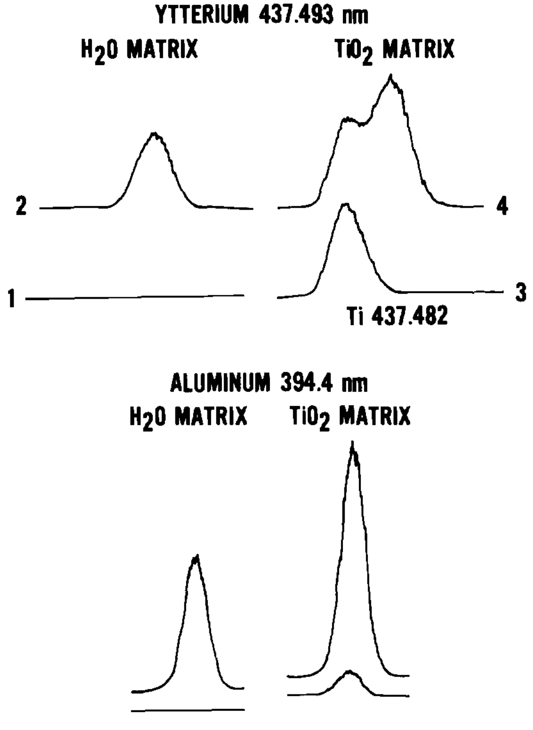


FIG. 1—*Wavelength region scans.*

The second set of scans (Fig. 1) is for aluminum at 394.4 nm. In this case, there is an emission line that exactly overlaps the aluminum emission line. The closest titanium emission line is at 394.78 nm. This is so distant that it would not show up on this scan, but it would probably present a spectral overlap with a conventional gratings. What this means is that we have either discovered a previously unreported titanium emission line or that another element is present in titanium, probably aluminum. To prove this, a scan at another aluminum emission line would be necessary.

One of the first multielement methods developed was the analysis of impurities in precious metals. Because of the large volume of material and the required purity, we had been analyzing for impurities in gold, silver, platinum, and palladium by arc emission spectroscopy. When we converted to a DCPES method, we analyzed specimens in duplicate for 13 impurities. The method for the analysis of fine silver, for example, is a very easy procedure [*8*]. A 2-g specimen is dissolved in nitric acid, diluted to 25 mL, and analyzed for impurities at the parts per million level. Emission wavelengths were chosen for their sensitivity and freedom from interferences. We use this method to analyze all the incoming fine silver as well as all the silver alloys made in our plant. Other precious metals are checked in a similar manner. The time saved over the arc emission method was about 20%.

Another analytical procedure development was the analysis of impurities in lead-tin solder [*9*]. This analysis was being performed by the solder supplier, but it took two to three weeks. We needed faster turnaround to insure the purity of the solder baths. The hardest part of this method was specimen preparation. As mentioned previously, the chemistry of the system is often the most important part of the analysis. Dissolution of lead and tin together is difficult by most procedures. We found that by heating the specimen in hydrobromic acid, just below the boiling point, complete dissolution was almost always achieved. Occasionally, a precipitate would remain. By the addition of a few drops of 10% nitric acid, we have been successful in complete solder dissolution. The advantage of this technique is that the purity of the acids is never in question. Other techniques, that is, fluoroboric acid dissolution, present purity problems.

After dissolution, the analysis was rather routine. Many of the same wavelengths used for precious metal analyses worked for solder analyses. Analysis time is less than 1 min per element when done in lots of at least ten specimens. This analysis is now a routine procedure in the lab. A one-to-two day turnaround time gives production much better control of their solder operations.

Analysis of steels was another method that easily lent itself to multielement spectrographic analysis. Anybody who has had to analyze steels by wet chemistry knows just how difficult that is. Direct reading arc emission spectrography is an excellent method, but it requires a dedicated instrument, more suited for use in a foundry. With plasma emission spectroscopy, we are now prepared to automatically analyze different steel alloys for up to 20 elements at once. This required a complete knowledge of emission lines, interferences, concentration ranges, and chemistry. With the proper emission wavelengths (Table 2), a single iron matrix standard can be used to analyze a number of different steel alloys including cast irons, carbon steels, low-alloy steels, and electric steels [*10*]. The analytical method is very straightforward; dissolve the specimen, prepare the proper standard, and analyze automatically. Dissolution involves the use of three acids: hydrochloric, nitric, and hydrofluoric, as well as a persulfate to help breakup carbides. The time involved is longer than by arc emission but considerably shorter than by wet chemical techniques. We are presently analyzing a large number of steel specimens for incoming inspection. The result is that the quality of incoming steel has improved, and our product rejection rates have dropped.

Precious Metal Analysis

The analysis of precious metals, whether they were bonded, plated, or in alloys, had to be both accurate and precise but was usually very time intensive. While instrumental methods would certainly save time, a study was undertaken to determine differences between fire assaying, the standard in the field, and DCPES or AAS. It was found that the DCPES is more accurate than fire assaying, does not have the interferences associated with AAS, and is faster than either of the other two when run in an automatic multielement mode.

Our lab does a large number of fire assay analyses. We wanted to determine whether DCPES could be used as an acceptable alternative to fire assaying. When comparing DCPES to fire assaying, the first test we ran was an

TABLE 2—*Wavelengths for steel analysis.*

Element	Wavelength, nm	Detection Limit, ppm	Linear Concentration Limit, mg/L
Al	394.4	5	300
B	208.8	10	300
Co	350.2	6	200
Cr	359.3	2	120
Cu	327.3	1	60
Mn	257.6	2	200
Mo	281.6	3	300
Nb	309.4	9	200
Ni	351.5	4	300
P	213.6	12	300
Si	288.1	3	500
Sn	326.2	28	300
Ta	240.0	12	200
Ti	338.3	2	200
V	270.0	10	300
Zn	249.6	10	100

analysis of the parted gold bead [*11*], that is, a precious metal bead that had been separated from the specimen's base metal in a furnace. In fire assaying, the parting technique is used to dissolve all other precious metals from the gold in a fire assay collection bead. The resulting gold bead should be, essentially, pure gold. We found substantial amounts of silver in the gold after parting, which indicates that the parting does not completely separate the precious metals from the gold.

The next step was to compare the entire fire assay operation to DCPES [*12*]. Figure 2 shows analyses of gold at the part per thousand (ppt) level in refinery specimens performed by the two methods. The straight line shows the curve that would result if the two methods gave identical results. The actual results all fall on the plasma emission side of the line, which means that, for gold, plasma emission gives higher results than fire assaying. Fire assaying does have two losses inherent in the method, evaporation and absorption in the slag [*13*]. Because of this, fire assaying values would be expected to be low.

Another analytical procedure involved the determination of gold in electrolytic gold plating baths. We had been determining the gold by AAS. An experiment was set up to compare gold analyses by AAS, DCPES, and fire assaying. The first thing we found was that the AAS analysis had to be very carefully controlled because the flame had a significant effect on the analysis

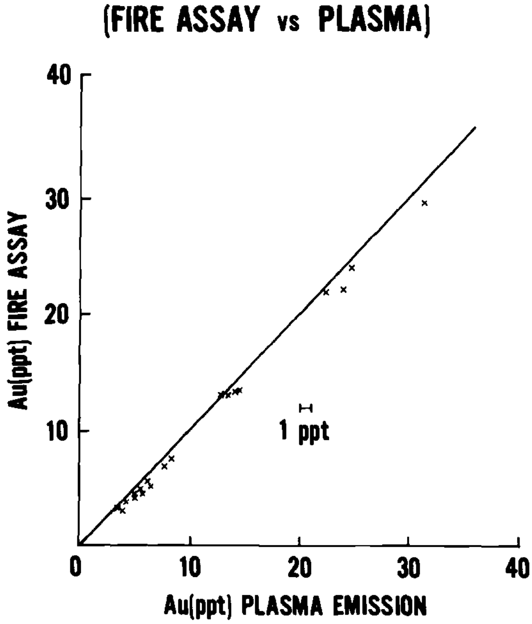


FIG. 2—*Gold in refiner specimens.*

[*14*]. A specimen of a gold bath that had been diluted to about 10 μg/mL was analyzed, using a 10-μg/mL gold standard in aqua regia. In an air-acetylene flame, the concentration of gold changed dramatically as the flame conditions were changed. The nitrous oxide/acetylene flame was a much better choice, but it also showed some variation. This meant that standards and specimens had to be very carefully matched, and flame conditions had to be controlled in order to get acceptable gold results using AAS. Five sample types were analyzed by AAS, DCPES, and fire assaying. The first four samples are gold plating baths; the last is gold plated beryllium copper. In all cases, precisions were determined by analyzing different dilutions or specimens, not by analyzing the same dilution or specimen many times. The AAS results were obtained under optimum AAS operating conditions. The precision of all methods is good. The two spectroscopic methods both have essentially the same precision, which is not as good as the fire assaying method. The accuracy is a different story. The DCPES results are all just slightly higher than the fire assay results. The difference between the two is constant at about 0.07, which was expected from the previous study. AAS results vary from the fire assay results by 0.16, more than double the DCPES results. Changing from AAS to DCPES for these analyses would mean no difference in analysis time and a 60% time savings compared with fire assaying.

The proof of the reliability of the DCPES method for the analysis of scrap material can be shown in total compositional analyses. For the gold and silver composition specimens, we have analyzed for all elements with concentrations greater than 0.2 parts per thousand (ppt). The total results are all very close to 100% with an average for 27 analyses of 99.90% (Tables 3 and 4).

Precision Improvements

During the first years using the DC plasma, our main objective had been to improve accuracy, that is, parameters not involved in the actual analysis. We investigated better specimen preparation, selection and characterization of wavelengths, understanding interferences and enhancement, and improved matching of standards and specimens. Little, however, was done to improve the precision of the analysis, that is, parameters directly affecting the actual analysis.

The manufacturer advertised analytical precision for this spectrometer in the order of ±2% relative standard deviation (RSD). In some of the work we are doing, we need to achieve precisions in the order of ±0.5% RSD. Internal standardization is generally used to increase precision in emission spectroscopy; however, developing internal standards for multielement analysis is a long and complex procedure. The internal standard must be properly selected for each element. Specimen preparation is longer and, therefore, more costly. As an alternative, a procedure for improving precision by linear correction of data using a computer was developed [*15*].

TABLE 3—*Comparison of gold results, fire assay, plasma emission, AAS.*

Specimen	Fire Assay	Plasma 242.8 nm	Emission 267.5 nm	AAS[a] 242.8 nm	 267.5 nm
24-kt. soft gold	6.14 ± 0.18%	6.20 ± 0.62%	6.22 ± 0.57%	6.30 ± 0.88%	6.34 ± 0.95%
24-kt. soft gold	3.28 ± 0.59%	3.34 ± 0.49%	3.36 ± 0.68%	3.44 ± 0.72%	3.42 ± 0.65%
23.8-kt. hard gold	4.81 ± 0.08%	4.89 ± 0.72%	4.87 ± 0.78%	5.00 ± 0.61%	5.02 ± 0.42%
23.8-kt. gold strike	4.23 ± 0.29%	4.26 ± 0.43%	4.28 ± 0.61%	4.37 ± 0.77%	4.37 ± 0.61%
Gold plated Be/Cu	0.76 ± 1.33%	0.81 ± 1.98%	0.83 ± 2.30%	0.90 ± 1.62%	0.88 ± 1.71%

NOTE: All results are in μg/mL.

[a] A nitrous oxide-acetylene flame was used.

TABLE 4—*Total composition by plasma emission concentration in specimen.*[a]

Specimen	ppt								
	Zn	Cd	Sn	Fe	Ni	Au	Ag	Cu	Total
Ag Component									
1	12.5	16.0	0.5	0.4	53.0	*	237.0	63.7	95.8
2	100.0	26.0	0.3	*	1.2	*	237.3	63.0	99.5
3	40.0	27.0	0.6	0.8	32.0	*	337.0	56.4	100.2
4	111.0	0.1	2.4	0.4	18.0	*	232.3	63.1	99.6
5	34.2	16.1	1.5	5.0	84.5	*	269.3	57.3	98.5
6	6.5	1.2	2.3	*	5.5	*	412.2	53.4	96.2
7	14.4	23.5	0.5	0.3	46.0	*	319.7	59.0	99.5
8	12.8	21.8	0.4	0.3	19.8	*	289.0	66.3	100.7
9	130.0	1.7	0.6	*	2.7	*	272.1	60.8	101.6
10	12.7	1.3	3.4	*	1.8	*	487.8	50.4	101.1
11	82.5	1.1	1.6	*	1.4	*	309.5	58.3	98.0
12	134.0	1.2	0.4	0.5	0.7	*	292.5	63.7	102.7
Ag Steel									
1	*	5.0	*	19.7	2.0	0.36	57.0	84.9	93.3
2	*	6.6	*	21.5	1.6	0.34	57.3	88.8	97.5
3	*	3.9	*	32.8	*	0.32	33.4	89.2	96.3
4	*	4.3	*	35.5	*	0.34	29.9	88.8	98.8
5	*	3.8	*	31.5	10.5	0.30	44.4	87.9	96.9
6	*	2.8	*	31.1	11.3	0.31	43.5	86.4	95.3
7	*	3.0	*	46.0	4.0	0.32	52.5	84.8	95.7
8	*	4.2	*	51.0	4.0	0.32	51.0	85.3	96.3
9	*	3.5	*	34.0	4.8	0.30	41.2	87.1	95.5
10	*	4.3	*	31.5	5.1	0.36	43.7	87.8	96.3
Au Component									
1	2.7	*	9.2	2.0	106.0	8.96	0.3	88.8	101.7
2	3.3	*	15.1	1.8	87.0	8.92	0.4	89.7	101.4
3	2.1	*	6.0	*	118.0	10.3	3.05	85.4	99.4
4	2.5	*	16.2	*	104.0	2.61	2.84	88.3	101.2
5	3.5	*	10.5	1.2	112.0	7.65	2.84	86.0	99.7
6	2.3	*	16.3	2.5	133.0	15.6	4.5	83.4	100.8
7	2.8	*	8.8	*	127.0	15.1	4.4	84.5	100.3
8	3.0	*	9.7	1.6	108.0	3.86	3.1	86.7	99.6
9	3.1	*	15.9	*	105.0	3.32	1.88	88.6	101.5
10	3.0	*	4.3	*	103.0	4.09	2.11	89.0	100.6
11	2.8	*	5.4	*	104.0	1.85	2.00	88.2	99.8
12	3.0	*	5.5	*	105.0	2.12	2.10	87.9	99.7
13	2.7	*	4.5	*	105.0	2.51	1.76	86.4	98.1
14	2.5	*	4.5	*	105.0	2.01	1.60	88.3	99.9
15	1.4	*	5.0	*	106.0	2.65	1.00	88.6	100.2

[a] * designates less than 0.2 ppt.

The method requires that when specimens are analyzed, high and low standards are run before and after each group of one to five specimens. Linear correction calculations assume that the instrumental drift is linear between the standards. Experimentally, we have proved it to be a reasonable assumption. First, corrected high and low standard values are calculated for the time each specimen is analyzed using a straight line equation. Next, the specimen concentration is calculated using the corrected standard values and the specimen reading. While this appears very time consuming, especially for multielement analyses, the calculations are easily and rapidly carried out in even the simplest of computers. A study was carried out comparing corrected and uncorrected values for the analysis of copper in 50 scrap specimens. Average precision per specimen improved from ±0.7 to ±0.3% RSD.

Linear correction calculations affect not only precision but also accuracy. Comparison of the corrected and uncorrected values with values from gravimetric analysis of copper indicates better accuracy for the corrected values. The average deviation from gravimetric results for corrected DCPES values was 1.2 compared to 1.9 for uncorrected DCPES data.

Another technique for improving precision is gas displacement flow injection sampling [*7,16*]. The gas displacement pumping system provides a continuous flow of sample matrix/solvent to the spectrometer nebulizer, eliminating any pulsing and providing a viscosity independent flow rate. To do this, a continuous stream of solvent is presented to the nebulizer of the spectrometer. A discrete reproducible microliter volume of sample is injected into the stream for analysis. The spectrometer integrates the intensity of the emission signal during the time the sample volume passes into the plasma. Analytical precision using the flow injection sampling technique is improved when compared to that of peristaltic pump sampling [*7*].

A second advantage of this technique is reduced specimen preparation time. Merging one or two solvent streams with the sample carrier stream provides a range of dilution ratios, thereby eliminating manual dilutions. The study of the analysis of refiner scrap for copper has demonstrated that analysis efficiency is improved by 20% using the diluting mode of the flow injection system without loss of precision or accuracy.

Computerization

Automatic, multielement plasma spectrometric analyses generate so much data that computer handling of data is a necessity. Most instrument manufacturers now provide computerized data handling and instrument control with their instruments. When we first automated our multielement spectrometer, such capability was not available. First a Zenith Z-80 microprocessor and later a Texas Instruments professional computer (TIPC) were interfaced with the spectrometer and sample turntable. We realized from our experiences that the computer should provide three functions: synchronize the operation of the turntable and spectrometer, monitor and provide a warning for any real-time problems in the analyses, and collect and manipulate data for final presentation. The remaining portion of this paper will explain how, using the TIPC, we accomplished this.

The TIPC is connected to both the spectrometer and automatic sampler by means of a parallel interface. Activation of the sampling mechanism of the turntable and initiation of the analysis routine of the spectrometer are accomplished by means of simple print statements from the computer software. The only hardware changes were the installation of a solid state relay and a latching relay in the turntable. This work was all completed in our lab by people with a basic knowledge of electronics and experience in interface programming [*18*].

Data manipulation required the use of the raw diagnostic data from the spectrometer. In order to gain access to this data, a modification was made in the instrument microprocessor by the manufacturer so we could collect this data by the Z-80 computer. This modification is not necessary when using the TIPC because of its larger storage capacity. The raw data, including electronic gains, standard values, and integrations of all elements for each analysis, are collected in a one-dimensional array. Any extraneous data are eliminated. The computer then checks the integration values and eliminates any that show more than a ±4% relative deviation from the mean. This eliminates spikes in the data caused by any phenomenon not directly related to the actual analysis. The mean value is then stored for the elements for each specimen and standard tested. At the end of an analysis set, consisting of one to five specimens and the standards run before and after the specimens, drift correction calculations are performed and the results printed out in the prescribed format. If desired, this data can also be stored and further manipulated for such things as weight correction, normalization, statistical analysis, control charting, and so forth.

Computer handling and manipulation of data are fast and accurate; however, if there is an error in specimen or standard preparation, spectrometer setup, or specimen sequencing, there is no way of knowing since neither the diagnostic data nor the data for standards can be reviewed. Using computer graphics, we developed an excellent method for displaying data for review. A moving bar graph of diagnostic data for a set of 13 specimens and standards is displayed. Display can be of any one desired element of the analysis. Bars are blue for the standard and green for the specimens. If the value for a specimen is outside the range of the standards, then the bar is displayed as red. The operator can immediately tell if there is a problem with the analysis. Comparison between high and low standards will tell if there is the appropriate intensity difference. Comparing standards before and after a sample group indicates the amount of instrumental drift. Finally, if the specimens are repeated, then precision of the analyses can be calculated. It is then the operator's responsibility to determine the cause of a problem if one appears. This type of monitoring real-time data can save valuable time when problems arise.

In summary, the DC plasma echelle grating spectrometer is a very useful industrial lab analytical instrument. Many analyses that are difficult or impossible by wet chemical or other instrumental techniques become very routine using the DCPES. This does not mean that there is nothing new happening in the field of plasma spectroscopy. There is still a very large area open for original ideas in the field, and industrial chemists should take advantage of this field to develop some new methods, theories, or equipment.

References

[*1*] Skogerboe, R. K. and Urasa, I. T., *Applied Spectroscopy,* Vol. 32, 1978, p. 527.

[*2*] Greenfield, S., McGeachin, M. McD., and Smith, P. B., *Tantala,* Vol. 22, 1975, p. 1.

[*3*] Sholes, P. H., *Analyst,* Vol. 93, 1968, p. 197.

[*4*] Cresser, M. S., Keliher, P. N., and Wohlers, C. C., *Analytical Chemistry,* Vol. 45, 1973, p. 111.

[*5*] Reednick, J., *American Laboratory,* Vol. 11, 1979, p. 53.

[*6*] Griffin, E., Bowen, R., and Savolainen, A., "Automation of a Multichannel DC Plasma Emission Spectrometer," *The 5th Federation of Analytical Chemistry and Spectroscopy Societies Meeting,* Boston, MA, 1978.

[*7*] Griffin, E. and Savolainen, A., "Wavelength Selection for a Multielement DC Plasma Emission Spectrometer," *The 5th Federation of Analytical Chemistry and Spectroscopy Societies Meeting,* Boston, MA, 1978.

[*8*] Savolainen, A., Griffin, H., and Olear, G., "Analysis of PPM Level Alkali Metals and Impurities in Fine Silver and Silver Alloys by Plasma Emission Spectroscopy," *The 9th National Conference on Spectrochemical Excitation and Analysis,* Edgartown, MA, 1984.

[*9*] Griffin, H. and McNulty, R., "Analysis of Impurities in Lead," *New England Conference on Current Developments in Spectrochemical Excitation and Analysis,* Woods Hole, MA, 1978.

[*10*] Belliveau, J., Griffin, H., and Savolainen, A., *New Analytical Techniques for Trace Constituents of Metallic and Metal-Bearing Ores, STP 747,* American Society for Testing and Materials, Philadelphia, 1981, pp. 77-90.

[*11*] Skwarto, J., Savolainen, A., Olear, G., Marvelle, B., and Griffin, H., "Multielement Analysis of Fire Assay Collection Beads by Multichannel DCP Spectrometer," *International Precious Metals Institute Seminar,* 1984.

[*12*] Griffin, E. and Savolainen, A., "Analysis of Silver Scrap by DC Plasma Emission Spectroscopy," *The 5th Federation of Analytical Chemistry and Spectroscopy Societies Meeting,* Boston, MA, 1978.

[*13*] Furman, N. H., *Standard Method of Chemical Analysis,* P. Van Nostrand Company, Princeton, NJ, p. 475.

[*14*] Griffin, H., Savolainen, A., and Haschke, R., "The Use of DC Plasma Echelle Grating Spectroscopy for the Analysis of Plated Gold," *New England Conference on Current Developments in Spectrochemical Excitation and Analysis,* Boston, MA, 1980.

[*15*] Savolainen, A., Griffin, H., and Olear, G., "Standard Updating and Linear Regression Correction for Automatic Analysis of DC Plasma Emission Echelle Grating Spectroscopy," *The 6th National Conference on Spectrochemical Excitation and Analysis,* Edgartown, MA, 1981.

[*16*] Shugar, G. T., Shugar, R. A., and Bauman, L., *The Chemists' Ready Reference Handbook,* McGraw Hill Book Company, New York, 1985.

[*17*] Savolainen, A., "Improved Precision with a Plasma Emission Echelle Grating Spectrometer," *Labcon New England '84,* 1984.

[*18*] Olear, G., Bernard, T., Savolainen, A., and Griffin H., "Automation of an Echelle Grating Spectrometer," *The 7th National Conference on Spectrochemical Excitation and Analysis.* Edgartown, MA, 1982.

Raymond K. Hertz[1]

General Analytical Chemistry of Beryllium

REFERENCE: Hertz, R. K., "**General Analytical Chemistry of Beryllium,**" *Chemical Analysis of Metals, ASTM STP 944,* F. T. Coyle, Ed., American Society for Testing and Materials, Philadelphia, 1987, pp. 74-88.

ABSTRACT: A number of classical methods for the determination of beryllium are described in the literature. Gravimetric methods in which beryllium is weighed as the oxide or the pyrophosphate are employed for relatively pure materials, but careful separation of interfering elements is required. A useful volumetric method is based upon the precipitation of beryllium hydroxide, addition of fluoride to complex beryllium, and titration of the liberated hydroxide; but this method is also subject to many interferences. Spectrophotometric reagents, such as aluminon and *p*-nitrophenylazoorcinol, and fluorometric reagents, such as morin, have been used to determine beryllium: but for most applications atomic emission spectrometry and atomic absorption spectrophotometry have replaced these methods. The emission of neutrons by gamma-irradiated beryllium is the basis for a rapid, relatively interference-free beryllium analyzer, which requires minimal sample preparation and may be used for practically any matrix.

KEY WORDS: beryllium, determination, gravimetric analysis, volumetric analysis, spectrophotometric analysis, fluorometric analysis, atomic absorption, emission, plasma emission, spectrometric analysis, separation

Although beryllium is a member of Group IIA of the periodic table, its chemical and physical properties differ markedly from the other elements of this group; thus, beryllium is usually not regarded as an alkaline earth metal. The bonds beryllium forms with nonmetallic elements (other than fluorine) are predominantly covalent in contrast to the ionic bonding prevalent in the compounds of the alkaline earth metals. Pure beryllium halides (except beryllium fluoride) can be sublimed readily and have low conductivities in the melt. The covalency of beryllium compounds can be explained by the high charge-to-radius ratio of the Be^{+2} ion (6.45 elementary charge units/Å), which is similar to the charge-to-radius ratio for the highly polarizing Al^{+3}

---

[1] Senior chemist, Analytical Development, Brush Wellman Inc., Elmore, OH 43416.

ion (6.00 elementary charge units/ Å). Beryllium, in fact, does exhibit many chemical similarities to aluminum. Both metals resist attack by pure, concentrated nitric acid because of the formation of a coherent oxide coating. Both elements form amphoteric hydroxides that dissolve readily in strongly alkaline solutions to form anionic complexes.

Beryllium also exhibits many similarities to the Group IIB metals, zinc and cadmium. Both beryllium and zinc form covalent oxide carboxylates. The crystalline structures of many beryllium compounds, such as beryllium oxide (BeO), beryllium hydroxide ($Be(OH)_2$), and beryllium sulfide (BeS), correspond to structures of their zinc analogs. Beryllium differs from both aluminum and the group IIB elements in its inability to expand its coordination sphere to six because of its small ionic radius and the inaccessibility of its 3d orbitals.

Several works covering the chemical and physical properties [*1-8*] and the analytical chemistry [*9-18*] of beryllium are available.

Safety

Beryllium and its alloys and compounds can be handled safely in the well-equipped chemical laboratory if reasonable precautions for dealing with toxic materials are rigorously followed.

In susceptible individuals, inhalation of dusts, fumes, or mists containing beryllium, its compounds, or its alloys may cause chronic beryllium disease, a serious chronic lung disease. In addition, acute pneumonitis may result from inhalation of soluble beryllium compounds. Contact of soluble beryllium compounds with skin or eyes may cause irritation or rash ulcers. Beryllium is listed as a potential carcinogen in the International Agency for Cancer Research Monograph Series and the National Toxicology Program Annual Report on Carcinogens, as beryllium compounds have produced tumors in several species. No convincing evidence exists that beryllium is carcinogenic in humans.

All operations that might produce airborne beryllium must be conducted under local exhaust ventilation. Spilled solutions containing beryllium must be wiped up immediately to prevent dried residues from becoming airborne. Provision must be made for the isolation and safe removal of beryllium-containing dusts. Liquid and solid wastes containing beryllium must be disposed of in accordance with all applicable federal, state, and local regulations.

Strong acids or bases can react violently with beryllium and some of its alloys, particularly when finely divided.

Those unfamiliar with the handling of beryllium-containing materials should consult Refs *1,3,8,* and *19* for appropriate safety practices. Further assistance in establishing safe procedures, as well as Material Safety Data Sheets for beryllium and its compounds, may be obtained from the supplier of the material.

Beryllium Standards

Relatively few beryllium-containing standard reference materials are available. The National Bureau of Standards[2] has offered six copper-beryllium standards: the wrought standards 1121 (1.89% beryllium), 1122 (1.75% beryllium), and 1123 (0.46% beryllium); and the chill cast standards C1121 (1.92% beryllium), C1122 (1.75% beryllium), and C1123 (0.46% beryllium). Only C1121 and C1123 are still available. Eight copper-beryllium standards have been fabricated by Centre Technique des Industries de la Fonderie[3]: 1593 (2.36% beryllium), 1677 (0.85% beryllium), 1678 (0.135% beryllium), 1707 (0.65% beryllium), 1708 (2.96% beryllium), 1722 (2.19% beryllium), 1723 (0.78% beryllium), and 1735 (1.12% beryllium). Beryllium metal standard reference materials are available in powder and chip form from the Department of Energy.[4] Beryllium contents range from 98.38 to 99.40%.

The analysts choices are also limited when a source of high-purity beryllium is required for standard preparation. Beryllium metal produced by magnesium reduction of beryllium fluoride is available from a number of laboratory supply houses. This material normally contains the metallic impurities magnesium, aluminum, silicon, titanium, chromium, manganese, iron, nickel, and copper, at concentrations above 100 ppm. Electrorefined beryllium flake, containing several hundred parts per million total metallic impurities (primarily lithium, potassium, and silicon, is not produced at the present time, but may be available from some suppliers in limited quantity.

Beryllium oxide can be used in standard preparation; but the commercial product, which is calcined at high temperature for ceramic production, is difficult to dissolve in most matrices. Highly pure beryllium oxide can be produced by recrystallizing reagent grade beryllium sulfate ($BeSO_4 \cdot 4H_2O$) several times from deionized water containing (ethylenedinitrilo)tetraacetic acid (EDTA) and calcining the purified salt at 900°C to constant weight. The acid form or ammonium salt of EDTA should be used to avoid contamination of the product with sodium. Beryllium oxide prepared in this manner dissolves readily in mineral acids and contains less than 10 ppm of any metallic impurity.

Beryllium sulfate ($BeSO_4 \cdot 4H_2O$) and beryllium nitrate ($Be(NO_3)_2 \cdot 3H_2O$) can be used to prepare standard beryllium solutions, but the salts vary in composition. The solutions prepared from these materials must be analyzed by a gravimetric or volumetric method to assign accurate beryllium concentrations.

Basic beryllium acetate, $Be_4O(C_2H_3O_2)_6$, is a covalent compound of well-

---

[2] Office of Standard Reference Materials, Room B311, Chemistry Building, National Bureau of Standards, Washington, DC 20234.

[3] Available in the United States from Brammer Standard Co., Inc., 14603 Benfer Road, Houston, TX 77069.

[4] Department of Energy, New Brunswick Laboratory, D-350, 9800 South Cass Avenue, Argonne, IL 60439.

defined stoichiometry, which is frequently used to prepare standard beryllium solutions. The commercially available compound, which normally contains less than 100 ppm total metallic impurities, can be further purified by sublimation or by recrystallization from chloroform. It is insoluble in water, but dissolves slowly in hot mineral acids.

Sample Dissolution

Beryllium metal dissolves readily in dilute or concentrated sulfuric, hydrochloric, or hydrofluoric acids. The reaction, which can be vigorous or even violent, can be controlled by covering the sample with water and adding the acid slowly and in small quantities. Pure concentrated nitric acid leaves beryllium virtually unattacked, but traces of hydrochloric, hydrofluoric, or sulfuric acid result in rapid reaction. Beryllium also dissolves readily in ammonium bifluoride or sodium hydroxide solutions. The choice of a dissolution matrix frequently depends upon the impurities that must be determined.

Most beryllium-containing alloys (including copper-beryllium, nickel-beryllium, and aluminum-beryllium alloys) dissolve readily in dilute nitric acid or a dilute mixture of nitric and hydrochloric acids.

Beryllium oxide calcined at 500°C can be dissolved in dilute sulfuric, hydrochloric, hydrofluoric, or nitric acids; however, as the calcination temperature is increased, the oxide becomes progressively more resistant to attack. Dissolution of beryllium oxide calcined above 1200°C usually requires hydrofluoric acid or an acid mixture containing hydrofluoric acid [*13,18*]. Alternatively, high-fired beryllium oxide may be dissolved by fusion with potassium pyrosulfate or potassium bisulfate [*18*].

Beryl ores are resistant to acid attack and are usually decomposed by fusion. In our laboratory, finely ground beryl ore is fused with sodium carbonate. The melt is dissolved in a mixture of sulfuric and hydrofluoric acids. Silicon tetrafluoride is driven off by evaporation of the solution to strong fumes [*20*]. If sodium or silicon is to be determined, the finely ground ore is fused with a mixture of lithium metaborate and lithium tetraborate, and the melt is dissolved in a mixture of nitric and hydrofluoric acids. Many other fusion methods for beryl ore have been described in the literature [*14,18*].

Separation

Beryllium is a member of the group of metals that is precipitated by ammonium hydroxide from weakly basic solutions. Since reagents for the determination of beryllium generally lack specificity, extensive separation schemes are often required to remove interferents. Aluminum, present with beryllium in many matrices, is chemically similar to beryllium and interferes in nearly all classical and spectrophotometric methods.

The precipitation of beryllium hydroxide with ammonium hydroxide at pH

8 to 9 forms the basis for the most common beryllium separation schemes. Coprecipitation of manganese, cobalt, nickel, copper, and zinc, is minimized by complexation of these elements with excess ammonia. The alkali and alkaline earth elements also remain in solution. Multiple reprecipitations may be required because the precipitate tends to occlude impurities. Species, such as tartrate, citrate, and fluoride, which complex beryllium, must be absent. Fluoride may be removed by evaporating a solution in sulfuric acid to strong fumes. Phosphate, which coprecipitates with beryllium hydroxide, may be removed by precipitation with ammonium molybdate.

The utility of this method is improved by adding EDTA before the addition of ammonium hydroxide [*21-23*]. Most of the divalent and trivalent metal ions form strong complexes with EDTA, whereas beryllium does not. Addition of EDTA minimizes precipitation of aluminum, chromium, and iron and further reduces coprecipitation of manganese, cobalt, nickel, and zinc. Excess EDTA should be avoided, as it will prevent complete precipitation of beryllium.

Ammonium beryllium phosphate (NH_4BePO_4) precipitates from slightly acidic solutions containing EDTA upon addition of ammonium phosphate [*23,24*]. The alkali and alkaline earth elements, aluminum, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, molybdenum, and lead, remain in solution. If hydrogen peroxide is present, the precipitation of small amounts of titanium can be prevented.

Several reviews discuss numerous other methods for separation of beryllium from interferents [*13,15,18*]. These include selective precipitation of interfering elements, solvent extraction of beryllium or of interferents, ion exchange, electrolysis using a platinum or mercury cathode, and selective volatilization.

Gravimetric Methods

Gravimetric procedures for determining beryllium are used primarily to obtain accurate analyses of beryllium products and standards that contain low levels of interfering elements. The ammonium hydroxide procedure for separation of beryllium from interfering elements provides the starting point for the most frequently used gravimetric beryllium method [*13,25-29*]. Interfering elements are removed by prior precipitation with 8-hydroxyquinoline or are complexed with EDTA. The precipitate is filtered and carefully heated to 600°C before ignition to beryllium oxide (BeO) at 1100°C. The ignited BeO is usually contaminated with silicon dioxide, which can be removed by adding hydrofluoric and sulfuric acids and reigniting to BeO. The ignited crucible should be cooled in a desiccator over the best drying agent available and weighed quickly to avoid the adsorption of water vapor.

The phosphate procedure for separation of beryllium has also been applied as a gravimetric method [*13,24,29-31*]. The NH_4BePO_4 precipitate is filtered and ignited at 1000°C to beryllium pyrophosphate ($Be_2P_2O_7$). Conditions must be carefully controlled to obtain the theoretical composition of the pyrophosphate.

Several other gravimetric methods for beryllium are discussed in Ref *15*.

Volumetric Method

One of the few classical beryllium methods still in general use is a titration procedure based upon the complexation of beryllium with fluoride. The sample to be analyzed is dissolved in sulfuric acid. Beryllium hydroxide is precipitated by adjusting the pH of the solution to 8.5 with sodium hydroxide solution. Excess sodium fluoride is added, redissolving the $Be(OH)_2$ to form the tetrafluoroberyllate complex (BeF_4^{-2}). The liberated hydroxide is titrated with sulfuric acid. The titration volume is used to calculate the amount of beryllium in the sample [*29,32,33*].

The complexation of beryllium by fluoride is not quantitative, so standards containing known amounts of beryllium must be analyzed along with the samples. Hold times and titration rates are critical; but, under carefully controlled conditions, relative precisions of 0.2% or better can be achieved (Table 1). An automatic titrator has improved the precision of the procedure in our laboratory.

Any species that complex fluoride interferes; therefore, aluminum, silicon, zirconium, hafnium, uranium, thorium, and the rare earth elements must be absent or (if present in small amounts) corrections must be made. This procedure is used in our laboratory for assay of beryllium metal, beryllium hydroxide, and beryllium specialty chemicals. Copper-beryllium and nickel-beryllium alloys can be analyzed by this method after separation of beryllium from copper, nickel, and cobalt by ammonium hydroxide precipitation.

Spectrophotometric Methods

The Be^{+2} ion in solution does not absorb in the ultraviolet (UV) visible region of the spectrum, so spectrophotometric reagents for beryllium must

TABLE 1—*Determination of beryllium by empirical tiration.*

	Percent Beryllium	
Sample	Certified	Found (Standard Deviation)
F-226[a]	98.46	98.42 (0.10)
C1122[b]	1.75	1.754 (0.002)

[a] Beryllium metal standard reference material, Department of Energy, New Brunswick Laboratory (see Footnote 4).

[b] Copper-beryllium alloy standard reference material, National Bureau of Standards (see Footnote 2).

carry chromophoric groups. Most spectrophotometric reagents for beryllium belong to one of three categories: polyhydroxyquinones, triphenylmethane dyes, and azo dyes [*15*].

Quinalizarin, a polyhydroxyquinone, was the first common spectrophotometric reagent for beryllium [*34–36*]; but it is seldom used now because of its instability.

One of the most frequently used spectrophotometric reagents for beryllium is *p*-nitrophenylazoorcinol (zenia), an azo dye that forms a red-brown lake with beryllium in alkaline solution [*9,13,29,36–40*]. The reagent is not particularly stable, so rigorous adherence to the experimental conditions is required. The calibration curve does not follow Beer's law. Major interferents include magnesium, zinc, and elements that form colored ions in solution. Interferents can be removed or masked with EDTA or citrate.

The ammonium salt of aurintricarboxylic acid (aluminon), a triphenylmethane dye, is used for the spectrophotometric determination of beryllium in ASTM Methods for Chemical Analysis of Copper-Beryllium Alloys (E 106). The analysis is carried out in acid solution. Hold times must be carefully controlled because of the instability of the reagent. The calibration curve deviates slightly from Beer's law. The major interferents, aluminum, calcium, iron, manganese, and species that form colored ions in solution, must be removed or masked with EDTA or tartaric acid [*39–42*].

Reviews that discuss other spectrophotometric reagents for beryllium are available [*15,36,40*].

Fluorometric Method

The yellowish-green fluorescence of the beryllium complex with 2′,3,4′,5,7-pentahydroxyflavone (morin) was frequently used for the determination of beryllium in environmental and biological samples before the advent of atomic absorption methods [*29,36,40,43–46*]. Beryllium concentrations of 0.5 μg/L can be determined by this method. Triethanolamine, EDTA, and diethylenetriaminepentaacetic acid (DTPA) have been employed to mask interferents, which include lithium, calcium, manganese, copper, zinc, silver, gold, and the rare earth elements. The morin fluorometric method for beryllium is used in ASTM Test Methods for Chemical Analysis of Aluminum and Aluminum Base Alloys (E 34).

Photoneutron Method

When subjected to gamma irradiation, beryllium undergoes the nuclear reaction

$$^{9}\mathrm{Be} + \gamma \longrightarrow {}^{8}\mathrm{Be} + {}^{1}n$$

This reaction is the basis for a rapid, relatively interference-free instrumental method for determining beryllium. Gamma radiation from a sealed antimony-124 source is used to excite photoneutron emission from beryllium. Emitted neutrons are counted by neutron detectors arrayed around the sample. The neutron counts for the sample and a standard are compared to obtain the beryllium concentration in the sample [*47-50*].

The sensitivity of the method depends upon the source activity, sample size, counting time, and distance between source, sample, and detectors. The instrument in our laboratory can determine beryllium concentrations ranging from 0.01 to 100% using a 200 mCi antimony-124 source, 25-g sample, and 200-s counting time.

Beryllium analyzers based upon photoneutron emission are widely used in the beryllium industry for the following reasons:

1. *Lack of Interferences*—The major interferents consist of neutron absorbing species such as lithium, boron, cadmium, and the rare earth elements. Relatively high levels of neutron-absorbing species can be tolerated if the sample size is kept small. Addition of 100-g cadmium/L to a 25-mL liquid sample containing 4-g beryllium/L suppresses the photoneutron count by less than 4%. The error caused by photoneutron absorption can be minimized by using matrix-matched standards, employing the method of standard additions, or decreasing the thickness of the samples and standards.
2. *Minimal Sample Preparation*—Liquids and powders require no preparation other than measurement of equal volumes of all samples and standards. Solids must be machined to a standard shape to obtain accurate results.
3. *Rapid Turnaround*—Analyses can be completed in several minutes.
4. *Nondestructiveness*—The sample can be recovered essentially unchanged.

The high cost of installing and operating a photoneutron beryllium analyzer has limited its use to laboratories that perform frequent beryllium analyses. Extensive lead shielding is required to protect the operator from gamma radiation. The half-life of the antimony-124 source is 60 days; therefore, it must be replaced several times per year to maintain a satisfactory counting rate. In the United States a license is required for the possession of the antimony-124 source.

Atomic Absorption Methods

The determination of beryllium by atomic absorption has become one of the principal methods for process control in the beryllium industry. The solution to be analyzed is aspirated into a fuel-rich, red nitrous oxide-acetylene flame. The 234.9-nm beryllium line is used for the analysis. A detection limit of 2 μg/L can be achieved using flame atomization [*51,52*].

The beryllium absorbance is suppressed by aluminum, titanium, magnesium, and silicon [*51–58*]. The aluminum and titanium interferences are reduced in the presence of hydrofluoric acid [*51–54*] or lanthanum [*58*]. The addition of 8-hydroxyquinoline has been suggested to minimize suppression by aluminum, magnesium, and silicon [*52,57*]. The enhancement of the beryllium absorbance by high concentrations of sodium, potassium, calcium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, selenium, strontium, zirconium, molybdenum, cadmium, tin, tellurium, mercury, lead, bismuth, thorium, and uranium, may be masked by adding potassium nitrate to sample and standards [*57*].

Because unrecognized interferences may exist, the sample and standards should be matrix-matched. Alternatively, the method of standard additions can be used; but care should be exercised, because the background absorbance may be elevated for the samples. Background correction techniques can help in addressing this problem. Separation techniques, such as solvent extraction [*56,58–61*] or ion exchange [*62,63*], have been employed to reduce interferences and to concentrate beryllium before atomic absorption analysis.

Beryllium in beryl ore is regularly determined in our laboratory by atomic absorption using the nitrous oxide-acetylene flame. The ore sample is dissolved using either the sodium carbonate or the lithium metaborate-lithium tetraborate fusion technique described in the sample dissolution section. Beryl ore lots of known beryllium concentration are carried through each procedure for use as standards.

Atomic absorption spectrophotometry using electrothermal (graphite furnace) atomization is virtually indispensible for the determination of trace levels of beryllium in biological and environmental samples [*64–68*]. Electrothermal atomization requires much smaller sample volumes than flame atomization, and much lower detection limits can be achieved. This technique can detect 0.5 pg of beryllium [*51*].

The thermal sequence for a typical beryllium determination involves drying at 100 to 110°C, charring at 1200 to 1600°C, and atomization at 2300 to 2700°C. Argon is the recommended purge gas. Pyrolytically coated graphite tubes are suggested for improved sensitivity [*69*]. At high charring temperatures, beryllium losses are reduced by the addition of a matrix modifier such as magnesium nitrate, aluminum nitrate, or calcium nitrate [*70*]. Background correction is required to compensate for broad-band molecular absorption and light scattering by particulates.

Direct insertion of solid samples into the graphite tube atomizer can be performed if the sample size is limited [*71*]; however, the loss of precision frequently outweighs the advantages of simplified sample preparation and lower relative detection limits.

Optical Emission Spectrometric Methods

Atomic emission spectrometry using DC arc and spark techniques has been employed in the beryllium industry for many years. More recently, plasma atomic emission spectrometry has been introduced. Atomic emission spectrometry has displaced most of the classical and spectrophotometric methods for beryllium because of its greater versatility, faster turnaround, and lower long-term costs. Chemical interferences, in general, are less severe with emission spectrometric methods than with classical methods, so less sample preparation is required.

Table 2 lists the analytically useful spectral lines of beryllium along with potential interferents. The lines are listed roughly in decreasing order of intensity; however, the order of intensities may vary somewhat depending on the excitation method. In the case of multiplets, only the most intense line is listed.

Copper-beryllium alloys are analyzed in our laboratory by direct reading spectrometer using low-voltage spark techniques. The 235.069-nm line is used for the determination of beryllium. Unfortunately, cobalt and nickel, which are present in the alloys, interfere with this line, so good matrix matching or interelement correction is essential. To minimize inaccuracy caused by metallurgical effects and sample inhomogeneity, many of our samples are remelted in a centrifugal casting furnace before analysis.

Plasma atomic emission spectrometry is becoming increasingly important in the determination of beryllium. Primarily a solution technique, plasma atomic emission spectrometry requires more extensive sample preparation than many arc-spark techniques; however, it offers a degree of versatility unavailable with other emission spectrometric methods. Matrix-matched standards may be prepared for plasma atomic emission spectrometry by dissolving pure metals, oxides, or salts. Metallurgical effects are eliminated in the dissolution process. Relatively large samples may be dissolved, minimizing the problem of inhomogeneity. Most plasma atomic emission spectrometers permit selection of alternate lines for a given element without the necessity of major equipment modifications.

TABLE 2—*Atomic spectral lines of beryllium.*

Wavelength, nm	Spectrum[a]	Interferences[b]
313.042 doublet	II	V
234.861	I	Fe
265.060 multiplet	I	Th, Os, Zr, Yb
332.134 multiplet	I	Th, Sm, V, Tb, Ti, Ho
249.473 multiplet	I	Th, Ru
235.069 multiplet	I	Co, Fe, Ni, Hf
217.507 doublet	I	Ir, Ni, Pt
298.662 multiplet	I	Fe, Cr, Ir, Rh
457.267 multiplet	I	Mn, Ti, Ta
205.590 doublet	I	Cr

[a] I, atom line; II, ion line.

[b] Refs *72* through *74*.

Interelement effects, including chemical and spectral interferences, can lead to erroneous results in plasma atomic emission spectrometry [*75, 76*]. Most interelement effects can be minimized by matrix matching or buffering with a high concentration of the interferent. A high-resolution monochromator or polychromator is required to deal with spectral interferences. Background compensation, interelement correction, and matrix matching can also assist with spectral interferences.

Complete solution of the analyte elements must be assured by careful choice of the dissolution matrix. This may be particularly difficult to achieve when refractory compounds are present or when many analytes are to be determined in the same solution.

Direct current argon plasma (DCP) atomic emission spectrometry is employed in our laboratory for the determination of beryllium in a number of matrices. Trace levels can be determined using the most intense emission line at 313.042 nm (linear range, 0.0003 to 60 mg/L). Weaker lines are more useful for determination of higher beryllium concentrations in alloys and ores. The line at 265.060 nm (linear range, 0.2 to 1000 mg/L) is used for the determination of beryllium in aluminum-beryllium, nickel-beryllium, and copper-beryllium alloys at levels ranging from 0.01 to 6%.

Beryllium in beryl ore is also determined in our laboratory by DCP atomic emission spectrometry using the 265.060-nm line. Either of the fusion techniques described in the Sample Dissolution section can be used to decompose the ore. Precision is comparable to atomic absorption.

The internal reference method [*74, 75*] is used for most routine DCP atomic emission spectrometric analyses in our laboratory. An element that is not normally present in the sample matrix, but which fluctuates in emission intensity in a manner similar to the analyte element, is added to all sample and standard solutions. This internal standard element must be present at equal concentrations in all solutions. The emission intensities of the internal standard and analyte elements are measured simultaneously for each sample and standard. The ratio of analyte emission intensity to internal standard emission intensity is calculated for each standard and sample. This ratio (not the raw emission intensity) is used to calculate the analyte concentration in each sample.

Properly applied, the internal reference method can improve the precision of some analyte determinations severalfold. Both short-term flicker and long-term drift can be compensated, but the proper internal standard must be chosen. The 257.610-nm manganese line and the 228.616-nm cobalt line are suitable for correction of the 265.060-nm beryllium line under our analytical conditions. The 303.936-nm indium line and the 396.153-nm aluminum line are not suitable, causing a degradation of precision if used with the 265.060-nm beryllium line.

The 257.610-nm manganese line is used for internal standard correction in the determination of beryllium in alloys. The cobalt line is not used because cobalt is present in many of the alloys and is determined simultaneously with beryllium. Table 3 shows the improvement in precision caused by internal standard correction.

When beryllium is determined in beryl ore, the 228.616-nm cobalt line is used for internal standard correction, since some beryl ores (containing helvite) exhibit high manganese concentrations.

Comparison of Beryllium Results Obtained by Several Different Methods

Several copper-beryllium samples have been analyzed for beryllium by five different methods. Results of these analyses are shown in Table 4.

Generally good agreement between the methods is observed. The aluminon spectrophotometric method tended to yield slightly lower results than the other methods. The best precision was obtained with the titration method.

TABLE 3—*Determination of beryllium in copper-beryllium alloys by DC plasma emission spectrometry.*

	Percent Beryllium (Standard Deviation)		
		Determined by DCP	
Sample	Certified	Uncorrected	Internal Standard Corrected
C1121[a]	1.92	1.911 (0.023)	1.902 (0.003)
C1122[a]	1.75	1.752 (0.011)	1.745 (0.006)

[a] Copper-beryllium alloy standard reference material, National Bureau of Standards (see Footnote 2).

TABLE 4—*Comparison of methods for determination of beryllium in copper-beryllium alloys.*

	Percent Beryllium (Standard Deviation)					
Sample	Certified	DC Plasma	Titration[b]	Spectrophotometric[b]	Atomic Absorption	Direct Reading Spectrometer
C1122[c]	1.75	1.745 (0.006)	1.754 (0.002)[d]	1.732	1.747 (0.013)	1.738 (0.014)
20C[e]	...	2.122 (0.031)	2.129 (0.014)	2.097 (0.015)	...	2.145 (0.017)

[a] Empirical titration method of Ref *26* adapted for automatic titrator.

[b] ASTM Method for Chemical Analysis of Copper-Beryllium Alloys (E 106).

[c] Copper-beryllium standard reference material, National Bureau of Standards (see Footnote 2).

[d] Range; only two samples were titrated.

[e] Copper-beryllium sample.

Acknowledgment

The author wishes to thank Roy Beck of Brush Wellman Inc. for supplying the copper-beryllium alloy data used in this report.

References

[*1*] White, D. W., Jr. and Burke, J. E., Eds., *The Metal Beryllium,* The American Society for Metals, Cleveland, OH, 1955.

[*2*] Darwin, G. E. and Buddery, J. H., *Beryllium,* Butterworths Scientific Publications, London, 1960.

[*3*] Everest, D. A., *The Chemistry of Beryllium,* Elsevier Publishing Company, Amsterdam, The Netherlands, 1964.

[*4*] Hausner, H. H., Ed., *Beryllium Its Metallurgy and Properties,* University of California Press, Berkeley, CA, 1965.

[*5*] Everest, D. A., *Comprehensive Inorganic Chemistry,* Vol. 1, J. C. Bailar, Ed., Pergamon Press Ltd., Oxford, England, 1973, p. 531.

[*6*] Ballance, J., Stonehouse, A. J., Sweeney, R., and Walsh, K., *Encyclopedia of Chemical Technology,* 3rd ed., Vol. 3, M. Grayson and D. Eckroth, Eds., John Wiley and Sons, New York, 1978, pp. 803-823.

[*7*] Walsh, K. and Rees, G. H., *Encyclopedia of Chemical Technology,* 3rd ed., Vol. 3, M. Grayson and D. Eckroth, Eds., John Wiley and Sons, New York, 1978, pp. 824-829.

[*8*] Petzow, G., Aldinger, F., Jonsson, S., and Preuss, O., *Ullmann's Encyclopedia of Industrial Chemistry,* 5th ed., Vol. A4, VCH Verlags-gesellschaft, Weinheim, Federal Republic of Germany, 1985, pp. 11-33.

[*9*] Vinci, F. A., *Analytical Chemistry,* Vol. 25, 1953, p. 1580.

[*10*] Metcalfe, J. and Ryan, J. A., Eds., "The Analytical Chemistry of Beryllium, Proceedings of a Symposium Held at Blackpool—June, 1960," PG Report 171(S), United Kingdom Atomic Energy Authority, Springfields, England, 1960.

[*11*] Vinci, F. A., *Standard Methods of Chemical Analysis,* 6th ed., Vol. 1, N. H. Furman, Ed., D. Van Nostrand Co., Inc., Princeton, NJ, 1962, p. 167.

[*12*] Kjellgren, B. R. F., Schwenzfeier, C. W., and Melick, E. S., *Treatise on Analytical Chemistry,* Vol. 6, Part 2, I. M. Kolthoff and P. J. Elving, Eds., John Wiley and Sons, New York, 1964.

[*13*] Kempchinskey, P. C., *Encyclopedia of Industrial Chemical Analysis,* Vol. 7, F. D. Snell and C. L. Hilton, Eds., John Wiley and Sons, New York, 1968, pp. 103-117 and 129-141.

[*14*] Snell, F. D. and Hilton, C. L., Eds., *Encyclopedia of Industrial Chemical Analysis,* Vol. 7, John Wiley and Sons, New York, 1968, pp. 118-129.

[*15*] Novoselova, A. V. and Batsanova, L. R., *Analytical Chemistry of Beryllium,* Israel Program for Scientific Translations, Jerusalem, Israel, 1968.

[*16*] Fresenius, R. and Jander, G., *Handbuch der analytischen Chemie,* Part 3, Vol. 2a, Julius Springer Verlag, Berlin, Germany, 1940.

[*17*] Rodden, C. J., *The Analysis of Essential Atomic Reactor Materials,* C. J. Rodden, Ed., Superintendent of Documents, U.S. Government Printing Office, Washington, DC, 1964, pp. 349-405.

[*18*] Smithe, L. and Florence, T., *Progress in Nuclear Energy,* Series 9, Vol. 3, 1963, p. 191.

[*19*] Stokinger, H. E., Ed., *Beryllium: Its Industrial Hygiene Aspects,* Academic Press, New York, 1966.

[*20*] Kallmann, S., Ledox and Company, Teaneck, NJ, unpublished procedure.

[*21*] Brewer, P., *Analyst,* Vol. 77, 1952, p. 539.

[*22*] Pribil, R. and Kucharsky, K., *Collection of Czechoslovak Chemical Communications,* Vol. 15, 1950, p. 132.

[*23*] Golovatyi, R. N., Oshchapovskii, V. V., and Alekseenko, L. I., *Ukrain s'kii Khimicheskii Zhurnal,* Vol. 26, 1960, p. 771.

[*24*] Chernikhov, I. A. and Goryushina, V. G., *Sbornik Nauchnykh Trudov Giredmeta,* Vol. 2, 1959, p. 97.

[25] Parsons, C. and Barnes, S., *Zeitschrift Fuer Analytische Chemie*, Vol. 46, 1907, p. 292.

[26] Frommes, M., *Zeitschrift Fuer Analytische Chemie*, Vol. 93, 1933, pp. 287, 295.

[27] Akiyama, T., *Japan Analyst*, Vol. 1, 1952, p. 133.

[28] Moser, L. and Singer, J., *Monatshefte Fuer Chemie*, Vol. 48, 1927, p. 673.

[29] Rodden, C. J. and Vinci, F. A., *The Metal Beryllium*, D. W. White, Jr. and J. E. Burke, Eds., The American Society of Metals, Cleveland, OH, 1955, pp. 641-691.

[30] Cupr, V., *Zeitschrift fuer Analytische Chemie*, Vol. 76, 1929, p. 173.

[31] Airoldi, R., *Annalidi Chimica (Rome)*, Vol. 41, 1951, p. 478.

[32] McClure, J. H. and Banks, C. V., *Proceedings of the Iowa Academy of Science*, Vol. 57, 1950, p. 193.

[33] McClure, J. H. and Banks, C. V., "An Empirical Titrimetric Method for the Determination of Beryllium," Report AECU-812, U.S. Atomic Energy Commission, Iowa State College, Ames, IA, 1950.

[34] Fischer, H., *Zeitschrift Analytische Chemie*, Vol. 73, 1928, p. 54.

[35] Fischer, W. and Wernet, J., *Angewandte Chemie*, Vol. A60, 1948, p. 129.

[36] Sandell, E. B., *Colorimetric Determination of Traces of Metals*, 3rd ed., Interscience Publishers, Inc., New York, 1959, pp. 304-324.

[37] Osborn, G. H. and Stross, W., *Metallurgia*, Vol. 30, No. 175, 1944, p. 3.

[38] Stross, W. and Osborn, G. H., *Journal of the Society of Chemical Industry*, Vol. 63, 1944, p. 249.

[39] Hayes, T. J., "The Analytical Chemistry of Beryllium, Proceedings of a Symposium Held at Blackpool—June, 1960." J. Metcalfe and J. A. Ryan, Eds., PG Report 171(S), United Kingdom Atomic Energy Authority, Springfields, England, 1960, pp. 15-24.

[40] Snell, F. D. and Snell, C. T., *Colorimetric Methods of Analysis*, Vol. 2A, D. Van Nostrand Company, Inc., Princeton, NJ, 1959, pp. 188-200.

[41] Kosel, G. E. and Neuman, W. F., *Analytical Chemistry*, Vol. 22, 1950, p. 936.

[42] Luke, C. L. and Campbell, M. E., *Analytical Chemistry*, Vol. 24, 1952, p. 1056.

[43] Sandell, E. B., *Industrial and Engineering Chemistry, Analytical Edition*, Vol. 12, 1940, p. 674.

[44] Sill, C. S. and Willis, C. P., *Analytical Chemistry*, Vol. 31, 1959, p. 598.

[45] Molineaux, H. F., Trowell, F., and Turnbull, G. B., "The Analytical Chemistry of Beryllium, Proceedings of a Symposium Held at Blackpool—June, 1960," J. Metcalfe and J. A. Ryan, Eds., PG Report 171(S), United Kingdom Atomic Energy Authority, Springfields, England, 1960, pp. 155-175.

[46] Sill, C. W., Willis, C. P., and Flygare, J. K., Jr., "The Analytical Chemistry of Beryllium, Proceedings of a Symposium Held at Blackpool—June, 1960," J. Metcalfe and J. A. Ryan, Eds., PG Report 171(S), United Kingdom Atomic Energy Authority, Springfields, England, 1960, pp. 177-178.

[47] Bisby, H. and Hale, F. H., "The Analytical Chemistry of Beryllium, Proceedings of a Symposium Held at Blackpool—June, 1960," J. Metcalfe and J. A. Ryan, Eds., PG Report 171(S), United Kingdom Atomic Energy Authority, Springfields, England, 1960, pp. 43-54.

[48] Milner, G. W. C. and Edwards, J. W., "The Analytical Chemistry of Beryllium, Proceedings of a Symposium Held at Blackpool—June, 1960," J. Metcalfe and J. A. Ryan, Eds., PG Report 171(S), United Kingdom Atomic Energy Authority, Springfields, England, 1960, pp. 55-69.

[49] Gaudin, A. M. and Pannell, J. H., *Analytical Chemistry*, Vol. 23, 1951, p. 1261.

[50] Kienberger, C. A., "Determination of Beryllium by Gamma Activation," AEC Research and Development Report Y-1733, Union Carbide Corporation, Oak Ridge, TN, 1970.

[51] Price, W. J., *Spectrochemical Analysis by Atomic Absorption*, John Wiley and Sons, New York, 1979, p. 292.

[52] *Analytical Methods for Atomic Absorption Spectrophotometry*, The Perkin Elmer Corporation, Norwalk, CT, 1971.

[53] Ramakrishna, T. V., West, P. W., and Robinson, J. W., *Analytica Chimica Acta*, Vol. 39, 1967, p. 81.

[54] Janousek, I., *Atomic Absorption Newsletter*, Vol. 16, 1977, p. 49.

[55] Amos, M. D. and Willis, J. B., *Spectrochimica Acta*, Vol. 22, 1966, p. 1325.

[56] Bokowski, D. L., *Atomic Absorption Newsletter*, Vol. 6, 1967, p. 97.

[57] Fleet, B., Liberty, K. V., and West, T. S., *Talanta,* Vol. 17, 1970, p. 203.

[58] Castillo, J. R., Belarra, M. A., Dominguez, M., and Aznarez, J., *Talanta,* Vol. 29, 1982, p. 485.

[59] Terashima, S., *Japan Analyst,* Vol. 22, 1973, p. 1317.

[60] Matsusaki, K., *Bunseki Kagaku,* Vol. 24, 1975, p. 442.

[61] Terashima, S., *Bunseki Kagaku,* Vol. 31, 1982, p. 727.

[62] Korkisch, J., Sorio, A., and Steffan, I., *Talanta,* Vol. 23, 1976, p. 289.

[63] Korkisch, J. and Sorio, A., *Analytica Chimica Acta,* Vol. 82, 1976, p. 311.

[64] Bettger, R. J., Ficklin, A. C., and Rees, T. F., *Atomic Absorption Newsletter,* Vol. 14, 1975, p. 14.

[65] Bolyard, M., *NIOSH Manual of Analytical Methods,* 2nd ed., Method 279, Vol. 4, U.S. Department of Health, Education and Welfare, National Institute of Occupational Safety and Health, Cincinnati, OH, 1978.

[66] *NIOSH Manual of Analytical Methods,* 2nd ed., Vol. 4, Method S339, U.S. Department of Health, Education and Welfare, National Institute of Occupational Safety and Health, Cincinnati, OH, 1978.

[67] *Methods for Chemical Analysis of Water and Wastes,* EPA Publication 600/4-79-020, Method 210.2, Environmental Protection Agency, Washington, DC, 1979.

[68] Geladi, P. and Adams, F., *Analytica Chimica Acta,* Vol. 105, 1979, p. 219.

[69] Lagas, P., *Analytica Chimica Acta,* Vol. 98, 1978, p. 261.

[70] Manning, D. C. and Slavin, W., *Applied Spectroscopy,* Vol. 37, 1983, p. 1.

[71] Owens, J. W. and Gladney, E. S., *Atomic Absorption Newsletter,* Vol. 14, 1975, p. 76.

[72] Boumans, P. W. J. M., *Line Coincidence Tables for Inductively Coupled Plasma Atomic Emission Spectrometry,* Vol. 1, Pergamon Press Ltd., Oxford, England, 1981.

[73] Harrison, G. R., *Massachusetts Institute of Technology Wavelength Tables,* The MIT Press, Cambridge, MA, 1969.

[74] Meggers, W. F., Corliss, C. H., and Scribner, B. F., *Tables of Spectral-Line Intensities,* Monograph 32, Parts 1 and 2, National Bureau of Standards, Washington, DC, 1961.

[75] Eastwood, D., Hendrick, M. S., and Sogliero, G., *Spectrochimica Acta,* Vol. 35B, 1980, p. 421.

[76] Thompson, M. and Ramsey, M. H., *Analyst,* Vol. 110, 1985, p. 1413.

Rudolph B. Fricioni[1]

Microprocessor-Based Determinator Design and the Impact of Future Trends in the Area of Computer-Controlled Automation of Analytical Chemistry Methods

REFERENCE: Fricioni, R. B., "**Microprocessor-Based Determinator Design and the Impact of Future Trends in the Area of Computer-Controlled Automation of Analytical Chemistry Methods,**" *Chemical Analysis of Metals, ASTM STP 944,* Francis T. Coyle, Ed., American Society for Testing and Materials, Philadelphia, 1987, pp. 89-96.

ABSTRACT: The design of analytical instrumentation has always made use of the latest electronic technology to provide the fastest and most accurate methods for analysis. The present and the future is no different than the past. Computer and microprocessor technology offers solutions to analytical problems that until this period of time had to be lived with.

Designers, while holding on to basic analytical techniques, cannot incorporate corrections for previously known but uncontrollable factors. Computer and microprocessor based design offers the designer the capability of automating manual analytical methods that previously were simply too complex. The design of such systems follows the same exacting evaluation process as used in the past. Evaluations for the most efficient extraction, isolation or separation, detection, signal process, and systems control methods are made and compiled to result in a fast, accurate, and easy to use system.

The combination of electronics, electro-mechanics, and analytical methods is continuing with the advent and development of robotics. Combined with the technology of todays instrumentation robotics can offer further productivity and efficiency of the analytical lab.

KEY WORDS: chemical analysis, computers, element extraction, element isolation, metal ions, gaseous element detection, analytical techniques, elemental oxides, sensitivity of detection, multiple regression, slope response, background element

Today, the electronics industry accounts for more than $100 billion in sales per year and is expected to reach sales of $325 billion to $400 billion by the

---

[1] Vice-president of Research and Development, Leco Corporation, 300 Lakeview Ave., St. Joseph, MI 48085.

late 1980s. It will then rank as the world's fourth largest industry, after steel, automobiles, and chemicals.

Microprocessors are used today in everything from hand-held calculators, digital watches, and TV games, to refrigerators, automobiles, and laboratory instrumentation of all types. The next decade will see such unimaginable applications as tiny inexpensive climate and soil sensors for agriculture, and infinitesimal medical devices sewn into ordinary clothing to monitor the heartbeat of the wearer.

As computer miniaturization advanced, computer capacity soared, and costs per function plunged; small, cheap, powerful mini-computers appeared virtually everywhere; nearly every branch office, laboratory, sales office or engineering department seems to have acquired one. Expenditures for microprocessor-based computers alone grew, in the United States, from $300 million in 1977 to over $3 billion in 1982.

In addition to the phenomenal growth of minicomputers, microprocessors and microcomputers are rapidly expanding throughout the entire range of American life. Apart from their applications in businesses and laboratories, they are already used, or soon will be, in everything from air-conditioners and automobiles to sewing machines and scales. They will soon monitor and minimize energy waste in our homes and factories. They already fine-tune automobile fuel systems. They tell us when a component of the automobile requires repair or service. Soon they will turn on the clock radio, the toaster, the coffee maker, and even the shower for us in the morning. They will warm the garage, lock the doors, and perform countless other tasks.

Today, the conversion of analytical chemistry methods to computer-controlled automation is accelerating. The acceptance of this trend is due to industrial demands for greater analytical accuracy, more analytical data, and more accurate process control.

As the steel industry progressed from open hearth melting to basic oxygen and electric arc melting, increased demands were placed on the chemical laboratory. The use of argon oxygen decarbonization increased these demands further.

The fuel laboratories of our energy industries have experienced increased demands from material process technology, government regulations, and material shortages. In other fields, such as plastics, foods, and environmental science, the technological advancements of the past several years have increased the same demands on their various analytical laboratories.

Automated Methods

Any automated method must consider the requirements of the laboratory, while at the same time, making the procedure simpler. When considering the automation of a particular method, the end element being determined is of primary concern. Also considered in the planning process is the expected content ranges, required accuracy, type of material to be analyzed, and the time allotted for analysis.

Defining both the type of material to be analyzed and the element to be determined allows the designer of the system to evaluate the most efficient method of extracting the element from the material. Which form of energy to employ is the first planning step. (If the element can be extracted from the material by heating in a controlled environment, combustion, fusion, carbon arcing, or X-ray bombardment in a controlled atmosphere, then the designer will consider the efficiency of each method in recovering the end element to be determined.) Methods of isolating the element from other elements that may evolve during the various extraction methods must be evaluated, as well as the efficiency of each extraction method.

The method of extraction determines the form of the element as it is extracted from the sample material. Establishing the form allows the engineer to choose the most efficient means of isolating, and then detecting, the extracted element. An element that evolves from a material at a specific temperature in an inert environment may be detected by weight loss, flame ionization, infrared absorption, or thermal conductivity. Elements that evolve in the form of a metal ion through arcing or etching may be detected by a flame photometer or colorimeter. Elements that evolve in a gaseous state through combustion or fusion may be detected by infrared absorption or thermal conductivity. Elements evolved by X-ray bombardment may be detected by pulse ionization, scintillation, or semiconductor detection.

The selected method of detection will be sensitive to certain interferences from other elements. After selecting both an extraction method and a detection method, the designer concentrates on further isolation of the element in regard to the detection system. Isolation of an element may range from simple temperature or environmental controls to chemical absorbers, wavelength filters, or dispersion crystals.

The engineer must incorporate the decisions on extraction, detection and separation into a system that will automatically control these functions, and, at the same time, process the data generated by the detection system into meaningful values. The designer's choices for control are mechanical, electro-mechanical, or electronic. At times, all three technologies will be employed to provide the most efficient method of control. As in other fields, the chemical analysis engineer makes use of electronic technology for detected signal processing, as well as system controls.

Making the correct design decisions is made easier by advancements that occurred during the past decades. Even though a particular method has never been automated before, the designer can learn from the work completed for other analytical techniques. For example, a designer may consider a resistance furnace as the heart of an extraction system. Resistance furnace systems have been used in the analytical process for nearly 50 years. The engineer considers the characteristics of an accurately controlled temperature environment to be the key to extracting the element to be determined. The material under analysis, however, cannot be introduced rapidly into high temperatures. The system designer may consider introducing the material at a reduced or ambient furnace temperature, then increasing the temperature to the prescribed level required for analysis. The adaptation, however, is more complicated. One must establish the fastest temperature response possible in the furnace to maintain minimal extraction time. Heating element materials are evaluated for heating response, temperature uniformity, and longevity. When the heating problems have been solved, the effect of the gradual heating process on the material being analyzed must be considered. An evaluation of elemental losses or interferences must be made regarding the chosen extraction method.

Elements that evolve in a specific form at a given temperature sometimes evolve in different forms at higher or lower temperatures. An example of this is moisture breaking down to hydrogen and oxygen at elevated temperatures in an inert environment. Study of these effects will determine whether any additional traps, filters, or converters are required.

The method of element extraction will not only determine the form that the element being determined will assume, but the associated elements in the material that will also evolve, and their forms. For example, when the carbon content of a material is being determined by a combustion method, carbon will evolve from the material in the form of carbon monoxide (CO) and carbon dioxide (CO_2). Along with these gases will be sulfur dioxide (SO_2), water (H_2O), and a wide variety of elemental oxides. The detection system would be designed to detect the carbon as CO_2. Therefore, any of the other elements that may cause interference in the detection system must be removed. Mechanical traps, such as metal screens, can be used to remove particulate oxides. Moisture can be removed with a dessicant, and sulfur dioxide with manganese dioxide. The engineer is left with the problem of the extracted carbon combining with a single oxygen molecule to form CO, while the detection system has been designed to detect CO_2. For this reason, a catalytic converter is added to the isolation process, causing CO to form CO_2, leaving only carbon dioxide and the carrier gas to go through the detection system. This type of gas isolation is used in conjunction with combustion or inert gas fusion extraction methods. In X-ray bombardment, the designer must select and properly place dispersion crystals that will alter the direction of energy wavelengths outside the wavelength of the element being determined.

Transfer of the extracted element through the isolation system to the detection system is provided by either a carrier gas medium or a high vacuum. One must be selective in the choice of transfer media. In some cases, the engineer will rely on the carrier gas to provide a reaction to the extraction or detection process; in a fusion method where the elements being extracted are already gaseous, an inert carrier is required to keep the gases from forming other compounds. When the element is being detected in the form of energy, as in X-ray fluorescence, a vacuum media is used to prevent a loss of energy in the atmospheric environment.

While considering all of these various factors, the designer must also keep in mind the sensitivity of the detection system. A thermal conductivity detection system, for example, is responsive to any change in its atmospheric environment. A carrier media must be selected that will have a greater or lesser conductivity in relation to the conductivity of the gas being determined. A carrier media that increases the difference in thermal conductivity in relation to the extracted gas will increase the detection system's sensitivity, causing a lower content detection.

A detection system's sensitivity establishes the content range. In X-ray fluorescence, the energy produced caused by X-ray bombardment is proportional to the elemental makeup of the material. Increasing the power of the X-rays and defining the target area of the material will increase the energy given off and increase the detection system's sensitivity. Infrared detection sensitivity can be varied by altering the measure chamber path length. In colorimetry, varying the material removal time and quantity of dye will alter the sensitivity. The engineer will use content range parameters to establish the required sensitivity of the detection system.

Defining each of the phases discussed provides the analytical requirements for element, material, content range, and time. These phases then have to be formed into a functional system. The designer considers the response of the detection system over the required content range, and the type of offset the detection system will provide. If one decides to collect the gases into a volume and measure the net offset of the detection system, the extracted element will need to remain stable and not change its form during the collection stage. If it has been decided to monitor the offset generated in the detection system, as the extracted element concentration changes during the extraction mode, then precautions have to be made to assure that the only offset produced will be due to the extracted element concentration. These requirements can be met by placing the detection system into a temperature, pressure, and flow-stable environment. Each type of detection will have its own characteristics in the area of background noise and response to varying concentrations. The engineer will make use of electronic technology to nullify, or filter out, background noise associated with the detection system.

Laws of physics associated with individual detection systems are applied to correct for nonlinear responses of the detector, such as Beer's law as applied in infrared detection systems, or possibly a multiple regression for an X-ray fluorescent system. The law that is applied allows the designer to use the same detection system for varying concentrations, and eliminates the need to regulate the maximum offset generated by the same concentrations when they are extracted differently.

In a collection type measurement, the net detector offset can be used to arrive at a content value. Offset measurements that occur over a period of time by concentration require an integration that is a sum of the total offset.

If the analysis is to be based on concentration by weight, a divisor must be established for this gross content. In order to provide an accurate content measurement, one must compensate for background sources of the element being determined, the slope response of the detection system as related to the actual content, and sample weight variations. Background sources of the element being determined are trace sources from carrier media or consumable contaminants. These contaminants are a constant or "blank value," which can be subtracted from the determined value. The slope response of the detection system is established by analyzing a sample of known content of the element being determined. The difference between the known and determined values is applied as a multiplication factor to the determined value to arrive at a final value. Barometric pressure changes or detector temperature changes will cause the slope correction to change over a period of time. By monitoring the changes in temperature or pressure and establishing a percentage of change, the designer can arrive at a multiplication factor to correct for these changes. All corrections are applied after the raw offset has been determined, starting with the subtraction of background element content, then multiplication of the slope correction. The multiplication factor for changes in detector temperature or barometric pressure fluctuations can be applied after the slope correction, if required. The final determined value is then divided by the sample weight if the value is to be reported on a weight basis. The corrections listed are basic corrections. The engineer will need to study the corrections required according to the material and element being determined. Incorporating corrections to the determined value into the system may be accomplished by manual calculation, electronic voltage manipulation, or microprocessor calculation.

All new designs require a control system to allow extraction on/off control, extraction time control, time for the separation process to take place, time for the measurement, and time for final result calculations. The designer will use the same electronic technology for the control system as was used for the detection signal processing system. An instrument's control system must control more than timing; it must also generate a mechanical or electronic switching of fluid or gas flows to the next process stage.

Once each phase of the system has been established, the physical assembly of the prototype system can begin. Developmental changes can be made to the system once the instrument is built and experimental analyses are performed. During the development stage, the engineer confirms the system's capabilities for both accuracy and analysis time. At the same time, the finer points of the design can be observed to make certain the system is easy to operate and simple to maintain.

Any chemical analysis procedure can be automated as long as there is a sound technological method of extracting, separating, and detecting the desired element. By making use of past technological advancements and investigating new technology, a system designer can follow the process just outlined and produce a functional, useful system. As industrial technology advances, the number of analytical procedures being automated will increase geometrically.

As far as the next decade is concerned, several technological breakthroughs should be noted. The latest microcomputers can already talk, interpret speech, and control entire groups of laboratory instruments.

"Voice data entry" terminals in existence today are already capable of recognizing and responding to a vocabulary of 1000 words, and many companies, from giants like IBM or Nippon Electric to small firms like Heuristics, Inc., or Centigram Corporation, are racing to expand that vocabulary, simplify the technology, and radically slash the costs. Advances in robotics have been equally impressive.

Impact of Automation on the Laboratory

The impact of all of this on the laboratory will be substantial. Even today, trained technicians, and some scientists, often perform repetitive tasks rather than delegate them to less skilled personnel. The new technologies will allow most of these tasks to be performed by machines, either alone or in conjunction with entry-level workers.

The scope of laboratory automation has been expanded to include specimen handling and specimen preparation, wet chemistry procedures, laboratory process control, and instrumental analysis.

Rapidly improving computer technology (particularly microprocessor) has made easy-to-use and low-cost programmable computers readily available. Robotics, combined with programmable computers, can be used in many applications to improve laboratory productivity. To accommodate these new trends, laboratory layouts are becoming more open, compared to the conventional small, enclosed laboratories. Robotic systems are being placed on islands with total access to the work area. Laboratories are also becoming more decentralized, thereby concentrating on the specific application to provide better data and faster turnaround.

When manual procedures are used, specimens are typically processed in batches, with one task performed at a time. Computers, on the other hand, are capable of simultaneously controlling many tasks, thereby permitting the serialization of automated procedures. Serialization offers several potential benefits, including the following:

- *Efficiency*—Serialized procedures make use of laboratory equipment continuously, with specimens loaded and unloaded by robotics throughout the work day.

- *Uniform Sample History*—In well-planned, serialized procedures, each specimen receives identical processing. This reduces or eliminates sources of error.
- *Fast Availability of Results*—Data acquisition and processing can be speeded up tremendously.

The key to improving specimen throughput in a serialized procedure is to determine the rate-limiting step or element in the procedure and to improve throughput at that step through design innovation. Automated specimen preparation can be integrated into higher level laboratory information management systems (known as LIMS). In an automated system, more replicates, standards, and controls can be run and interpreted to verify satisfactory operation, and improve quality control.

Laboratory instrumentation manufacturers must recognize their growing role as systems architects, compared to their conventional past role as makers of laboratory tools and equipment.

Conclusion

Laboratory automation is essential for increasing the productivity of skilled scientists and technicians. Robotics is a rapidly emerging technology for the laboratory. User experience, product capability, and the range of applications are all rapidly increasing. The time to begin incorporating tomorrow's technology into instrument and laboratory design has arrived.

Ford A. Blair,[1] *Jon M. Arritt,*[1] *and Larry J. Lundy*[1]

Analytical Laboratory Information Management System (ALIMS)

REFERENCE: Blair, F. A., Arritt, J. M., and Lundy, L. J., "**Analytical Laboratory Information Management System (ALIMS),**" *Chemical Analysis of Metals, ASTM STP 944,* Francis T. Coyle, Ed., American Society for Testing and Materials, Philadelphia, 1987, pp. 97-107.

ABSTRACT: A computerized system has been developed that closely approaches total laboratory data automation. The system is menu driven, permitting the analyst to easily step through a hierarchy of works instructions. Data generation, calculations, dissemination, and retention are fully automated for instruments and automated for wet-chemical analyses prior and subsequent to raw data collection.

The system begins with the log-in of samples for which unique identification numbers are automatically generated. The total routine workload can then be scheduled by the computer. Overrides permit appropriate variations. Work centers query the system for assignments. The system not only controls and monitors work flow but invokes analytical and quality control procedures as well. For management control, sample status is readily available.

Instruments controlled by the system include inductively coupled plasma, atomic absorption spectrophotometer, optical emission spectrophotometer (ICP, AAS, OES), analytical balances, LECO analyzers, ultraviolet-visible spectrophotometer (UV-VIS), and automatic titrators. Report capability exists for back-logs, sample status, quality control, cost accounting, and periodic performance.

KEY WORDS: data processing, data generation, data dissemination, calculations, analytical instruments, analytical sample, log-in, work scheduling, sample status, quality control, management control, past due reports, backlog samples, analyst performance, laboratory performance, menu driven, password control

In the last 50 years the field of analytical chemistry has changed dramatically. Classical wet techniques have given way to instrumental methods for routine analysis. There will always be a need for wet chemical methods, but even these have grown, and will continue to grow, in sophistication. These events have produced changes in analytical terminology, and for some a com-

---

[1] Manager of Analytical Laboratory Section, senior chemist, and chemist advanced, respectively, Inco Alloys International Inc., Huntington, WV 25720.

pletely new vocabulary. Formal educational requirements are significantly different, and planned continuing education is a must for all.

Fifty years ago our laboratory handled analytical data just as all others did: handwritten calculations with pencil and paper. In addition to the analysis, each chemist was responsible for recording finished data in an assay log book and for maintaining his own raw data files for some time period. As the laboratory grew and the workload mushroomed, these tasks became somewhat easier as the advancing technology provided slide rules, mechanical calculators, and the present day programmable electronic calculators. However, the problems associated with storage, retrieval, and dissemination of analytical data were not effectively addressed until computers became available.

The advent of computers in the laboratory is probably the singly most important change agent ever in terms of effects on total laboratory operation. This certainly is true with respect to the handling and dissemination of data. The Analytical Laboratory at Inco Alloys International, Inc., (IAII) performs approximately 875 000 analytical determinations on approximately 80 000 samples per year. This presentation describes a computer controlled information management system designed and implemented by the analytical staff at IAII. The system runs on a Digital Equipment Corporation VAX 11/750 computer and contains some features specific to our needs that were unique when we began the system design.

ALIMS: The System

The Analytical Laboratory Information Management System (ALIMS) consists of a modular design that allows easy maintenance (including modifications) and operation.

The system is MENU driven, incorporating the use of programmed forms (or templates). ALIMS has been divided into four subsystems, which are shown in the following Main Menu:

ANALYTICAL LABORATORY PROGRAM

1. Exit
2. Sample Entry/Scheduling
3. Laboratory Assignments
4. Analytical Results/Sample Status/Assay
5. Methods/Personnel

From these categories all laboratory functions operate. Entering a number, from 2 through 5, automatically calls another menu to the screen. Selections from succeeding menus allow the analyst to step through any desired sequence in establishing and controlling the work flow.

This can be demonstrated by assuming that the analyst has entered the number, 2, from the main menu. The following menu would appear on the screen:

SAMPLE ENTRY/SCHEDULING

1. Exit
2. Log-in Samples
3. Schedule Samples

From this menu the analyst will either log samples into the laboratory or will schedule work on samples previously logged in. Let us examine both cases. First, assume the analyst selected Option 2. The following menu would appear on the screen:

LOG-IN SAMPLES

1. Exit
2. Escape (To Main Menu)
3. Enter Samples
4. Modify An Entry
5. Reprint A Label
6. Delete An Entry

Assuming further that the analyst is performing the initial log-in of samples, he would enter Option 3 from the menu. The following menu would appear on the screen:

ENTER SAMPLES

1. Exit
2. Ladle
3. Ingot
4. Weld Pad
5. Miscellaneous
6. Remelted Ingot
7. Experimental Heat
8. Process Control

This menu lists the seven different categories that define all the samples we might analyze. One further selection of a specific category from this menu will bring to the screen a form. This form has been specifically designed to contain all the information that is pertinent to the identification of that sample type. The analyst simply is required to fill in all applicable blanks as he or she is automatically prompted through the form. Some blanks must be filled and the computer will not allow the analyst to proceed further until that occurs. After all information has been entered, the computer prompts the analyst for a review to insure that all information has been entered correctly. Having verified that he or she has correctly entered the identifying data, the analyst stores this in a file, and the computer simultaneously assigns a unique laboratory identification number to that sample. Also occurring simultaneously is the printing of a label that is immediately attached to the sample container.

All sample types from the above menu can be logged-in in this manner. These data are stored and are available for scheduling work to be performed on each sample. The Log-In menu contained three other categories: Delete An Entry, Modify An Entry, and Reprint A Label. These can be taken literally in that a sample entry can be totally deleted from the system at any time or changes can be made to the entry at any time. New labels can also be reprinted at any time.

Assume, now, that all samples have been correctly logged-in and the analyst is ready to schedule all required work on these samples. In our laboratory this may or may not be done by the same analyst. In most cases the scheduling will be done by a second individual because this tends to provide a cross check on the log-in process.

Now let us assume that the analyst has entered Option 3 from the Sample Entry/Schedule Menu. The following menu will appear on the screen:

```
                 SCHEDULE SAMPLES

1. Exit
2. Escape (To Main Menu)
3. Schedule Samples
4. Reschedule Samples
```

From this menu the analyst again chooses Option 3 for scheduling samples, and the following menu will appear on the screen:

```
                   SCHEDULE SAMPLES

1. Exit            _____ Ladle            _____ Miscellaneous
2. One Sample      _____ Ingot            _____ Experimental
3. Some Samples    _____ Weld Pad         _____ Process Control
4. All Samples     _____ Remelted Ingot
```

This split screen display shows the numbered choices on the left and the sample types, which can occur with each of these choices, on the right. This allows the analyst to schedule any number of samples of any type in any desirable fashion. Of all the samples logged-in, the analyst might wish to schedule only one, or all the ingot samples of one alloy, or all the samples that are available.

Computer files containing all analytical methods in use in the laboratory have been developed. The files also contain three arrays that describe analysis characteristics such as the number of replicate specimens to be analyzed, whether or not the specimen is an over-check, and the method priority. Routine scheduling combines these three arrays with an elementary methods file to select the routine methods needed. Routine scheduling also incorporates nonelemental methods. Using a computer assigned method number, all methods remain unique.

When the choice has been made, the computer automatically, and transparent to the operator, sequences through five different scheduling options. These internal options are

A. If scheduled samples are routine, all routine methods are displayed. The computer then prompts the analyst with the following screen:

1. Exit
2. Schedule These
3. Make Methods Changes
4. Schedule Manually, By Alloy Independent Methods, Or Change Current Routine Methods

If the sample types are routinely analyzed in the laboratory, the computer files contain all specific information relative to elements to be determined in each different alloy type. The analyst selects Option 2 from the menu and all scheduled determinations are automatically transferred to a pre-weigh file awaiting method application. This action simultaneously deletes the sample from the Log-In file and creates a data receiving file.

If Option 3 or 4 is chosen, other menus appear that prompt the analyst through necessary changes or additions. However, these options will eventually direct the analyst back to Option 2 for completing the scheduling process.

B. If the sample cannot be routinely scheduled, the following menu appears:

1. Exit
2. Need to Create/Modify Methods
3. Schedule Manually
4. Schedule By Alloy Independent Methods

Option 2 is used to input data relative to procedures that have not already been filed and does not refer to the development of new analytical procedures. Option 3 permits manual scheduling of samples, but this is still accomplished within the computer. Option 4 refers to methods that are primary in nature and do not require an alloy matrix calibration standard:

C. If The Sample Is An Ingot, it will be scheduled according to previous ingot requests.

D. If The Sample Is Miscellaneous Type, all established miscellaneous methods will be scrolled for review. The system will attempt to schedule like known routine samples. Failing this, the sample will be scheduled manually in Option 3 above.

E. If The Sample Is Experimental, it will be processed as a miscellaneous sample.

This system permits scheduling and rescheduling of work with a great deal of flexibility. Sample information and analytical methods are easily manipulated. Moreover, scheduling keeps track of certain sample types moving through the system. The system can schedule additional analyses or a different set of analyses after a designated number of samples has passed through the system or after a designated number of days has elapsed. This provides for automatic over-checking on performance of analytical instruments.

Assume, now, that all samples have been scheduled. The next option, 3, from the Main Menu controls assignment of work throughout the laboratory. The scheduling procedure creates files that are specific to individual work centers. The analysts query these files for daily work assignments. Assuming that the analyst has chosen Option 3 from the Main Menu, the following menu appears:

ANALYTICAL ASSIGNMENTS

1. EXIT
2. Atomic Absorption Spectroscopy
3. Balance (Mettler A-30)
4. Balance (Mettler A-160)
5. Inductively Coupled Plasma (JACO)
6. Inductively Coupled Plasma (ARL)
7. LECO (CS-344)
8. LECO (NOA)
9. Manual Data Input
10. Potentiometric Titration
11. Spectrophotometric (HP)
12. Dissolving/Sample Preparation
13. Routine Sheets For Instruments Not Currently Interfaced
14. X-Ray Fluorescence (MRS 300)
15. X-Ray Fluorescence (MRS 400)
16. Optical Emission Spectrograph (JACO)

This menu demonstrates the diversity of the computerized system. Each of these menu options has additional operating menus associated with it. Consequently, a detailed explanation of each is too lengthy to be addressed here. However, an understanding of the work assignment process can be gained from the following general description.

The first step in sample processing is the weighing of analytical specimens. The electronic balances are interfaced to the computer and the analyst is prompted through the weighing process. Appropriate specimen weights have been previously assigned, and filed, based upon known or estimated concentrations of the elements to be determined. The computer enforces process quality control by imposing limits on acceptable specimen weights, prompting the analyst to the next sample, and printing adhesive backed labels for transferring to beakers.

All the parameters associated with dissolving specimens and preparing them for further analysis have also been predetermined and filed. The analyst querries the computer for a listing of all weighed specimens. This listing provides information for each specimen relative to the type, or types, and quantities of dissolving acid to be used. It also supplies notes on unusual specimen characteristics that might impact the solution process. When properly dissolved, the specimens become the responsibility of another work center. This can be a preparation area for instrumental analysis or an area for wet chemical separations. In either case, the analysts there query the computer for work instructions. For instrumental analysis, the analyst receives a listing of specimens with specific instructions as to aliquot volumes and volumetric flask sizes. With gravimetric procedures, precipitate weights are automatically entered into the computer from interfaced balances, and the computer calculates desired elemental concentrations.

Analytical instruments attached to the system include: two AA spectrophotometers; simultaneous ICP spectrometer; sequential ICP spectrometer; two simultaneous XRF spectrometers; OE spectrograph; carbon/sulfur analyzer; nitrogen/oxygen analyzer; UV/VIS spectrophotometer; and a potentiometric titration analyzer.

Both ICP spectrometers and one XRF spectrometer have attached control computers that operate the instruments with the manufacturer's commercial software package. These computers, however, are interfaced to the main laboratory computer, which cues all operating sequences. With these instruments ALIMS serves as a repository for all generated data and maintains all quality control functions. All other instruments are interfaced directly to the main computer, and ALIMS serves as the complete control system.

The most important aspect of ALIMS as a control system is the quality control function. Quality control begins with the computerized selection of the proper standard to be analyzed with each suite of weighed specimens. Groups of standards to be used with each alloy type have been previously selected and inserted into the methods files. The computer selects the correct alloy standard based on concentration levels of the elements to be determined. Subsequent acceptance of analytical data from unknown specimens is based on performance on analytical standard specimens. Performance is monitored by statistical applications that compare generated data to established limits. Statistical applications include the Grubbs Test for outliers, two sided normal distribution test, Chi square test for variances, Cometto test for weighted means, and standard deviation.

ALIMS prompts the analyst through required calibration procedures and will not allow analysis to proceed until all statistical requirements have been met. Additionally, the system monitors the analysis of unknown specimens on a continuing basis and instructs the analyst to recalibrate if necessary. If recalibration is necessary, the system defines the last acceptable specimen data and instructs the analyst to reanalyze specimens from that point forward. Ultimately, all data generated by analytical instruments are statistically acceptable. We define this as instantaneous, or real time, quality control. Wet gravimetric procedures are different in that the analyst is not aware of the quality of performance until the analytical procedure has been completed. However, we are quickly aware of the quality after the data are entered into the computer. These data are tested statistically the same way as instrumental data, and those requiring rechecking will not be accepted.

The next option in the main menu deals with the collection, handling, and dissemination of analytical data. Selection of Option 4 from the Main Menu produces the following menu on the screen:

ANALYTICAL RESULTS

1. EXIT
2. Assay
3. Standards
4. Chemistries
    A. Composition Ranges
    B. Average
5. Sample Status
6. Reports

An assay of all samples develops from the collection of processed data. Data from instruments, as well as manual input from gravimetric procedures, build a raw data file. This file will generally contain elemental data generated by two or more analytical methods. Quality control applications will have been previously invoked at the individual method source, and the data transferred to this file are all statistically acceptable. Ultimately this file will contain a single elemental value from each source method. At this point an analyst will review all submitted data, and if acceptable, initiates a transfer to the final assay file. The final assay utilizes all single value source data in arriving at the statistical mean elemental values appearing in the final assay. This mean value calculation prioritizes the source values with respect to the variance associated with the individual method. Since all data are statistically acceptable, the most precise method has the greatest influence on the final assay elemental values.

ALIMS maintains an inventory of some 500 standards, which include SRMs, CRMs, and internally developed standards. The quantity of internal alloy standards is monitored to insure that an ample supply of each is available. These files list complete assays on each standard. The quality control applications access these files for certified elemental values for comparison to analyzed values in routine analysis. This section also contains a file of open text, brief descriptions of all elemental methods in current use.

Option 4 in this menu provides access to defined alloy elemental concentrations for commercial products. All final assay chemistry for each heat produced is compared to listings in this file to insure that the product meets defined alloy compositional requirements. This section also maintains a historical running average for each element in each alloy produced. This file is accessed by the scheduling function in determining proper specimen weights and aliquots relative to known average elemental concentration in each alloy.

The status system links all processes operating within ALIMS. Specimens follow a status "blueprint," which identifies the previous and next work stations. After the specimen has been through the scheduling process, all changes to the specimen and its scheduled analyses must be done in the status program. Since all laboratory work stations periodically refer to the status system, the analyst receives immediate notification of the termination of or changes in analytical requests.

All reports are made possible by status codes which are established during the scheduling process. From these codes analysis times can be determined. These can then be compared to known, and filed, turn around times for each analytical method. At the time of scheduling a projected finish date is entered, and actual analysis times are compared to this date. From this the system produces past due information and projects new finish dates. These status codes make possible the complete evaluation of our analytical processing system.

ALIMS provides for a variety of reports that can be viewed either from a CRT screen or as printed reports. As a management control device, information is generally reviewed from the CRT screen. This, in conjunction with electronic mail capabilities, provides for a rapid communications device among the management staff. Option 6 from this menu provides access to the following reports:

- *Quality Control*—These can include all of the statistical tests, but those most frequently viewed are the weighted mean and precision statements. Direct comparison of analytical values from different methods is available.
- *Sample Status*—These reports provide information on progress of samples through the laboratory. The analyst can easily determine the last procedural step completed, the length of time spent on each step, as well as total elapsed time, and projected time to completion.
- *Past Due Reports*—Information from the status files automatically provides daily, or as desired, reports showing the specimens already past the projected finish date.

- *Backlog Samples*—The status files, in conjunction with the scheduling system, automatically provides a daily listing of samples that have been backlogged.
- *Analyst Performance*—The system provides for easy assessment of individual analyst performance on standards. Turn around times can also be monitored on an individual basis and can be indicative of individual efficiency. This provides for management a means for determining and correcting bottlenecks in laboratory processing.
- *Laboratory Performance*—The system can provide monthly accounting reports in great detail. These include: total work units produced during the month; analytical costs by alloy, by heat, or by individual cast ingot; the number and types of samples analyzed, and, if desired, analytical costs associated with these; analytical costs by department, by experimental project, or by individual requester; and costs associated with laboratory administration. The system also provides calculations relative to analytical cost per determination or per sample.

The final selection from the main menu relates to methods of analysis and laboratory personnel. If Option 5 from the Main Menu is selected, the following menu appears on the screen:

METHODS/PERSONNEL

1. EXIT
2. Methods
   A. Elemental
   B. Non-Elemental (eg., Specific Gravity)
   C. Current Needs
   D. Print Alloys Loaded/Method
   E. Edit Report Requesters
   F. Change Std In Method File
   G. Print Method Codes
   H. Establish Routine Method Codes
   I. Load Files Names/Workstations
   J. Load Method File Addresses
   K. Copy Method File Addresses
3. Qualified Personnel
4. Calculator

The files containing information necessary to schedule and process all specimens through the laboratory are found in this section. This includes both elemental and nonelemental methods. These are not written analytical procedures but computer codes that refer to analytical methods. Once method information for a particular sample type has been loaded, the sample becomes routine to the computer. Changes, however, can be made at the scheduling level for a single specimen. Permanent changes are made only by developing new method information.

Vital functions necessary for laboratory operation are protected using a password system. Without the correct password for a specific function, that part of the system cannot be accessed. Each analyst has been qualified to perform certain analytical procedures by our laboratory quality control program. Personnel files contain this qualification information. These files are accessed each time an analyst logs on and the computer verifies proper qualification to perform the analysis.

Summary

A computerized system has been developed that closely approaches total laboratory data automation. The system is menu driven, permitting the analyst to easily step through a hierarchy of works instructions. Data generation, calculations, dissemination, and retention are fully automated for instruments and automated for wet-chemical analyses prior and subsequent to raw data collection. The system not only controls and monitors work flow, but invokes analytical and quality control procedures as well. For management control, sample status is readily available. Report capability exists for backlogs, sample status, quality control, cost accounting, and periodic performance.

Robert L. Watters, Jr.[1]

Quality Assurance in Metals Analysis Using the Inductively Coupled Plasma

REFERENCE: Watters, R. L., Jr., "**Quality Assurance in Metals Analysis Using the Inductively Coupled Plasma,**" *Chemical Analysis of Metals, ASTM STP 944,* Francis T. Coyle, Ed., American Society for Testing and Materials, Philadelphia, 1987, pp. 108–127.

ABSTRACT: The inductively coupled plasma (ICP) technique is a useful approach for multielement analysis of a wide variety of materials. Published reports have described the successful application of the ICP technique for the analysis of trace, minor, and major elements in metal alloys. When assessing the quality of analytical results using the ICP or any other technique, one must consider the contribution of various parts of the measurement process to the total error. In addition to random error, a careful evaluation of all possible sources of systematic errors must be undertaken, so that the appropriate corrections can be applied to the analytical results. Emission spectroscopists are well aware of the problems caused by spectral interferences in ferrous matrices. The inherent linearity of the ICP technique offers a correction scheme for dealing with spectral interferences, but the method of measuring correction factors and accounting for their variability warrants close examination.

Most descriptions of ICP applications report relative freedom from matrix effects. Although the magnitude of systematic errors may be less than for other spectrometric techniques, such errors can cause analytical bias, which can appreciably affect the final results. For example, it has been shown that differences in acid concentration between pure element standards and the sample can cause systematic error. This type of problem can occur when complex alloys are dissolved for ICP analysis. Examples of these kinds of errors and approaches to correcting for them are presented.

KEY WORDS: inductively coupled plasma, spectral interference, matrix effects, precision, accuracy, analysis of variance

The accurate determination of major, minor, and trace elements in metals using the inductively coupled plasma (ICP) represents one of the most difficult applications of an emission spectrometric technique. Although the ICP

---

[1] Research chemist, Inorganic Analytical Research Division, Center for Analytical Chemistry, National Bureau of Standards, Gaithersburg, MD 20899.

technique has fewer interferences than other spectrometric techniques, ICP quality assurance requires that measurable biases be corrected. The three basic components of quality assurance in any measurement process are the control of random errors, the measurement and correction for all significant known sources of systematic error, and the evaluation of all uncertainties in these corrections. In the ICP analysis of metals, one of the basic indicators of random error in the measurement process is the variability of replicate instrumental integrations. Most commercial instruments control this source of error by providing stable electronics, rigid optical systems, and well-tested solution nebulizer devices. Furthermore, the available analytical software usually provides a convenient routine for calculating the average and standard deviation of replicate integrations during the aspiration of a sample or standard solution. An inherent danger of this convenience is to assume that this is the only source of random error.

It is important that the basic instrumental variability be controlled sufficiently to allow sources of bias in the analytical measurement to be discernible above the noise. The major sources of systematic error that should be evaluated are spectral interferences, chemical and physical differences between calibration standards and samples, and instrumental drift. In the analysis of metals, where one of the principal constituents is often iron, the problems of spectral interferences are well known among emission spectrometrists. The variety of metal alloys that must be dissolved for ICP analysis will also require a combination of acids and fusion fluxes that will be difficult to match in the calibration standard solutions. Differences in viscosity, acid concentrations, and alkali element concentrations between samples and standards may cause bias in the analytical results. The following discussion will focus on the problem of spectral interferences because of its importance to metal analysis using the ICP. Certain approaches to measuring and correcting for spectral overlaps are specifically applicable to polychromators, whereas sequential spectrometers may require a different procedure. Identification of other significant sources of random and systematic error are also discussed. Procedures for matrix effect and instrumental drift corrections are suggested that ensure accuracy in the ICP analysis of metals.

Spectral Interferences

In designing a method for the analysis of metals, particularly ferrous alloys using any form of emission spectrometry, a set of spectral lines for all analyte elements must be chosen. One usually considers spectral sensitivity, freedom from spectral overlap with matrix element lines, and freedom from spectral interference from other emission lines of minor or trace constituents. There are several literature sources for checking the most sensitive analyte emission lines for spectral interferences from iron or other analyte lines. The commonly used National Bureau of Standards (NBS), Massachusetts Institute of

Technology (MIT), and Zaidel tables [*1-3*] provide a comprehensive list of spark and arc emission lines but give little information concerning the relative sensitivities and degree of interferences that arise from ICP excitation.

Of more use to ICP spectrometry are the line coincidence tables by Boumans [*4*], the tables of iron emission lines by Michaud and Mermet [*5*], and the ICP wavelength scans by Winge et al. [*6*]. The Boumans tables relate ICP sensitivities, calculated from an algorithm applied to the NBS table sensitivities, to the bandpass of the spectrometer to predict the severity of spectral interferences from many possible elements. The Michaud and Mermet reference lists iron emission lines from 200 to 300 nm. This table is most useful for selecting analyte emission lines for ferrous matrices.

In the consideration of a set of spectral lines for the ICP analysis of ferrous materials, many spectral interferences can be predicted by consulting these and other references. However, the next step must be the actual experimental verification of interference-free analyte spectral lines for the range of matrices of interest. The results of such a study have been reported by Snyder [*7*] for the analysis of cast irons, carbon steel, low-alloy steel, silicon steel, ingot iron, and wrought iron matrices. To ensure that the results of this study are attainable by most commercial instrumentation, a spectrometer with 0.028-nm resolution was used. The author's proposed list of interference-free analyte lines is reproduced in Table 1. The table also indicates whether the emission line results from an excited atomic or ionic state of each element.

TABLE 1—*Wavelength list for ICP analysis of low-alloy steels.*

Element	λ, nm	Sensitivity Rank	Sensitivity Factor
Al I	396.153	2	1.3
As I	189.042	5	2.6
B I	182.641	...	...
Ce II	456.236	11	1.5
Cr I	427.480	10	2.7
Co II	228.616	2	1.2
Cu I	327.396	3	1.8
La II	408.672	3	1.0
Mg II	280.270	2	2.0
Mn I	280.106	9	15.0
Mo II	281.615	8	1.8
Ni II	231.604	3	1.5
Nb II	319.498	6	2.0
P I	178.280	...	...
Si I	288.160	2	2.2
Sn II	189.980	1	1.0
Ti II	334.941	1	1.0
W II	207.911	1	1.0
V II	311.071	5	2.0
Zr II	339.198	2	1.0

It is instructive to examine the consequences of choosing these lines for interference-free analysis at a spectral resolution of 0.028 nm or better. The third column in Table 1 lists the rank of each spectral line in the order of its sensitivity as given by Boumans [*4*]. A rank of 1 means that the spectral line gives the best detection limit for the ICP determination of that element. Higher numbers in this column mean the sensitivity has been sacrificed to ensure freedom from spectral interferences. The fourth column contains a measure of how much sensitivity is lost relative to the detection limit of the most sensitive line for a given element. This factor is obtained by dividing the detection limit of the listed spectral line by the detection limit of the most sensitive line. Again, the data are from Boumans [*4*]. A factor of two in this column means that the most sensitive line for this element is twice as sensitive as the listed interference-free line.

It is apparent that the sensitivity for a number of elements has been reduced by a factor of two or more in an effort to avoid interferences. The list includes arsenic, chromium, magnesium, manganese, niobium, silicon, and vanadium. The most seriously compromised element is manganese, where the selected line is over 15 times less sensitive than the first ranked line at 257.610 nm. Whether or not these compromises in sensitivity are important for the analysis of low alloy steels can be estimated by examining the lowest analyte concentrations found in some Standard Reference Materials (SRMs) in the appropriate classes of alloys. If one assumes that 0.5 g of the alloy is dissolved and diluted to a volume of 100 mL, the resulting analyte concentration in solution can be compared to the detection limit for the spectral line of the analyte element. When this comparison is made for spectrographic ingot irons and low alloy steel SRMs [*8*], it is found that the detection limits for the spectral lines of arsenic, chromium, magnesium, manganese, niobium, silicon, and vanadium are at least three times lower than the lowest certified concentrations likely to be encountered in the analysis of these materials. It can therefore be concluded that no serious compromises in sensitivity have resulted from the line selection process.

The selection of analyte element lines must also take into account possible interferences from spectral lines of elements other than iron. Some analyte element concentrations can range over three orders of magnitude for the alloys of interest. For the spectral lines that are ranked 4 or higher, one can examine the tables of Winge et al. [*6*] to check for interferences from aluminum, calcium, copper, lithium, magnesium, manganese, titanium, and vanadium, as well as iron. Of these possible interferents, aluminum, calcium, lithium, and magnesium are not likely to be high enough in concentration to be of concern. However, one does find a few possible interelement interferences when the other concomitants are present at levels 200 times the analyte concentration. Inspection of these tables of spectral scans bears directly on the application of commonly available spectrometers since the spectral line widths at half-maximum intensity are stated to be about 0.025 nm. The analyte lines and possible interferences found are listed in Table 2. Since Winge et al. have furnished spectral scans for the four most sensitive lines of the elements, lines of lower rank in Table 1 must be checked by consulting other references, such as Boumans [*4*], or by direct experimental observation. Snyder [*7*] has checked for interferences among the elements listed in Table 1. Although boron and nickel were found to interfere with cobalt; no interference from titanium was found. An interference from phosphorus was the only one listed for copper as the analyte, and no interferences for magnesium and silicon were found.

The interferences on cobalt and silicon were not detected by Snyder, although they appear to be quite significant in the wavelength scans from Ref *6*. The analyte concentrations used by Snyder were chosen to simulate actual sample concentrations (0.050 μg/mL). Interference effects can be partially masked by the noise at this level. It is interesting to note all of the interference effects except one recorded by Snyder are no less than 10% relative to the analyte concentration. It is possible that interference effects less than 10% were not considered to be significant.

Although no interferences caused by titanium were listed in Ref *7*, inspection of the Boumans [*6*] tables indicates a possible interference from titanium at 427.458 nm on the chromium line at 427.480 nm. At a spectral resolution of 0.030 nm, titanium is expected to give a signal equal to that of chromium if the titanium/chromium concentration ratio is 150. Although there are only a few examples of ferrous materials with a titanium concentration over 100 times the chromium concentration, significant errors could occur even at lower titanium/chromium concentration ratios. For example, SRM 465, Ingot Iron E has a titanium/chromium concentration ratio of 0.20%/ 0.004% = 50. A spectral scan of the wavelength region around 427.480 nm is presented in Fig. 1 for 1.0-μg/mL chromium and 50-μg/mL titanium. The spectrometer used for this scan has a spectral resolution of 0.014 nm. Although these spectral lines are almost completely resolved at this resolution, a spectrometer of 0.028-nm resolution would be unable to resolve the pair, and an error in the chromium determination would result.

Another example can be found by checking the Boumans tables [*4*] for interferences of the vanadium line at 311.071 nm. Again titanium is predicted to give an equal signal if its concentration is 100 times that of vanadium.

TABLE 2—*Analyte wavelengths and interferences from Ref* 6.

Analyte	λ, nm	Interferent	λ, nm
Co	228.616	Ti	228.618
Cu	327.396	Ti	327.405 (slight)
Mg	280.270	V	280.280
Si	288.160	Cr	288.193

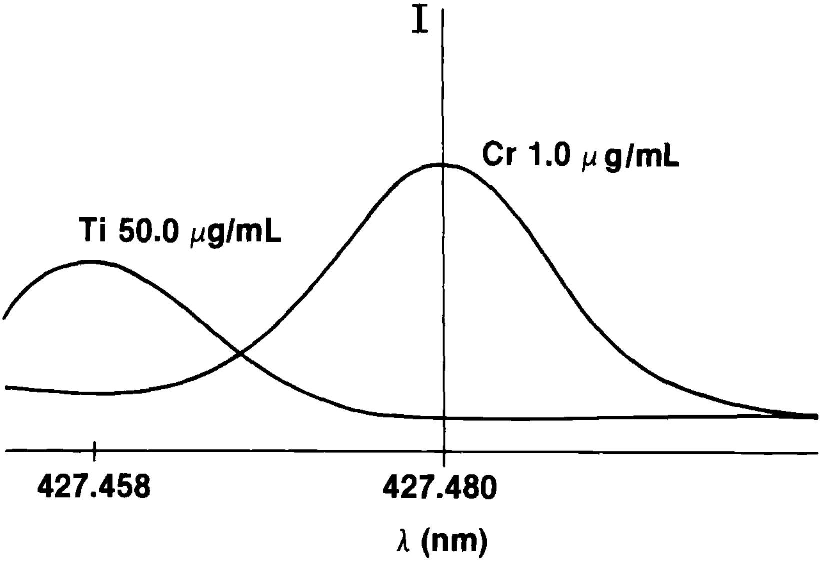


FIG. 1—*Spectral scan of titanium and chromium at 427.480 nm with a resolution of 0.014 nm.*

SRM 465 serves as an appropriate example with a titanium/vanadium concentration ratio of 0.20%/0.002% = 100. A spectral scan of the 311.071-nm wavelength region for 0.5-μg/mL vanadium, 5000-μg/mL iron, and 0.5% solution of SRM 465 is presented in Fig. 2. It is apparent that although iron does not interfere with vanadium, the shape of the vanadium line is distorted and shifted by the presence of the titanium line at 311.067 nm. This degree of line overlap cannot be resolved even with the spectrometer resolution of 0.007 nm used for the scans in Fig. 2.

In such cases one might employ a spectral interference correction procedure to subtract the titanium contribution from the vanadium intensity at 311.071 nm. If a series of solutions with varying amounts of titanium are aspirated into the ICP, the resulting wavelength scans can be displayed as in Fig. 3. The dependence of the apparent vanadium intensity on the titanium concentration can then be calibrated and used to calculate the correction factor for the sample. When the sample is analyzed, the determination of titanium must be made first, and in this case the 334.941-nm line is free from other interferences. The wavelength scan for titanium is given in Fig. 4, and the concentration of titanium in SRM 465 can be calculated. This value is then used to calculate an apparent vanadium concentration caused by titanium in the spectral window of the vanadium line at 311.071 nm. This value is then subtracted from the total concentration calculated from the measured intensity at 311.071 nm, and the corrected vanadium concentration is obtained.

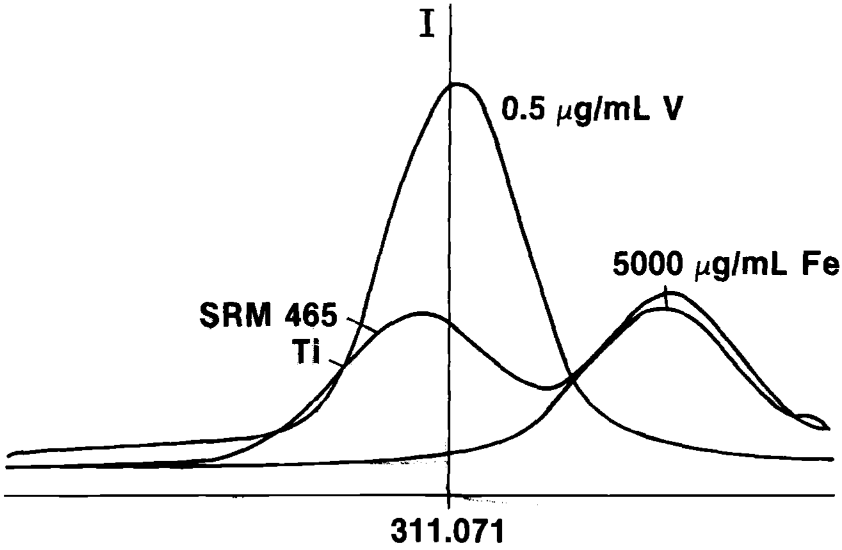


FIG. 2—*Spectral scan of vanadium at 311.071 nm for SRM 465 with possible interferences from iron and titanium.*

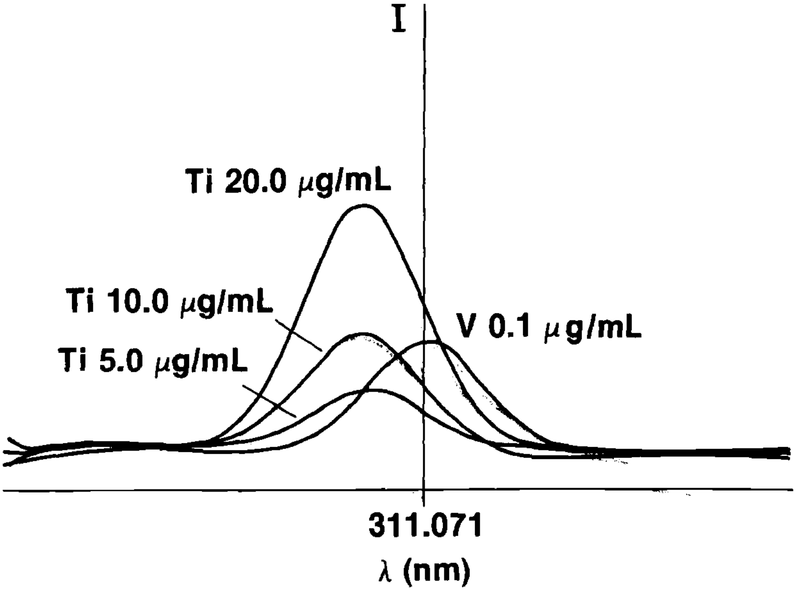


FIG. 3—*Spectral interference correction for titanium on vanadium by aspiration of increasing amounts of titanium.*

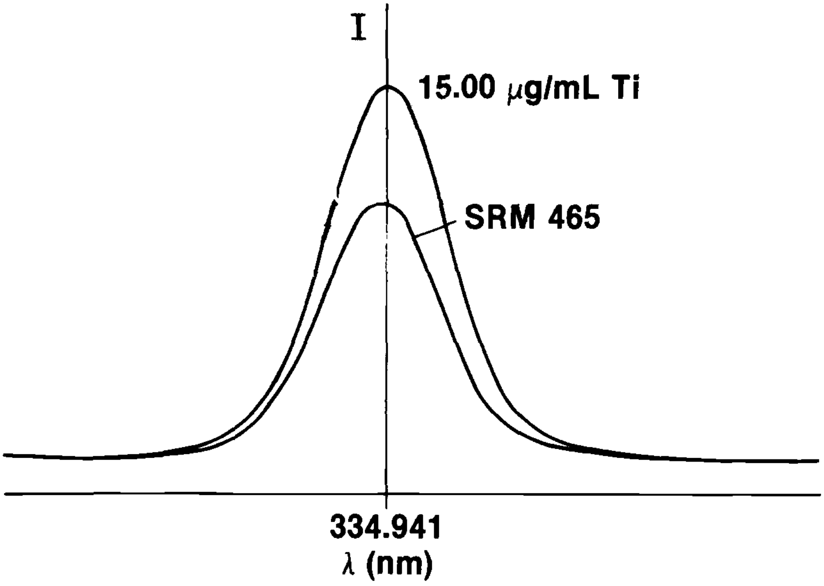


FIG. 4—*Spectral scan of titanium at 334.941 nm.*

The data for this approach are given in the second case of Table 3. These data are to be compared to the data in the first case of the table, where no interference correction has been made.

One of the problems associated with scanning sequential ICP spectrometers can be defined by careful examination of the scans in Fig. 3. When the standard solutions of titanium are analyzed to calibrate the interference function, the spectrometer finds the titanium peak within the spectral search window and centers on it. Since the titanium peak is slightly shifted from the vanadium peak, the measured intensity for apparent vanadium caused by ti-

TABLE 3—*Spectral interference correction schemes for vanadium in SRM 465. Duplicate data are given for each case. Vanadium in SRM 465 is certified at 0.002%.*

Case	Observed V, μg/mL	Apparent V Caused by Ti, μg/mL	Corrected V, μg/mL	V, wt. %
1. No correction	0.213	...	...	0.0043
	0.210	...	...	0.0042
2. Ti only used	0.213	0.098	0.115	0.0023
for correction	0.210	0.099	0.111	0.0022
3. V + Ti used	0.213	0.085	0.128	0.0026
for correction	0.210	0.086	0.124	0.0025

tanium is higher than it should be. The proper measurement would be on the side of the titanium peak at the central vanadium wavelength. One way to force a scanning spectrometer to make the measurement nearer to the vanadium peak wavelength is to add titanium to a solution that already contains an appreciable quantity of vanadium. Such is the case for the data plotted in Fig. 5. Successive amounts of titanium were added to 0.5-μg/mL vanadium so that the principal spectral feature in the peak search window is centered at the vanadium peak wavelength of 311.071 nm. The apparent vanadium concentration thus obtained, and the resulting values for corrected vanadium concentration are listed in the third case of Table 3. This improved correction scheme results in a change of over 10% relative in the final vanadium concentration value, compared to the first correction scheme. Both correction procedures yield values for vanadium that are significantly more accurate than the uncorrected value.

The procedures for implementing spectral interference corrections using polychromator ICP systems are more straightforward, since the exit slits are always centered on the analyte wavelength of interest. Unfortunately, spectral overlaps, for which corrections must be applied, are likely to occur more frequently with polychromators than with some sequential spectrometers. The reason is that most polychromators have focal lengths of 0.75 to 1.0 m and cover a spectral range of from 175 to 450 nm using both first and second order

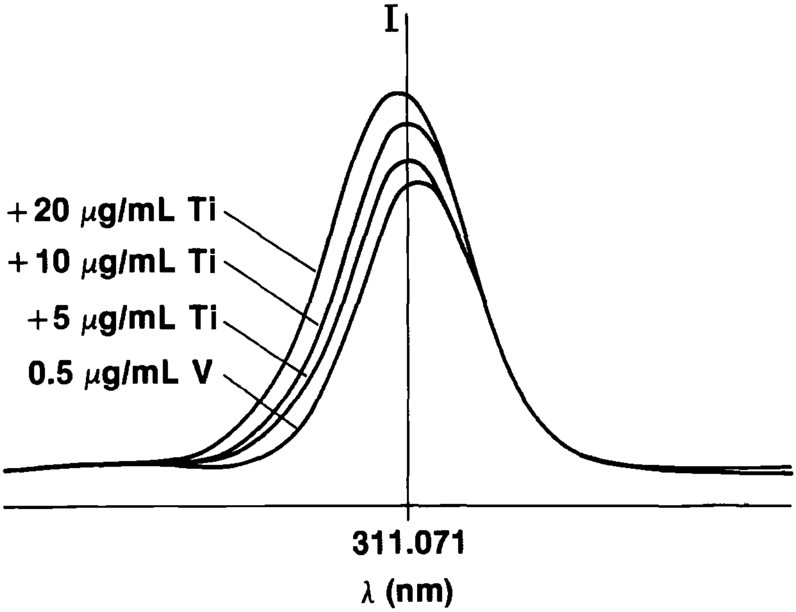


FIG. 5—*Spectral interference correction for titanium on vanadium by aspiration of increasing amounts of titanium added to a fixed amount of vanadium.*

lines. The resulting practical limit of spectral resolution is about 0.03 nm. The resolution limit is set by the size of the focal curve, optical aberrations at either end of the focal curve, and slit widths necessary to ensure optical stability.

By comparison, a 1-m Czerny-Turner monochromator with a 3600-line/1mm grating occupies the same laboratory space, and does not incur the off-axis aberrations of the concave grating. Consequently, such a monochromator is quite capable of a spectral resolution of 0.007 nm. This resolution approaches the typical widths of spectral lines emitted by the ICP, and therefore eliminates many spectral interferences that are caused by low-resolution spectrometers rather than true spectral line overlaps from the ICP itself. If one has to sacrifice the speed of simultaneous multielement analysis using a polychromator for the flexibility of a scanning sequential spectrometer, spectral resolution should not also be sacrificed.

Matrix Effects

Assuming that one can obtain spectral intensity measurements free from spectral interferences, other sources of bias must be evaluated and corrected. The final statement of uncertainty must include the variability of any correction factors as well as the random variability of sample preparation procedures, calibration procedures, and instrumental integrations. For the analysis of metals or any other complex matrix, systematic error can be caused by contamination of samples during dissolution, and differences in acid and matrix element content between samples and standards. Accurate estimates of contamination can be made by replicate preparations of blank solutions. The procedures used must be exactly the same as those for the sample, including all transfer, dilution, and digestion steps. Enough blanks must be prepared to acquire a good estimate of the uncertainty in the average blank values.

Differences in matrix content between samples and standards can cause up to 15 or 20% relative error, depending on the matrix, analyte element, and ICP operating conditions. Such bias manifests itself as a multiplicative error that can be corrected for by standard addition. Since the ICP exhibits linear response over a wide concentration range, single-point standard additions, or spike recoveries, often prove sufficient for correcting matrix effect bias. This approach is only suitable if background-subtracted intensities are measured, and enough spikes are run to allow estimation of the matrix effect correction factor variance. In general, it is not advisable to attempt matrix matching of the samples and standards. Usually it is difficult to avoid contamination of analyte elements in the standards when high concentrations of matrix elements are added. Perhaps the addition of 0.5% iron to the standards for low alloy steel and ingot iron analysis can be accomplished successfully. However, this concentration of iron will not match that found in all samples exactly, and therefore incomplete matrix effect correction will result. For the analysis of minerals and ores, dissolution procedures involving fusions are relatively easy to employ for both standard and sample solutions, making this a reasonable approach to matrix matching.

Other Sources of Random and Systematic Error

Results from ICP analytical measurements are usually summarized by an estimate of the "true" value and its uncertainty. Most often the estimated value is obtained by computing the average of a number of replicate analyses, and the uncertainty is expressed in terms of the standard deviation of these replicates. The standard deviation of the average or a confidence interval can also be reported. Treatment of the analytical data in this way assumes that the replicate measurements are mutually independent, normally distributed, and are from the same population that has a mean value μ and a standard deviation σ. Furthermore, the overall uncertainty statement implies that all sources of variance have been evaluated. Therefore, this statement applies to the sample homogeneity as well as the analytical measurements themselves.

Most sampling and analysis schemes contain steps that are related to one another in a hierarchic manner. Such a relationship is outlined in Fig. 6, which could represent the analysis of a number of bottles of a metal chip material. Duplicate samples are taken from each bottle, and each sample is measured using a number of instrumental integrations. Most commercially available software packages with ICP instrumentation provide automatic calculation of the average and standard deviation of replicate instrumental integrations. All too often analytical results consist of these data only, without proper regard to the variance of other steps in the analysis scheme. One can estimate the likelihood that instrumental replicates are the chief source of variance by inspection of the plot in Fig. 7. The relative standard deviation (RSD) is plotted against the detection limit multiple, indicating that at concentrations near the detection limit, instrumental variance may indeed domi-

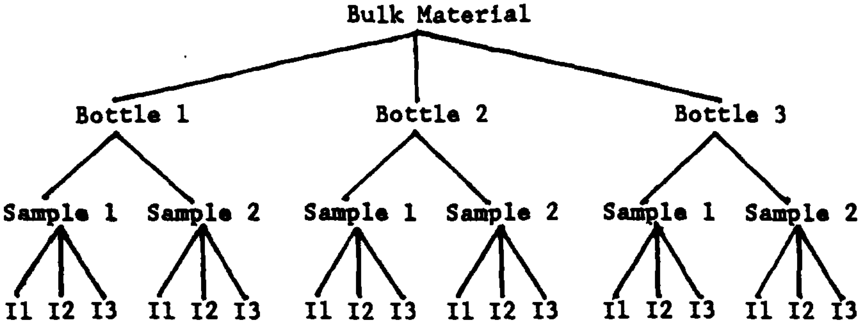


FIG. 6—*Hierarchic relationship of a typical metal SRM analysis.*

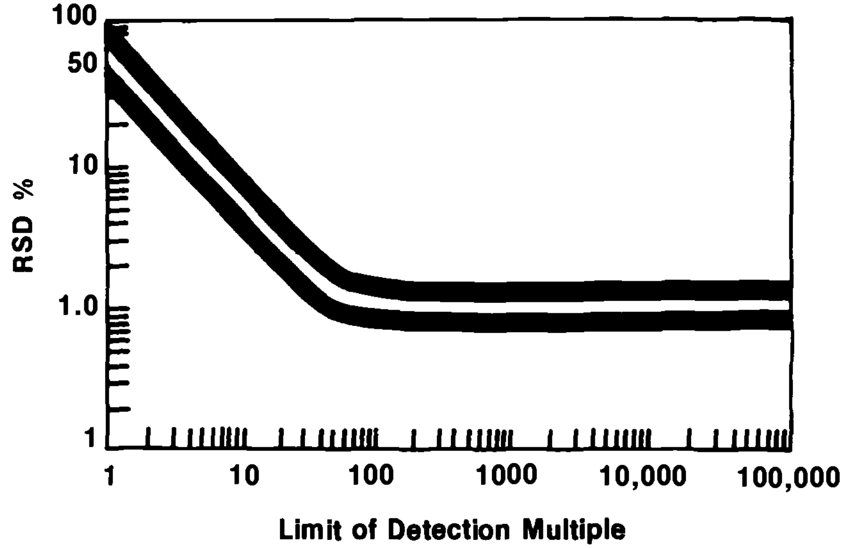


FIG. 7—*The relationship between relative standard deviation (RSD) of a determination and the concentration of the analyte in terms of detection limit multiple.*

nate. However, at analyte concentrations above 100 times the detection limit, other sources of variance, such as errors in volumetric dilutions, may be as significant.

The relative contribution of each of the steps in Fig. 6 to the total variance can be estimated by a classical analysis of variance (ANOVA). Although we are primarily interested in the application of the ICP to analysis of metals, the underlying concepts of the ANOVA and its results apply to ICP analysis in general. Analytical data for the determination of magnesium in powdered milk, SRM 1549, provide a good example for evaluating sources of variance. The data and corresponding ANOVA summary are presented in Table 4. Two samples were taken from each of eleven SRM bottles, and each result listed in the table is the average of four instrumental integrations. Estimates for variance between bottles, between samples within a bottle, and among instrumental integrations are obtained. In this case the sample-to-sample variance appears to be the most important, and a reasonable estimate of the random error of the method would be the standard deviation of the 22 numbers listed. A confidence interval based on this standard deviation and the *t* value for 21 degrees of freedom would also include the instrumental variability. Results based on bottle averages only would decrease the number of degrees of freedom to 10, when we have actually made 22 measurements. The approach used in the foregoing analysis can help to improve the efficiency of ICP analyses of a new sample matrix. For instance, analyzing a few samples from a single bottle of SRM 1549 would yield the same results, while saving a significant amount of time in sample dissolution and measurement.

TABLE 4—*Data and ANOVA for the determination on magnesium in SRM 1549, powdered milk. Concentrations are in μg/g.*

SRM Bottle	Sample 1	Sample 2
12-2	1201.1	1210.0
06-2	1213.3	1185.6
10-2	1247.6	1177.7
01-1	1177.1	1265.7
11-1	1248.9	1186.4
03-2	1224-1	1256.7
07-1	1240.5	1202.3
02-1	1168.4	1213.7
09-2	1204.4	1186.3
08-1	1210.1	1204.9
04-1	1206.5	1196.7

ANALYSIS OF VARIANCE FOR ELEMENT MG

Source of Variation	Sum of Squares	DF	Mean Square
Between groups (SRM Bottles)	16 246.843	10	1624.68
Between samples within groups	45 017.498	11	4092.50
Within samples	12 732.556	66	192.92
Total	73 996.900	87	

The mean squares estimate the following

$$\begin{aligned} 1624.68 &= V(0) + 4\,V(1) + 8\,V(2) \\ 4092.50 &= V(0) + 4\,V(1) \\ 192.92 &= V(0) \end{aligned}$$

where

$V(2)$ = variance caused by SRM inhomogeneity
$V(1)$ = variance caused by sample preparation and instrument drift
$V(0)$ = variance caused by instrumental integrations.

The estimates are

$$\begin{aligned} V(2) &= -309 \text{ (essentially 0)} \\ V(1) &= 975 \\ V(0) &= 193 \end{aligned}$$

Once the analysis steps with the most significant variability are identified and replicated, it is essential to examine the validity of the assumptions that the replicate measurements are indeed independent and normally distributed. Figure 8 is a smoothed histogram of the magnesium data, which indicates a tri-model distribution. Referring to the ANOVA summary in Table 4, it must be noted that each sample measurement requires a finite amount of time. Therefore, the estimate of sample-to-sample variance also includes the effect of instrumental drift during the course of the analysis.

Filliben [9] has described a convenient graphical method for testing mea-

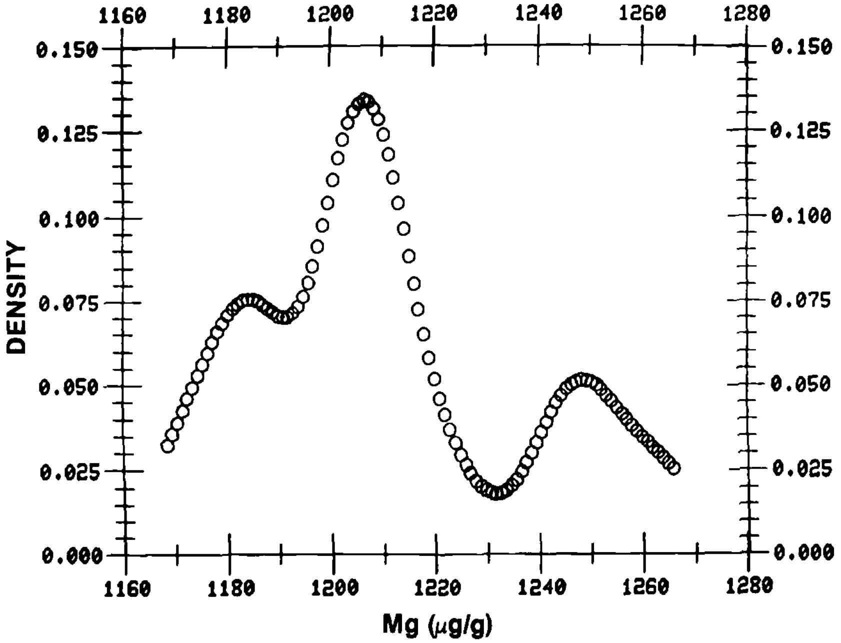


FIG. 8—*Smoothed density distribution of results for magnesium in SRM 1549, powdered milk.*

surement independence. This approach has been shown to be useful in detecting ICP instrument drift, which for the most part can be ascribed to changes in nebulizer performance [*10*]. An effective procedure for minimizing the effects of instrument drift is to follow each sample measurement with one of a standard. Provided the measurement time is much shorter than a half-cycle of any periodic drift in the system, the ratio of the true standard concentration to the observed standard concentration can be multiplied by the observed sample concentration. This correction assumes that drift errors are multiplicative and not caused by uncorrected changes in the spectral background. If each data point is a peak-minus-background measurement, additive errors caused by background shifts are minimized.

Interspersing measurements of a standard with sample measurements lengthens the analysis time. However, drift corrections can also be accomplished by the same procedures that are used to correct for matrix effects. If each sample measurement is followed by the measurement of the corresponding spiked sample, the corrected observation is obtained by

$$\text{corrected sample} = (\text{observed sample}) \times (\text{spike added/spike found})$$

where

$$\text{spike found} = \text{observed spike} - \text{observed sample}$$

If one applies some drift correction (DC) to each sample and spike measurement, the combined equations are

$$\text{corrected sample} = \frac{\text{DC (observed sample) (spike added)}}{\text{DC (observed spike)} - \text{DC (observed sample)}}$$

Notice that the term DC cancels, and the spike-recovery corrects for both drift and matrix effects. This makes intuitive sense since both drift and matrix effects are considered to be multiplicative errors.

As an example, the determination of aluminum in a limestone sample was accomplished by analyzing four samples from each of four bottles. Each sample solution was prepared with its corresponding spike solution, and the sample-spike pairs were nebulized into the ICP in random order. Each spike measurement immediately followed its sample measurement. All measurements consisted of four instrumental integrations. Under stable instrument conditions, 90% recovery is observed for this matrix, but in this case a significant amount of instrument drift was purposely introduced. This was accomplished by tuning the monochromator to a wavelength slightly off the peak wavelength used for aluminum and beginning the analysis immediately after starting the ICP. The ensuing temperature drift of the system caused the aluminum peak to gradually shift out of the spectral window. After six of the sample-spike pairs had been analyzed, the monochromator was retuned onto the aluminum peak before running the remaining solutions. Run-sequence plots of both uncorrected and corrected aluminum concentration versus instrument integration number are presented in Fig. 9. Instrument drift is quite evident in the uncorrected case, whereas the plot of the corrected data shows that bias caused by drift and matrix effects can be effectively minimized. In cases where the drift is pronounced, measurement of the spike solution before and after the sample and averaging the spike results is advisable. The amount of instrumental drift indicated by the data plotted in Fig. 8 is appreciably greater than that exhibited by most commercial ICP systems. For most applications of ICP spectrometry, long-term drift on the order of 1 or 2% is often quite tolerable. However, for the high-accuracy analysis of SRMs, or when excessive drift is caused by samples containing greater than 1% solids, these procedures have been found to be useful.

When such correction procedures are employed, the sample is homogeneous, and the variance of ICP instrumental measurements is below 0.5% RSD, sources of error caused by calibration must be taken into account. Even if the measurement of the standards is very precise, errors caused by sequential di-

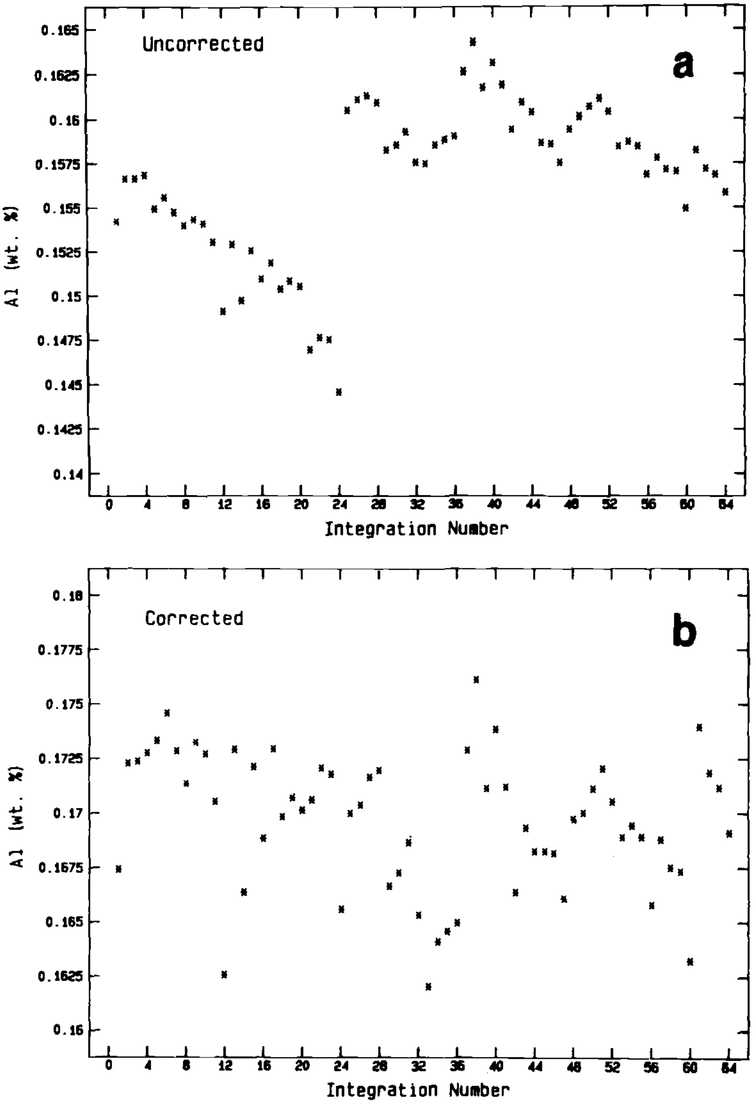


FIG. 9—*Run sequence for aluminum:* (a) *uncorrected data and* (b) *data corrected for matrix effects and drift.*

lutions of stock standard solutions can often exceed 0.25% RSD depending on the volumetric equipment used. Capacity tolerances for flasks and pipets [*11*] can be used to estimate the total error incurred by multiple dilutions. These effects can be reduced by restricting the use of transfer pipets smaller than 5 mL and volumetric flasks smaller than 25 mL. If primary standards are made in terms of weight of analyte per unit weight of solution, gravimetric dilutions can appreciably reduce the random error associated with such dilutions.

For many instrumental methods of metal analysis that use direct solid sample introduction, previously analyzed reference materials are often used as calibration standards. Recently, the use of dissolved SRMs has been suggested as a feasible approach to matrix-matched calibration for ICP solution analysis [*12,13*]. Since the certified values of SRMs have associated uncertainties, concentrations of the standard solutions of such SRMs will also have uncertainties. Even if the metal SRM is dissolved quantitatively for all elements of interest, the uncertainty of the concentration axis of the calibration curve for each element can appreciably affect the overall uncertainty of the sample analysis. This effect can easily be discerned by inspection of the series of plots in Fig. 10.

Figure 10*a* depicts the linear calibration of instrument response versus standard concentration for ICP analysis. A high standard and a standard with an analyte concentration of zero are used for two-point standardization. A measurement of the sample analyte intensity is made, and the concentration is calculated by inverse transformation of the calibration curve function. No uncertainties are indicated in this inset.

Figure 10*b* depicts the uncertainty in sample concentration that results from the variability of replicate sample intensity measurements. Intensity measurements associated with the high and low standard are assumed to have no random error. The assumption that the calibration constants have no uncertainty may cause an underestimation of the overall analytical uncertainty.

Figure 10*c* is a graphical representation of the uncertainty limits of a calibration curve that result from the variance of the standard solution intensity measurements. Notice that the variance for the low standard measurement is smaller than that of the high standard measurement. The linear confidence band that is drawn around the calibration curve is not intended to represent the exact shape of the true confidence band. Rather, it is drawn so that the effect of calibration uncertainty can be simplistically indicated by intersection of the sample measurement uncertainty band with the calibration uncertainty band. The resulting sample concentration uncertainty interval is appreciably wider than the interval indicated in Fig. 10*b*.

Figure 10*d* graphically represents the effect of adding the uncertainty of the concentration of the high standard. This is the uncertainty associated with using an SRM or other analyzed reference material as the source of the high standard. The uncertainty band of the calibration curve is widened at the high concentration end, and its effect of increasing the uncertainty in the sample concentration is evident. It is interesting to note that if the uncertainty band limits of the calibration curve are symmetric and nonparallel about the curve (line) itself, the confidence interval about the average sample concentration is asymmetric.

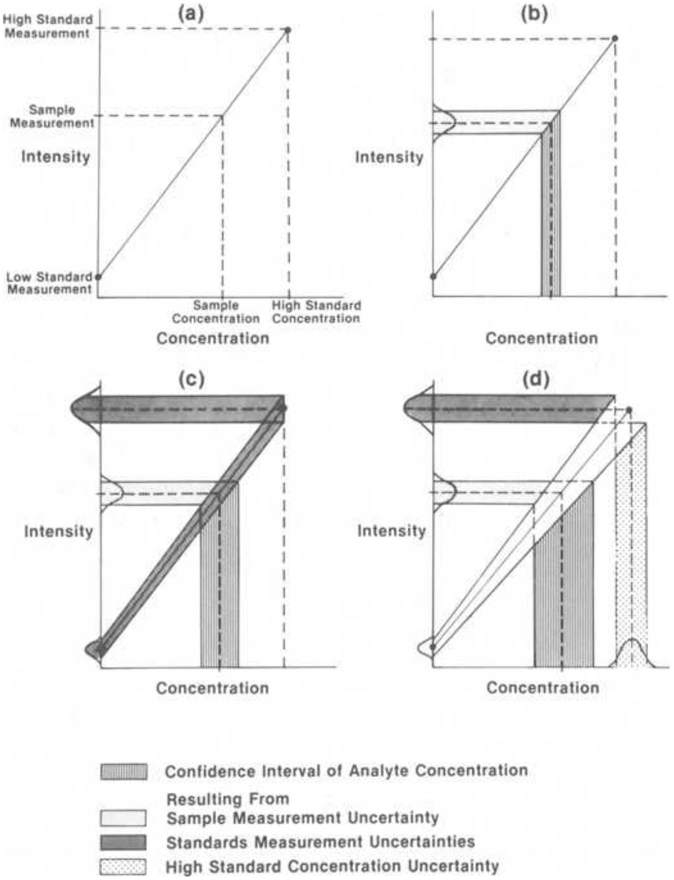


FIG. 10—*Effect of various sources of variability in calibration on the uncertainty of a measured analyte concentration.*

Conclusions

Despite the difficulties encountered in the application of the ICP technique to the analysis of metals, accurate and precise data can be obtained by correcting for specific sources of error. Spectral interferences are the most likely sources of bias that can cause gross errors in the analytical results. Since the degree of spectral overlap is very often a function of the spectrometer, the occurrence of specific interferences should be examined on each ICP instrumental system. When choosing between two ICP sequential systems, the analyst should view spectral resolution as a specification of primary importance. The ability of both polychromator and sequential systems to display spectral wavelength scans is also important.

The designing of a generalized ICP method for metals analysis requires detailed study such as the one reported by Snyder [7]. Such investigations are essential for defining useful matrix and analyte concentration ranges, as well as minimizing interferences for a wide variety of instrumental systems. When interference corrections must be made, the procedure used may have to be specific for a particular type of spectrometer.

Other sources of bias caused by matrix effects should be evaluated and corrected to ensure the best possible accuracy for the technique. In all cases, the variability of each correction factor must be included in the final statement of uncertainty. This may be accomplished either by replication of the correction factor measurement with each sample measurement or by mathematical propagation of error.

The evaluation of random error should begin with an experimental design that allows the relative importance of all sources of error to be estimated. Only the most significant sources of variability need be replicated for the efficient application of the ICP technique. When these steps are taken, the final confidence interval for an analytical result should encompass the true value with a high degree of probability.

Acknowledgment

Grateful acknowledgment is made to the Office of Naval Research for its financial support of the experimental studies contained in this report under Contract NR-042544. The author also wishes to thank Prof. Augusta Syty, Chemistry Department, Indiana University of Pennsylvania, for her assistance in obtaining the spectral interference data, and Clifford H. Spiegleman for the graphical analysis of the magnesium data in Fig. 8.

References

[*1*] Harrison, G. R., *Massachusetts Institute of Technology Wavelength Tables*, John Wiley and Sons, New York, 1956.

[*2*] Meggers, W. F., Corliss, C. H., and Scribner, B. F., "Tables of Spectral-Line Intensities," NBS Monograph 145, U.S. Department of Commerce, Washington, DC, 1975.

[*3*] Zaidel, A. N., Prokofiev, V. K., and Raiski, S. M., *Tables of Spectral Lines*, Veb Verlag Technik, Berlin, West Germany, 1955.

[*4*] Boumans, P. W. J. M., *Line Coincidence Tables for Inductively Coupled Plasma Atomic Emission Spectrometry*, 2 Vols., Pergamon Press, Elmsford, NY, 1980.

[*5*] Michaud, E. and Mermet, J. M., "Iron Spectrum in the 200-300 nm Range Emitted by an Inductively Coupled Argon Plasma," *Spectrochimica Acta*, Vol. 37B, 1982, p. 145.

[*6*] Winge, R. K., Fassel, V. A., Peterson, V. J., and Floyd, M. A., *Inductively Coupled Plasma-Atomic Emission Spectroscopy. An Atlas of Spectral Information*, Physical Sciences Data Series, No. 20, Elsevier, New York, 1984.

[*7*] Snyder, S. C., "Testing Inductively Coupled Plasma for Steel Analysis," *ASTM Standardization News*, Vol. 13, No. 4, April, 1985, pp. 35-38.

[*8*] Certificates of Analysis, SRM 460-468 and SRM 1260-1265, Office of Standard Reference Materials, National Bureau of Standards, Gaithersburg, MD 20899.

[*9*] Filliben, J., "Testing Basic Assumptions," Ch. 2 in *Validation of the Measurement Pro-*

cess, DeVoe, J. R., ed., ACS Symposium Series No. 63, American Chemical Society, Washington, DC.

[*10*] Watters, R. L., Jr. and Norris, J. A., "Factors Influencing Precision and Accuracy of Analysis with Inductively Coupled Plasmas," in *Applications of Inductively Coupled Plasmas to Emission Spectroscopy, Proceedings of the 1977 Eastern Analytical Symposium*, R. M. Barnes, Ed., Franklin Institute Press, Philadelphia, 1978.

[*11*] Testing of Glass Volumetric Apparatus, NBS Circular 602, National Bureau of Standards, Gaithersburg, MD, 1959.

[*12*] Brätter, P., Berthold, K. P., Gardiner, P. E., *Winter Conference on Plasma Spectrometry*, Paper No. 69, Orlando, FL, 1982.

[*13*] Schramel, P. and Li-qiang, Xu, *Fresenius Zeitschrift für Analytische Chemie*, Vol. 314, 1983, p. 671.

Silve Kallmann[1]

Interdependence of Chemical and Instrumental Methods of Analysis

---

REFERENCE: Kallmann, S., "**Interdependence of Chemical and Instrumental Methods of Analysis,**" *Chemical Analysis of Metals, ASTM STP 944,* Francis T. Coyle, Ed., American Society for Testing and Materials, Philadelphia, 1987, pp. 128-133.

ABSTRACT: Chemical methods of analysis are inherently more precise than purely instrumental methods. With the exception of trace metal determinations chemical methods are also more accurate than instrumental methods and have a wider range of application, since final measurements are absolute and do not depend on the availability of standards. The main disadvantage of the classical chemical approach is the length of time required to carry out the analysis.

It will be shown in this paper that chemical methods of analysis can be greatly simplified, and their application range enhanced by incorporating into the procedure various instrumental features. The instrument allows the analytical chemist to (1) examine filtrates for solubility products, (2) avoid reprecipitations by determining specific contaminants by instrumental means, and (3) act as final measuring device, after removing matrix elements by selective or specific separations such as ion exchange, solvent extraction, and precipitations. While the interdependence of chemical and instrumental methods is demonstrated in this paper to be particularly striking in the case of precious metal analysis, an area the author has been concentrating on during the last 15 years, examples of the applicability of the "interdependence" theme to base metal analysis are also provided.

KEY WORDS: chemical analysis, instrumental methods, interdependence

At the 1983 Eastern Analytical Symposium, I discussed at some length the "Interdependence of Chemical and Instrumental Methods for Determining Precious Metals" in a variety of materials. A similar theme entitled "Preparation of Precious Metal Bearing Solutions for Instrumental Analysis" was presented by the author at the 1985 International Union of Pure and Applied Chemistry (UIPAC) Meeting in Pretoria, South Africa. At both meetings I pointed out that only a limited number of precious metal substances can be analyzed by purely instrumental techniques. While in instrumental methods random errors frequently can be limited to ±1% relative, systematic errors

---

[1] Research director, Ledoux Company, 359 Alfred Ave., Teaneck, NJ 07666.

often are significantly greater unless standard samples of the same composition, both chemical and physical, are available and employed.

In addition, although with the instrumental approach at 1% relative error may be acceptable if the concentration of an element is 10% or less, for greater concentrations of an element, a 1% relative error is unacceptable, particularly when applied to the determination of precious metals.

Where a higher degree of accuracy is required or when the precious metals are present in ultra trace amounts, the precious metal analyst has to take recourse to classical methods. It should be pointed out, however, that chemical methods, whether they are based on some form of classical or neoclassical form of fire-assay or on wet chemical techniques, can be extensively modified to take advantage of the ability of instruments to measure minor concentrations of many elements with adequate precision. Thus, it is possible to reconstruct or revitalize many of the older procedures that previously suffered from such defects as solubility or contamination of the compound being determined gravimetrically.

Experimental Procedures

As an example, the determination of platinum in platinum alloys can be cited. These alloys usually contain between 75 and 95% of platinum and 1 to 7% of such alloying elements as rhodium, iridium, ruthenium, palladium, and sometimes gold. The determination of the alloying elements can be carried out expeditiously and with adequate precision by dissolution of the specimen in aqua regia and direct measurements of the elements by direct current plasma or inductively coupled plasma. The determination of platinum, however, requires its separation from the alloying elements. The most efficient way to achieve this is by the hydrolytic precipitation of the alloying elements at a pH of about 7 under oxidizing conditions. This method was originally proposed some 40 years ago by Gilchrist of the National Bureau of Standards. It suffered however from the fact that coprecipitation of platinum with the alloying platinum metals was significant. In addition, Gilchrist for reasons that may have been valid at that time rejected the ammonium chloride precipitation of platinum because the resulting compound $(NH_4)_2PtCl_6$ was not completely insoluble. Consequently, the method was considered quite cumbersome and required repeated retreatments of precipitates and filtrates.

Taking advantage of modern instrumentation, however, it is now possible to cut the analysis time for determining platinum by more than 60% while simultaneously improving both precision and accuracy. This is achieved by precipitating with ammonium chloride (NH_4Cl) and finally weighing more than 98% of the platinum in ultra pure form with a precision of 0.05%. The remaining platinum is measured in various fractions by instrumental methods with a precision of 1 to 2%. Two percent of 2% calculates to 0.04%. So the precision of the procedure is about 0.1%. This is significantly better than that which can be achieved by using a strictly instrumental approach and much more rapid than the purely chemical technique described by Gilchrist.

In precious metal analysis many more examples could be cited demonstrating the value of supplementing chemical methods with attractive features of various instrumental measurements. This interdependence of chemical and instrumental methods, however, is not limited to the precious metal field.

There are potentially many applications in the base metal field. One that comes immediately to mind is the determination of copper in blister copper, which usually has a copper content of 85 to 99% of copper and which frequently is contaminated with varying amounts of tin, antimony, bismuth, selenium, and tellurium, all of which make it difficult, if not impossible, to determine the copper content directly by the electrolytical approach. We discovered that if a sulfuric acid solution of 5 to 10 g of such a blister copper sample is heated with a small measured amount of a thiosulfate solution, a small amount of cupric sulfide is precipitated (say 20 mg), which on heating reacts with the impurities, such as tin, antimony, and bismuth, which can be filtered off. Copper can now be determined by electrolysis with great precision in the main solution, while the small amount of copper retained in the sulfide fraction is determined with adequate precision by atomic absorption spectroscopy (AAS) or plasma emission spectroscopy (PES).

Another example of an effective instrumental supplement is the determination of lead in lead concentrates containing barium or other elements that cause retention of lead in the insoluble fraction from which most of the lead has been extracted with ammonium acetate. While the bulk of the lead is determined by ethylenediaminetetraacetate (EDTA) titration or, if preferred, by chromate precipitation, the lead retained by the residue is determined simply by fusion of the residue in sodium dioxide (Na_2O_2), followed by AAS determination. In addition, there is no need to be concerned with the solubility of lead sulfate ($PbSO_4$) in various media, since the soluble fraction can easily be determined by AAS. In our laboratory, we have extended the principles outlined above to many other determinations of base metals and have succeeded to cut to a considerable extent both cost and analysis time.

The most extensive application for the interdependence of chemical and instrumental methods lies in the area of chemical preparation of sample solution followed, if need be, by limited chemical separations and finally by an instrumental measurement of one or more constituents of the sample. Innumberable examples could be given here, a few have to suffice.

In precious metal analysis, the beads obtained by fire assay (a chemical procedure) can be dissolved and analyzed for silver, gold, platinum, and palladium by AAS or PES or both. This can be done in a cyanide medium (gold, silver, and lead) or in a fairly strong hydrochloric acid (HCl) medium (gold, silver, platinum, and lead). It should be mentioned that beads obtained by fire assay can also be analyzed rapidly and inexpensively by neutron activation. Using a similar approach, the precious metals can be collected, by what we may call neoclassical procedures, into nickel or copper sulfide. The sulfides can be dissolved in acid and all precious metals determined in the same solution by PES and sometimes by AAS techniques. In a limited number of cases, direct dissolution of samples in acids or fusion with sodium peroxide followed by direct PES measurements is feasible. In other cases, sodium peroxide fusion followed by a selective separation to remove alkali salts or the matrix elements or both is more appropriate before submitting the sample solution to instrumental measurements.

The situation is similar in base metal analysis. The repertoire of ASTM Committee E-3 on Chemical Analysis of Metals standards is full of examples of dissolution of a sample in acids and direct measurements of one or more constituents of a sample by AAS and more recently by PES procedures. Into this category, I guess, belongs the more traditional approach of acid dissolution and spectrophotometric measurements, a technique that we should remember is instrumental and that has been or is in the process of being streamlined by various microprocessor devices.

There remains one area where basic knowledge of analytical chemistry remains essential. I am referring to the instrumental determination of an element requiring prior chemical separations.

For instance, the classical method for determining antimony in its sulfide concentrates involves separation of the antimony from iron and arsenic by precipitation of antimony sulfide and expulsion of arsenic trichloride. The antimony is finally determined by titration with an oxidant such as bromate or permanganate. The method can be greatly simplified by applying instrumental techniques in place of the time-consuming classical separations. Thus, antimony, iron, and arsenic can all be reduced to known oxidation states then titrated together with permanganate. Iron is determined by AA in the titrated solution, and arsenic can be determined by X-ray spectroscopy in the original sample. The total titration is then corrected for the contributions of iron and arsenic to provide excellent results for antimony with but a fraction of the work required by the classical method.

The determination of traces of arsenic in various sulfide ores presents another difficult analytical problem. The purely classical technique of distillation of arsenic trichloride followed by iodometric titration has an inherent uncertainty of a few hundredths of a percent. The instrumental approach of hydride generation AAS fails in the presence of large amounts of such elements as copper. Straight atomic absorption at a wavelength of 193 μm is plagued by background interferences made totally unmanageable in the presence of a large variety of matrices. However, it is a simple matter to distil the arsenic from a sample of several grams as the trichloride, oxidize it with a little nitric acid, evaporate to dryness, redissolve in a small volume, and measure the arsenic by AAS using background correction. Thus, 5 g of a sample containing 100 ppm of arsenic will yield 500 μg of arsenic, which is conveniently placed in a 25 mL volume for a concentration of 20 μg/mL, easily read by AAS.

Ion-exchange separations are frequently useful for removing the bulk of a sample, leaving the minor elements available for measurement in a small volume. For example, a method currently being tested for ASTM for gallium in aluminum involves putting a 1-g sample of aluminum into a solution of 6 *N* HCl and passing the solution through an anion exchange column. The aluminum and many other ions pass directly through the column while the gallium is totally adsorbed. The gallium is subsequently eluted with 0.5 *N* HCl, concentrated by evaporation and determined by AAS. The stated scope of the method is from 0.005 to 0.05% of gallium. By increasing the sample weight, the applicable range could be extended to 10 ppm or lower.

Similarly, traces of lead and zinc can be adsorbed on an anion exchange column from 1 *N* HCl, subsequently eluted by 1.5 *N* nitric acid (HNO_3) and determined with high sensitivity by AAS.

ASTM Method for Chemical Analysis of Nickel (E 39) represents a good example of the combination solvent extraction atomic absorption spectroscopy. Traces of lead and bismuth present in high-temperature alloys in the low parts per million range are first separated from a matrix solution containing nickel, iron, cobalt, and so forth, by a tri-n-octyl phosphine oxide (TOPO) extraction in a medium containing bromide, then are determined by AAS.

Impurity elements including tin, lead, antimony, bismuth, and molybdenum can be determined in tungsten ores by coprecipitating their sulfides into copper sulfide from a tartrate medium, collecting the precipitate on a membrane filter, and determining the elements by X-ray spectroscopy.

Similarly, selenium and tellurium have been precipitated as the metals from an HCl medium, collected on a membrane filter, and determined by X-ray.

The method for determining zinc in zinc concentrates recently developed by ASTM Committee E-16 on Sampling and Analysis of Metal-Bearing Ores and Related Materials involves extraction of the zinc as its thiocyanate complex followed by EDTA titration. The analysis is complicated by the presence of cobalt, which is similarly extracted unless it is removed by a preliminary treatment. We find that it is much simpler to titrate the zinc and cobalt and subsequently deduct the cobalt determined by AA.

One last example, it is commonly required to determine cobalt in cemented tungsten carbides. A simple procedure is to fuse the sample in a zirconium crucible with a mixture of sodium peroxide and sodium carbonate, leach in water, and filter. The tungsten passes into the filtrate while the cobaltic oxide is quantitatively retained by the paper. The cobalt oxide is readily dissolved through the paper into hot 6 *N* HCl, diluted to a convenient volume and determined by AAS. Iron can be determined in tin ores by essentially the same method.

Summary

The above survey represents an attempt to demonstrate the interdependence of chemical and instrumental methods as a discipline of great value, which presumably is what ASTM Committee E 3 is all about.

Author Index

Subject Index

ISBN 0-8031-0942-3