SAMPLING, STANDARDS AND HOMOGENEITY

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W. R. Kennedy, symposium chairman
J. F. Woodruff, co-chairman

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Foreword

The Symposium on Sampling, Standards and Homogeneity was presented at the Seventy-fifth Annual Meeting of the American Society for Testing and Materials held in Los Angeles, Calif., 25–30 June 1972. The symposium was sponsored by ASTM Committee E-2 on Emission Spectroscopy. W. R. Kennedy, American Cast Iron Pipe Co., presided as the symposium chairman, and J. F. Woodruff, Armco Steel Corp., served as co-chairman.

Related
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Contents

Introduction

While the analyst is always confronted with a sample problem, he encounters a definite homogeneity problem less often and he seldom has to deal with the "standards making" problems.

While many have been aware that the three entities, sampling, standards and homogeneity, are all closely bound, it has been only recently recognized through E2 Subcommittee 04 discussions how necessary it is that we define these three aspects of the sample.

All of the papers presented at the symposium could not be included in this Special Technical Publication for various reasons, but problems in the manufacture of some standards are covered. Sampling of various products, such as ferrosilicon and cement are covered as well as the two foremost subjects of ecology—air and water: probably the two most difficult fields today.

The difficulty in these latter two fields probably arises in a definition of homogeneity. While air and water may be polluted, they are only polluted locally. Where the sample is taken, and when, are very important things to know.

The statistics of homogeneity is needed to help define the direction in finding a needed handle to measure its goodness or poorness. The paper given in this publication certainly points in the right direction.

In emission spectroscopy, one cannot discuss the sample without considering the means of volitilization or excitation or both to produce the spectra. Such a fundamental picture of excitation appears here. One hopes that further efforts in this direction will help us understand the sample problem.

An outstanding problem of criminal investigation is not the sample, *per se,* but what was the sample prior to the catastrophe, and this is discussed.

The problem of sampling large masses such as a mountain, or large areas, for mineral identification is only diminished in the real problem of that of sampling the moon to help discover how it was formed. Both subjects are adequately covered.

The publication shows that the sampling problem is dynamic and present in all analytical methods. It is inherent in all good analytical methods, that they are independent of the sample and it is incumbent on the "standard method producers" to make them so. Homogeneity can be good or bad, depending on ones point of view, but we must first learn to measure it.

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Finally, we cannot have good analytical methods without good standard reference materials and we must find the best ways to manufacture these in sufficient quantities.

W. R. Kennedy
American Cast Iron Pipe Co.,
Birmingham, Ala.,
symposium chairman.

J. F. Woodruff
Armco Steel Corp.,
Middletown, Ohio,
symposium co-chairman.

FIG. 1—*A preliminary lunar regional geology map. D. Wilhelms and J. McCauley, U.S. Geological Survey, 1966.*

FIG. 9—*A color enhanced far UV-photo of the earth. Note the two, little understood, equatorial airglow belts.*

A. W. England[1]

To Sample the Moon

REFERENCE: England, A. W., **"To Sample the Moon,"** *Sampling, Standards and Homogeneity, ASTM STP 540,* American Society for Testing and Materials, 1973, pp. 3–15.

ABSTRACT: Within the framework of engineering constraints and of scientific uncertainties, the Apollo project has proved a great scientific success. A brief history is presented of the lunar exploration as it evolved through the unmanned probes to Apollo 16.

KEY WORDS: sampling, lunar geology, lunar rock, lunar probes, manned spacecraft

This article was intended as a talk and, as such, lacks the precision of either an historical work or of a scientific paper. It will have achieved its goal if the reader senses the scientific challenge of the lunar sampling program.

A Lunar Sample

The grandaddy of all sampling problems undertaken to date has to be that of sampling the moon. The earth, while bigger and perhaps more diverse, is easily accessible and has been the subject of detailed studies relevant in today's context for several hundred years. The moon is 60 000 earth radii from us, is one quarter the earth's size, is 1/81 as massive, and is not geologically simple. Through Apollo 17, we have obtained samples from eight locations on the moon's near side and, of course, none from the far side. There will have been six relatively sophisticated Apollo expeditions extensively sampling discrete regions of up to 10 km in diameter, and two of the Russian Luna series which obtained soil samples from Mare Fecunditatis and from the Apollonius Mountains. With this limited sampling there can be no thought of generating detailed geologic

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[1] Mission scientist for Apollo 16, National Aeronautics and Space Administration, Manned Spacecraft Center, Houston, Tex. Dr. England is presently with the U.S. Geological Survey, Denver, Colo. 80225.

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maps. The task prior to Apollo was cast as follows: within the constraints of the Apollo program, obtain sufficient lunar samples and related data to specify generally the lunar origin; to understand, in general terms, the state and composition of the lunar interior; to understand the processes controlling the lunar physiography; and to relate generally the moon's evolution to that of the earth and solar system.

One better understands the lunar scientific program when it is placed in its political context. Apollo did not become a scientific program until after Apollo 11. The goal until that time had been to reach the moon, not to explore it. The United States had been badly shaken by Russia's many space successes and by our own multiple failures. The technological feat of a manned lunar landing was all important and couching the program in the peaceful language of scientific exploration merely masked a hard edge of international competition.

Developing the Apollo vehicles was unquestionably difficult. Few hardware managers could afford concessions to enhance their vehicle's scientific utility. It was during this period that the scientist-engineer rift ran deepest. As the time for Apollo 11 approached, however, confidence grew to the point where NASA began looking beyond Apollo 11. The lunar program could have been stopped after the initial landings, or it could have been greatly enhanced with the possibility of lunar bases. A middle ground was chosen, that of flying a slightly enhanced vehicle on lunar missions at the rate of about two per year as long as public support permitted flying Apollo and, simultaneously, beginning new programs. Programs such as shuttle were believed to be all important to NASA's future. Initially, there were ten lunar missions; this later shrank to seven. Fortunately, the science that came to Apollo arrived with sufficient quality and vitality to ensure that the billions of dollars spent on space technology purchased a creditable scientific achievement as well.

In preparation for manned lunar exploration, NASA funded the Santa Cruz and Woods Hole conferences, lunar radar studies, telescopic IR and photogeological studies, etc. Figure 1 shows a preliminary photogeological map produced by the U. S. Geological Survey. Note that even at low resolutions available from earth based telescopes (roughly 1 km), the moon is geologically complex. The microwave, IR, and visual observations yielded a fair understanding of the physical state of the upper few centimeters of the lunar surface. Except in the vicinity of blocky, fresh craters, this upper layer of soil was composed of loosely packed 10 to 100 micron-sized grains of dry, nonmetallic material. Blocky areas appeared as radar bright spots and as areas of high thermal inertia. Albedo variations were mapped in both the maria and highlands. The average albedos were 5 percent for the maria and 10 percent for the highlands. Unfortunately, at that time small variations in albedo could not be related to composition. As a result of data from the orbiting geochemical sensors flown on Apollo

15 and 16, we know that there is strong correlation between albedo and the aluminum/silicon ratio for areas which are not freshly cratered.

To appreciate the problem of planning a limited lunar program, one should review what was known about the moon prior to the first unmanned landing. In addition to the previously mentioned surficial properties, we knew that the moon's average density was 3.34 g/cm^3 compared to the earth's 5.54; that the maria and highlands were physiographically different; that unlike the earth, the moon's moment of inertia indicated an absence of a large metallic core; that the differences in principal moments indicated a rather cold, strong lunar interior; and that the moon had little, if any, dipolar magnetic field. There was abundant speculation about the moon's origin, about currently active volcanism, about dust layers that might be hundreds of meters thick, and about life on the moon. Then, there were the legion of unknowns. The moon was thought to have undergone some chemical fractionation on a global scale. Perhaps the highlands were rough analogs to the earth's continents and the maria were similar to our ocean basins. The degree and complexity of the fractionation would dictate how extensive the lunar sampling program would have to be in order to adequately characterize the moon's chemical evolution. An understanding of the ages of the moon and its formations would be required to construct a model of the lunar evolution and to link the earth's and the moon's histories. We did not know many of even the most basic physical properties such as details of the moon's shape, its gravity field, and whether or not landing spacecraft might sink out of sight in an unconsolidated, powdered lunar surface. These questions and the possibility of the unanticipated were threads in the fabric of the scientists enthusiasm for Apollo. In retrospect, Surveyor told us more than we were ready to

TABLE 1—*A list of the successful United States and USSR unmanned lunar probes.*

1959	September	Luna 2—struck 270 miles northwest of moon's center
	October	Luna 3—photographed 70% of moon's far side—low resolution
1964	July	Ranger 7—4,308 pictures before impact
1965		Rangers 8 and 9—more pictures before impact
	July	Zond 3—medium resolution pictures of far side
1966	January	Luna 9—soft land with pictures
	March	Luna 10—72° orbit with magnetometer and gamma ray
	May	Surveyor I—soft land
	August	Lunar Orbiter 1—12° orbit
	October	Luna 12—equatorial orbit, 15–20 m resolution
	November	Lunar Orbiter 2—12° orbit
	December	Luna 13—soft land, pictures and gamma ray
1967		Lunar Orbiters 3, 4, and 5—medium and high resolution
		Surveyors 3, 5, and 6—the last two with chemical analysis
1968	January	Surveyor 7—lander with chemical analysis
	April	Luna 14—moon's gravity field and radiation environment
1969	July	Apollo 11

accept. Principally, we learned that the lunar surface would support man and his vehicles, that the terrain was reasonably smooth and presented few landing hazards, and, from the alpha back-scatter experiment, that the highlands and maria were compositionally different. The maria appeared compositionally similar to basalt. In contrast, the highland area near Tycho was apparently richer in alumina and poorer in the iron group elements such as chromium, iron, cobalt, and nickel. Although the compositional data from Surveyor were crude, they required that the highlands and the maria had experienced different chemical histories.

In their race to the moon, both the United States and the USSR launched numerous unmanned probes. Table 1 is a chronological list of the more successful of these. One might note that the United States did rather poorly in the beginning. Our three successful unmanned lunar programs were Ranger, Orbiter, and Surveyor (Fig. 2). Ranger, a hard lander, was essentially an engineering vehicle and had little scientific impact. Orbiter is significant for its medium and high resolution (often as good as 2 m) photography. Surveyor, a soft lander, was the most advanced and paved the way for the manned missions.

The first Apollo landing sites were selected for operational reasons. Lack of confidence in our ability to hit a predesignated target plus our inexperience with landing in rugged terrain mitigated against most geologically interesting sites. The first landings were to be in the nearly featureless maria. All early Apollo missions were to be within the "Apollo Zone,"

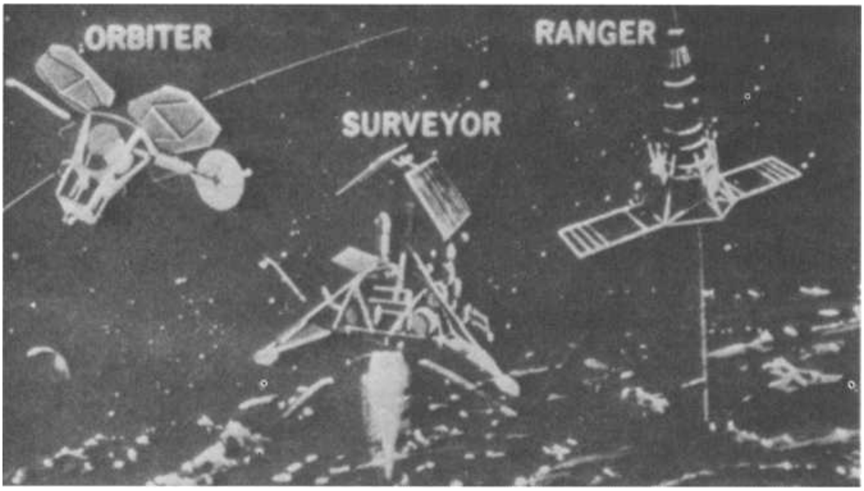

FIG. 2—*Lunar spacecraft. Ranger, a hard lander, obtained the United States' first medium resolution pictures of the moon. Orbiter obtained medium and high resolution pictures of possible Apollo landing sites. Surveyor, a soft lander, tested soil strength, returned detailed pictures of the lunar surface, and, on Surveyor V, VI, and VII, performed a limited chemical analysis (Turkevich et al, J.P.L. Technical Report 32-1262, 1968).*

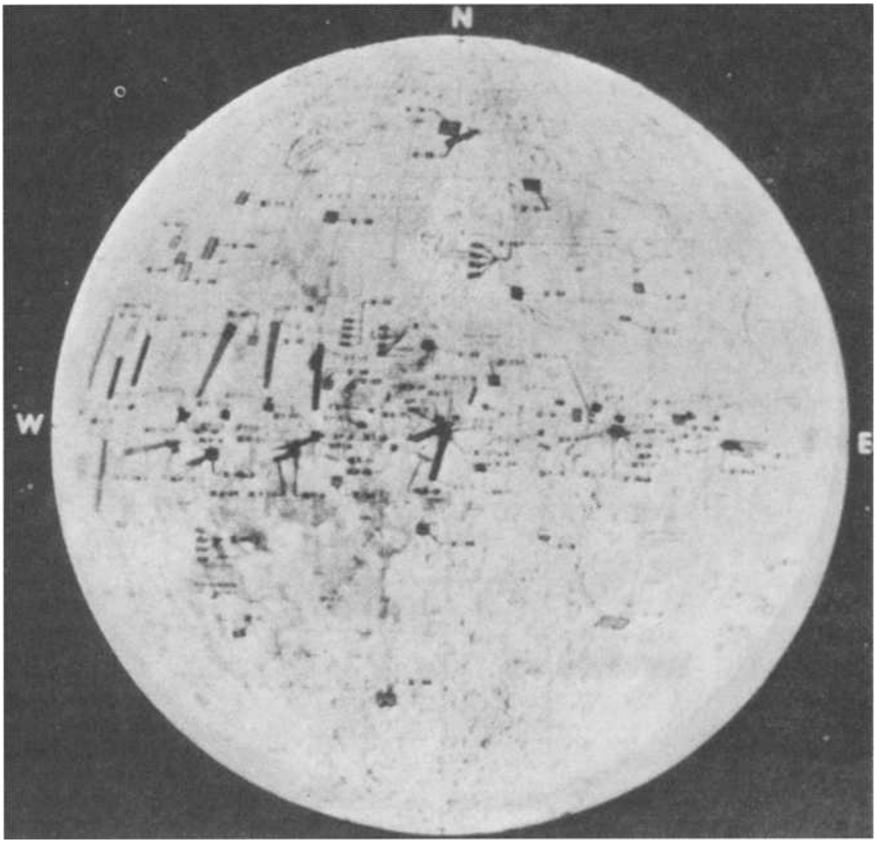

FIG. 3—*Lunar exploration sites. The colored blocks indicate areas for which high resolution Orbiter pictures exist. The roman numeral is the Orbiter mission involved.*

a lunar quadrangle of ±5 deg latitude and of ±45 deg longitude. The "A" sites were to be within the Apollo-Zone while the "B" sites were to be a compromise between operational accessibility and scientific desirability. For each of the A and B sites, Orbiter obtained sufficient medium resolution photographs to plan the approach trajectories and enough high resolution photography (the colored strips in Fig. 3) to support the actual landing. As a precursor to Apollo, Surveyor (Fig. 4) was used to test the sites in the Apollo Zone for soil strength and to insure that they were free of obstacles. The geochemical experiment that yielded soil compositions flew on Surveyor V, VI, and VII. The results of Surveyor I through VI were sufficiently encouraging that Surveyor VII was released from its operational task and sent to the highlands near Tycho.

The Apollo 11 landing site was an "A" site in the eastern Apollo Zone

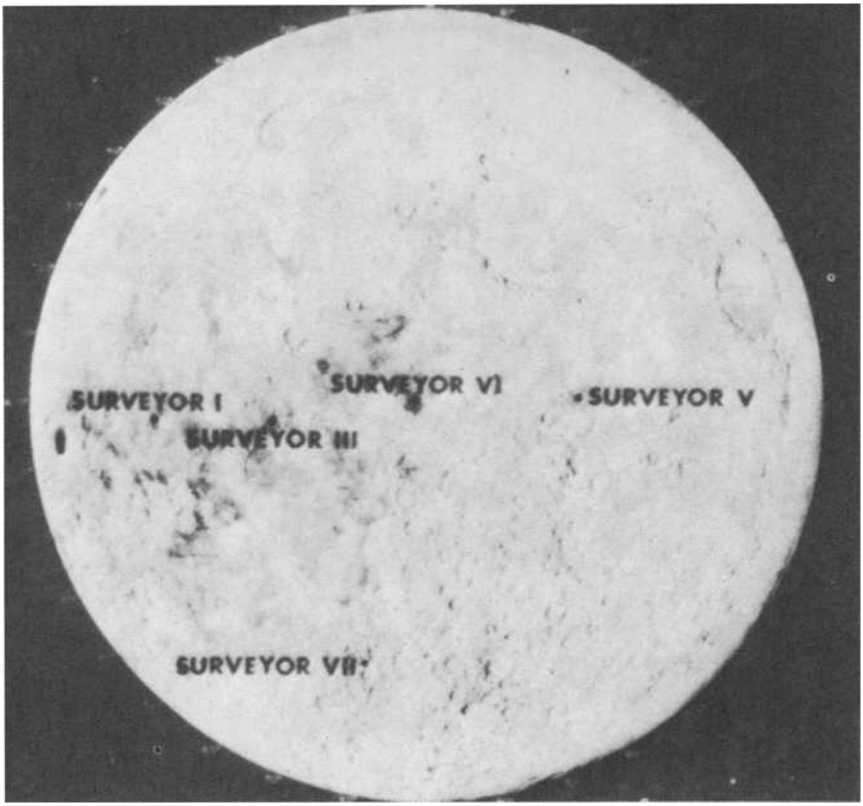

FIG. 4—*The Surveyor landing sites. Surveyor missions II and IV failed.*

laying within the relatively featureless Mare Tranquilitatis, a region tested by Surveyor V. Similarly, Apollo 12 landed in the western Apollo Zone within Oceanus Procellarum and within 100 m of the Surveyor III spacecraft. The Apollo 13/14 and 15 landing sites, Fra Mauro and Rima Hadley were chosen from the "B" list (Table 2). Because of high resolution cameras available on later Apollo spacecraft, possible landing sites for Apollor 16 and 17 were not limited by Orbiter photography. We were "boot-strapping," that is, some of the photography necessary for Apollo 16 was taken by Apollo 14, and all of the photography of the Apollo 17 site was obtained by Apollo 15.

As mentioned, scientists initially believed they had at least ten lunar landing missions. Around the time of Apollo 14, this number was cut to seven, one of which had already failed. Apollo 11 and 12 landed on maria, Apollo 14 landed on material ejected from Imbrium Basin, and Apollo 15 landed on a relatively young mare next to the Apennine Mountains—

TABLE 2—*A list of the more advanced lunar landing sites covered by Orbiter photography. Only two were visited, Fra Mauro and Rima Hadley.*

LUNAR EXPLORATION SITES

Recommendation
Designate by name of nearest named lunar feature of interest, but not beyond alphabetical tabulation

Set B Candidate Sites	Censorinus	0°17′S	32°39′E[a]
	Rimae Littrow	21°35′N	28°56′E
	Abulfeda	14°50′S	14°00′E[a]
	Rima Hyginus	07°52′N	06°07′E
	Rima Hadley	25°02′N	02°55′E
	Tycho	41°08′S	11°35′W
	Copernicus		
	Peak	09°36′N	19°53′W
	Wall	10°22′N	19°59′W
	Schroter's Valley	24°36′N	49°03′W
	Marius F	15°10′N	56°31′W
	Fra Mauro	3°45′S	17°36′W[a]
	Mosting C	1°55′S	8°03′W
	Hipparchus	4°36′S	3°40′E
	Prinz	25°57′N	43°40′W
	Gossendi	17°50′S	40°20′W
	Dionysius	2°31′N	17°49′E
	Alexander	37°46′N	14°06′E
	Alphonus	13°35′S	4°11′W
	Rima Bode II	12°47′N	3°49′W
	Copernicus CD	6°32′N	14°58′W[a]
	Tobias Mayer P	13°18′N	31°11′W
	Aristarchus	24°24′N	47°50′W

[a] 1:200,000 not available.
Coordinates from Lunar Aeronautical Charts.

also ejecta from Imbrium Basin. As the time of Apollo 16 approached, scientists were acutely aware that with only two Apollo missions left, they had yet to sample what was clearly old, lunar highlands. Such highlands cover 30 percent of the nearside and most of the farside. That is, we had not yet sampled material representative of around 65 percent of the lunar surface. There were simply no Orbiter pictures of suitable highland sites. To obtain the photography, an 18 in. focal length camera was flown in the command module of Apollo 13. When that mission aborted, the camera was added to Apollo 14. That camera broke before obtaining the photography. In an attempt to recover, the Apollo 14 crew used a 70 mm Hasselblad with a 500 mm lens to take pictures of the highland Descarte site. This photography from a 100 km altitude yielded 20 m surface resolution—images far inferior to those of any previous sites. That Hasselblad photography along with medium resolution Orbiter pictures were used to plan the Apollo 16 mission.

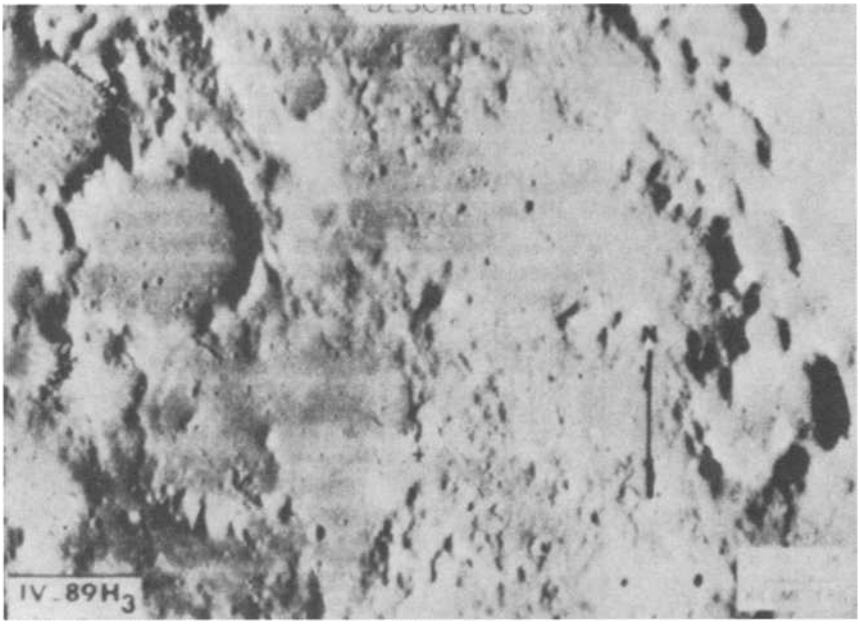

FIG. 5—*The Descarte region. Orbiter IV pictures such as this and the Hasselblad photography were all NASA had in support of the Apollo 16 landing.*

Figure 5 is an Orbiter IV frame of the Descarte region. The small cross (lower center) is about 2 km northwest of the actual landing site. The hilly and furroughed region east of the site is the Descarte Highlands and the relatively smooth plains unit to the west is the Cayley Formation. These two units are typical of much of the lunar highlands. Our primary objective, on Apollo 16, was to sample these units in relatively great detail. Figure 6 is a Hasselblad photograph with the Apollo 16 geological traverse overprinted. Stations 4, 5, 6, and 14 were designed to sample the Descarte Highlands. The remaining 13 stations were on the Cayley Formation. Various sized craters were used as excavation tools. That is, by sampling material ejected from craters of from 10 m to 1 km in diameter, one might hope to reconstruct a cross section of Cayley valid to depths of several hundred meters. A much more elaborate sampling protocal than had previously been attempted was designed to take maximum advantage of the opportunity to sample highlands (see the NASA Apollo 16 Preliminary Sciences Report). Over 200 lb of samples were collected including a 2.8 m core, 7 short cores, and many special samples. In addition, a geophysical station was emplaced yielding seismic velocities and electrical properties (which can be related to temperature) for the Descarte Highland region.

It is beyond the scope of this talk to present in detail the scientific results of Apollo. The reader is referred to the NASA Preliminary Science Reports and to the many volumes of the Houston Lunar Science Conferences. However, it is constructive to consider the types of problems that now have at least a partial solution. Table 3 is a list of basic questions concerning the moon and a chart of progress on them. One of the most interesting discoveries is the age of the moon. Apparently, the moon has been inactive for over 3 billion years. It experienced its dynamic evolutionary phase during its first 2 billion years. In contrast, because

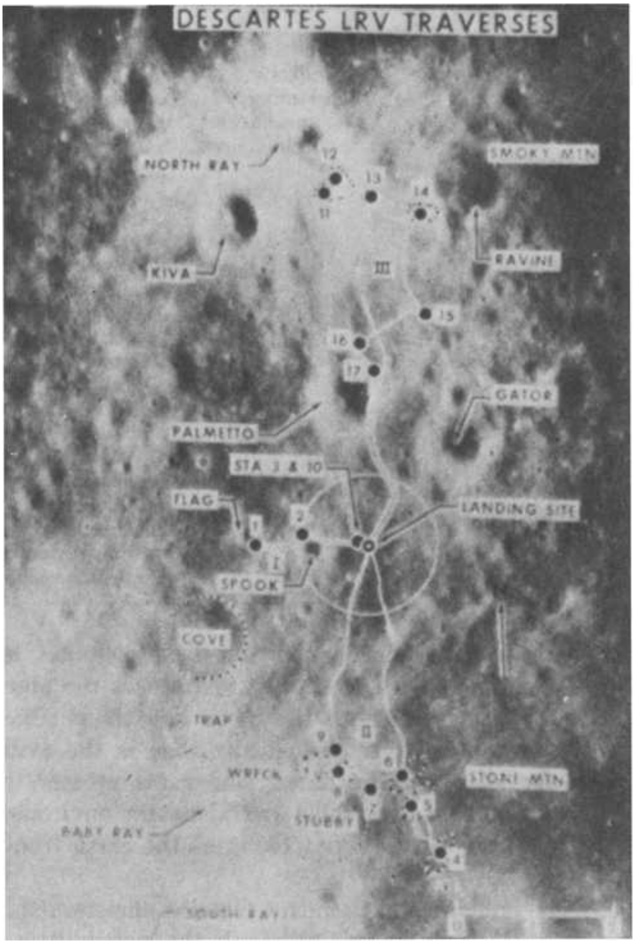

FIG. 6—*The Apollo 16 traverse plan at Descarte. The photographic base was obtained from the Apollo 14 Command Module by a 70 mm Hasselblad camera with a 500 mm lens. While it was the best photography available, it had only a 20 m resolution. The traverse routes and stations were slightly modified during the mission.*

TABLE 3—*A chart of our progress with basic lunar problems.*

Basic Questions	Pre-Unmanned Probes	Pre-Apollo	Apollo
Age of surface	old	young	old
Character of surface	very thick dust	fresh	thin dust
Present volcanic activity	little, if any	recent	very little, if any
Internal temperature	cool	hot	~900°C
Magnetic field	?	little	dipole—very small locally—significant
Composition	?	earthlike	earthlike but with its own uniqueness
Differentiated	maybe	probably	definitely
Life	unlikely	unlikely	no
Lunar processes and characteristics	?	cratering mechanics volcanic flows	cratering mechanics volcanic flows cinder cones ash falls? volatile element mobility Tidal adjustment electrostatic dust mobility? diffusion of seismic energy locally strong magnetic fields? internal differentiation internally inhomogeneous mascons CG offset different mare compositions highlands badly jumbled solar record in soil generation of soil seismic velocities in certain areas to nearly 100 KM

the earth has been so active during the past 3 billion years, most of the earth's early history has been erased. Figure 7 shows the abundances of rocks as a function of age for both the moon and the earth. The moon appears to be somewhat simpler geologically than is the earth and is a mature planet. By studying the moon, one gains greater insight into planetary processes and into the solar and planetary environment in the early solar system. It is a little like looking at the earth from a new dimension.

One of the more fundamental problems remains unanswered. The origin of the moon is still an unknown, although the possibilities are better defined. However, the scientific adventure of Apollo is far from over. It will be a decade before the Apollo data are digested and the results assimulated. Certainly, answers to many problems are locked in the raw data, perhaps the solution to the moon's origin lies there as well.

Since I argue that the geologic principles discovered from the lunar studies are applicable to geological problems on earth, it is appropriate to mention an additional experiment flown for the first and only time on Apollo 16. Figure 8 shows the lunar far UV-camera/spectrometer. This instrument is sensitive to many more astronomical ultraviolet sources than can be seen from earth. It is the first astronomical observatory emplaced on the moon. Figure 9 is a color enhanced photograph taken by the far UV-camera of the earth. The polar auroral zones are easily discerned and, in addition, two equatorial airglow belts may be seen.

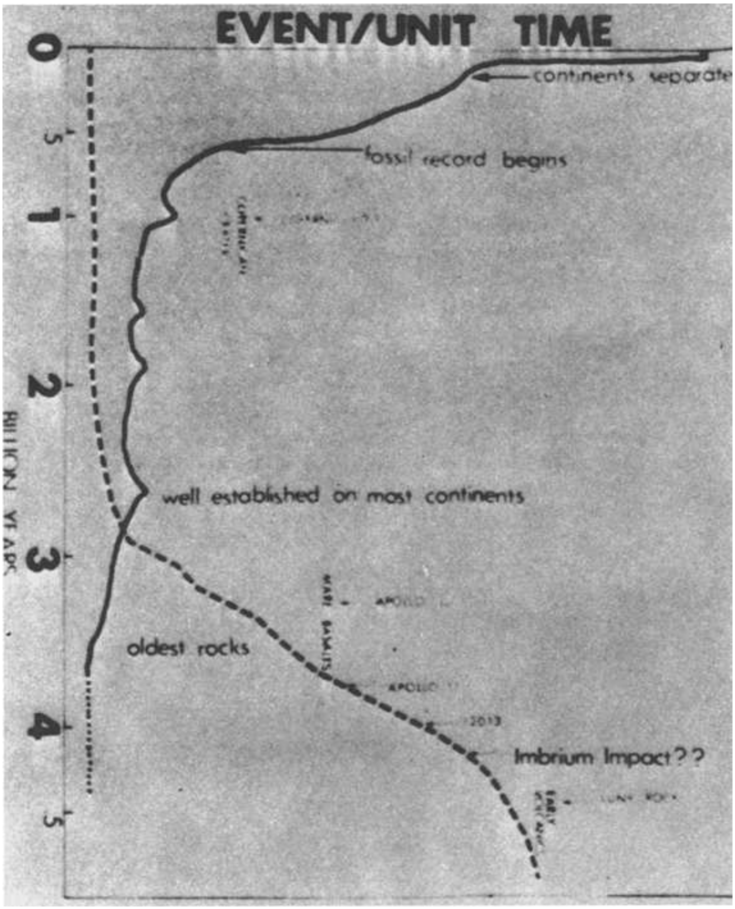

FIG. 7—*A time log of rock abundances for the earth and moon. Note that most earth rocks have ages of less than 1 billion years while most lunar rocks are older than 3 billion years. By studying lunar materials, one has access to a record of events that is far older than is available on earth. (Through the courtesy of Dr. R. Brett, NASA Manned Spacecraft Center.)*

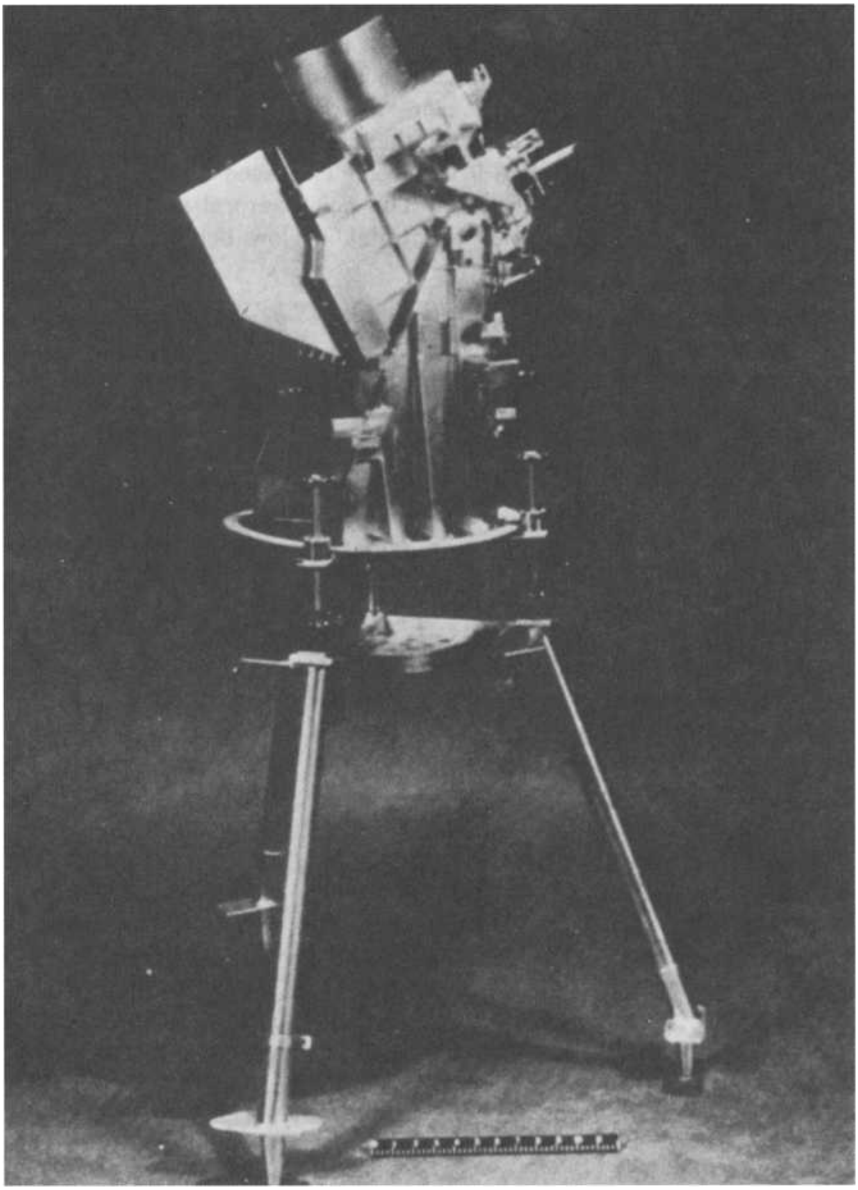

FIG. 8—*The far UV-camera/spectrograph. This is the first astronomical telescope placed on the moon. It is an electronograph sensitive to UV in the 500 to 1600 Angstrom range. It takes an automatic sequence of time exposures of both images and spectra.*

These were not anticipated and may very well prove to be a new phenomenon.

Conclusion

The Apollo scientific program has to be considered a success. There have been pains and, occasionally, unnecessary compromises, but the country is far richer for having spent the effort to explore the moon rather than simply being satisfied with the technological victory of having landed there. The problem of obtaining a sufficiently complete lunar sample is an appropriate subject for an entire volume. I hope, however, that this outline provides insight into the magnitude of that problem.

C. L. Grant[1] *and P. A. Pelton*[1]

Role of Homogeneity in Powder Sampling

REFERENCE: Grant, C. L. and Pelton, P. A., **"Role of Homogeneity in Powder Sampling"** *Sampling, Standards and Homogeneity, ASTM STP 540*, American Society for Testing and Materials, 1973, pp. 16–29.

ABSTRACT: When chemical analyses fail to satisfy the precision and accuracy requirements of a problem, it is common to attribute this difficulty to heterogeneity. In this paper, relationships between the properties of samples and standards and the methods used to analyze them are examined with respect to the influence of homogeneity.

The majority of chemical analyses are intended to characterize bulk composition. In this situation, a homogeneous material is one in which the unit that determines segregation is "very small" compared to the size of the analytical sample and in which the defining units are randomly distributed in the bulk. Both theoretical and experimental evidence is presented to demonstrate the magnitude of error contributed by various sizes of analytical samples and segregation units.

The error contributed by heterogeneity cannot be completely eliminated. Therefore, the analyst must attempt to devise a total analytical system with an acceptable sampling error.

KEY WORDS: homogeneity, samples, powder (particles), standards, sampling

A homogeneous material is of uniform or similar nature throughout. Stated another way, there is no detectable segregation in the system. Of course, we know that such an idyllic situation seldom, if ever, pertains to the materials an analytical chemist is asked to characterize. Therefore, if the analyst is to achieve acceptable levels of precision and accuracy, he must give careful attention to the type and extent of heterogeneity in both samples and standards. Coping with this problem presents difficulties with gases and liquids as well as solids, but the problems are most severe with solids. For this reason, the following discussion will concentrate on solids only.

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[1] Professor of chemistry and chemist, respectively, Center for Industrial and Institutional Development, Kingsbury Hall, University of New Hampshire, Durham, N.H. 03824.

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For any analytical result to be useful, it must be sufficiently precise and accurate to satisfy the purpose for which the analysis was made. It should be remembered that the precision and accuracy which can be achieved with any analytical system depends on the cumulative effects of sampling error, sample preparation errors, and determinative errors. In general, sample preparation errors and determinative errors associated with various methods have been well researched. Accordingly, the analyst can usually predict in advance the approximate magnitude of error to be expected from these sources. In contrast, sampling errors have been much less intensively investigated; and most analysts are unable to predict their magnitude.

It should be possible to plan a total analytical program more intelligently if the approximate size of the sampling error could be predicted in advance. A major component of this planning is a knowledge of the degree of homogeneity of the material to be sampled. Similar considerations apply to both samples and standards although the problem should be less severe for standards which receive special attention in order to render them as homogeneous as possible.

In the analysis of bulk lots of solid material, at least two sampling steps are generally required. First, a sample of the bulk material is obtained for submission to a laboratory. Bicking [*1*][2] has presented a comprehensive review of the problems of establishing a sampling scheme for various types of bulk material such as railroad car lots, fertilizers packaged in bags, and ore deposits in place. He emphasizes that the requirements of sampling depend upon (*a*) material type, (*b*) location such as in place in a mine or in storage in piles or bins, (*c*) form such as solid, molten, or other, and (*d*) distribution such as homogeneous and continuous, homogeneous within a lot, or stratified. Some of the tools and procedures for extracting samples from solids are described by Taschler [*2*].

Too often, the analytical chemist considers that, once a laboratory sample has been obtained, the sampling problems have been largely overcome. However, this sample is generally too large for direct analysis so it must be further subdivided by an acceptable sampling scheme. Sandell and Elving [*3*] state

> Chemists are inclined to use "grab" sampling, assuming the material to be homogeneous within the desired accuracy of the experimental results. There is a tendency to overlook the possible heterogeneity that may exist in small scale samples, e.g., that due to relative particle size distribution where the particles may not all be of the same type. The chemist must recognize the need of obtaining a valid (representative) sample; it is a truism which bears constant reiteration that the analytical data will be no better—indeed, can not be better—than the care exercised in sampling.

The ASTM Style Manual [*4*], seems to leave the nomenclature situation

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

unclear. According to this Manual, "In general, the word 'sample' should be used only to describe a chunk or lot of bulk material that has been selected by some sampling process. A piece or portion taken from the sample for testing or analysis is called a 'specimen.' Quantities of liquid or bulk aggregate usually are called 'samples', because a sampling procedure is usually used to obtain them." The last sentence of this quote suggests that bulk materials which are essentially continuous as opposed to discrete units are sampled. However, in the same Manual, directions are given "To describe the piece on which a test or analysis is made, use 'specimen,' not 'piece' nor 'sample.'" This would seem to say that a unit which is analyzed should be called a specimen and is an apparent contradiction to the earlier statement if we are to analyze a portion of material which has been isolated by a sampling scheme. The main thrust of this paper will deal with the reduction of laboratory size powder samples to suitable aliquots for analysis; and, since we will emphasize that this process requires an intelligently planned sampling scheme, we will continue to employ the term sample rather than specimen.

Sampling Theory

If the particles of a lot of material are identical with respect to their chemical makeup, then sampling is very simple. Any sample taken from the lot will be representative. However, for most particulate systems, the particles do differ chemically and physically or both; and we must sample with these variables in mind. The degree of chemical nonuniformity can range from only slight differences between particles such as a "pure" material with a nearly ubiquitous distribution of contaminant to particles that are distinctly different such as gold particles in mineral sand.

For laboratory sampling, some of the same tools used for bulk sampling are suitable. However, in a comparative study of various splitters, Allen and Khan [*5*] showed that a spinning riffler is most effective in producing representative samples for small lots of material that can be completely processed. A spinning riffler has a series of sample receivers arranged on the perimeter of a disc which is located under a delivery shute with a conic feeder. Charlier and Goossens [*6*] found that the homogeneity of samples obtained with a properly operated spinning riffler is independent of the degree of heterogeneity of the original powder mixture. Using a vibratory feeding channel, they reported that, "the total number of revolutions made by the spinning riffler during the feeding of a batch is of primary importance." Clearly, with very small batches, the feeding rate must be slow in order to keep the number of revolutions large.

The error associated with sampling either bulk or laboratory size samples is due to particle segregation and random particle distribution. Segregation occurs according to particle size, shape, and density [*7–9*]. Under the influence of gravitational forces, the smallest, the most free flowing, and the most dense particles will settle downward. Segregation is enhanced by movement of the total particle system. Such motion may be of small magnitude such as that due to natural vibration; or it may be of major proportions such as when grain, sand, coal, and the like are discharged from a storage bin [*9*].

The effect of random particle distribution is more subtle. To understand this effect, simply apply binary statistics to an ideal mixture of 5000 white beads and 1000 red beads [*10*]. From this mixture, samples of 24 beads are extracted. Despite the fact that the mixture may have been homogenized as completely as possible, there will not always be four red beads in each sample. Because of the random manner in which the particles are extracted, between zero to eight red beads per sample would be expected if we only consider 95 percent of the samples. The magnitude of this effect depends on the number of particles extracted per sample, that is, the greater the number, the smaller the relative variation. Consequently, random variations may be of greatest influence when subdividing for small laboratory size samples rather than in the case of large bulk samples. In contrast, particle segregation is most serious for large bulk samples, because they are difficult to mix and process through a device that eliminates particle segregation such as can be done for small laboratory samples.

Visman [*11*] incorporated the above concepts in a general sampling equation written below.

$$S^2 = A/W + B/N \tag{1}$$

where

S^2 = the total variance for the system,
A = sampling constant; a component of the random variance,
B = sampling constant; a component of the segregation variance,
W = size of the gross sample, and
N = number of samples collected.

The random variance constant A is estimated by taking a series of small samples where the sampling variance is primarily due to random effects, and it is assumed that the segregation variance is negligibly small. On the other hand, the segregation variance constant B is estimated by taking a series of large samples where the sampling variance is due primarily to segregation effects; and it is assumed that random effects are negligibly small.

Further, W and N in Eq 1 are in the nature of operating variables that can be regulated within certain limits by the sampler, for instance after A and B have been determined and for a given S^2 and N, the sample weight, w, can be determined by substituting the equality $Nw = W$ into Eq 1. This substitution gives

$$w = \frac{A}{(NS^2 - B)} \tag{2}$$

Conversely, by specifying w, N can be determined. Therefore, the number and size of samples can be calculated for a specified sampling variance.

There has been much discussion relative to Visman's concepts [*12*, *13*] which serves to emphasize the need for much more work in this area.

Since segregation of particles in laboratory sampling can be largely eliminated, we decided to focus our attention on errors resulting from random particle distribution.

Benedetti-Pichler [*10*] considered this situation; and for a binary population, he applied the Bernoulli theorem and developed the equation

$$\sigma_p \doteq \frac{d_A d_B}{d^2} (P_A - P_B) \sqrt{\frac{p(1-p)}{n}} \tag{3}$$

where

σ_p = the absolute standard deviation of the percent of component x in a mixture of particles A and B,
d_A = the density of the A particles,
d_B = the density of the B particles,
d = the weighted average density assuming all particles have the same volume,
P_A = the percent of the component x in the A particles,
P_B = the percent of the component x in the B particles,
p = the fractional number of the total particles which are type A,
$1 - p$ = the fractional number of type B particles, and
n = the total number of particles.

This equation is idealized by assuming only two species of particles. However, this restriction can be overcome by assuming the components are either rich in x, the analyte, or poor in x. If similar densities can be assumed, the equation can be expanded to consider three or more species. Equation 3 is also idealized by assuming that all particles are the same size.

Equation 3 is somewhat cumbersome because the relative numbers of particles for the different species are inconvenient units of expression. However, Wilson [*14*] modified Eq 3 to put the units in terms of particle size, sample weight, concentration, and density. Thus, for the simple case of two distinct particulate species of the same particle size, we have

$$S_E = (t_1 - t_2) \sqrt{W_1 W_2 \left(\frac{d_1 d_2}{d}\right)\left(\frac{V}{w}\right)} \tag{4}$$

where

S_E = the absolute standard deviation of the concentration of element E,
t_1 = the weight fraction concentration of element E in Species 1,
t_2 = the weight fraction concentration of element E in Species 2,

W_1 = the weight proportion of Species 1,
W_2 = the weight proportion of Species 2,
d_1 = the density of Species 1,
d_2 = the density of Species 2,
d = the weighted average density,
V = the volume of the particles, and
w = the weight of sample taken.

In light of this equation, consider the determination of trace analytes in powder samples. If the analyte under consideration is a minor ingredient of one or more of the major constituents, its relative sampling error will be comparatively small because $t_1 - t_2$ will be very small. If, on the other hand, the trace ingredient is present as a major constituent of the species of minor abundance, its relative sampling error will be comparatively large. For example, the latter situation would pertain to analytes in certain minerals such as zircon, gold, and many others in ores.

If we assume none of the minor ingredient is present in Species 2, then t_2 equals zero. Also, if we express the sampling error, C_E, as the percent relative standard deviation, then Eq 4 becomes

$$C_E = \frac{100 S_E}{t_1 W_1} = 100\sqrt{\frac{W_2}{W_1}\left(\frac{d_1 d_2}{d}\right)\left(\frac{V}{w}\right)} \qquad (5)$$

From this equation, we see that the relative sampling error varies directly with the square root of W_2, d_1, d_2, and V, and inversely with the square root of W_1, d, and w. However, for trace analytes, d is approximately equal to d_2 so they cancel each other; and changes in W_2 can be ignored because of the greater effect on the term, W_2/W_1, of a small change in W_1. Therefore, the significant aspects of Eq 5 are that C_E varies directly with the square root of the density of the minor species, d_1, and the size of the particles, V; and inversely with the square root of the concentration of the minor species, W_1, and the weight of the sample taken for analysis, w. Since we have no control over the density or the concentration of Species 1, we must either decrease the volume of individual particles or increase the sample weight, in order to decrease the sampling error.

For the case of more than two mineral species and with the simplifying assumption that all species have the same density, Wilson derived the equation:

$$S_E = \sqrt{(t_1 - t_2)^2 \frac{W_1 W_2}{n} + (t_2 - t_3)^2 \frac{W_2 W_3}{n} + (t_3 - t_1)^2 \frac{W_3 W_1}{n}} \qquad (6)$$

However, for this study, our interest is primarily in determining trace elements which are major components of species in minor abundance. This condition pertains for many real samples and for many synthetic powder standards. Therefore, we can assume a binary system in which everything other than the species of interest is the second component. This assumption does not introduce serious error and allows us to use Eq 5.

The assumptions, in addition to those already cited, are that all of the particles are spherical and of uniform size. Therefore, knowledge of the particle size distribution is required in order to estimate the average particle size. In general, this distribution varies with the type of material and the method of grinding and sieving. Herdan [*15*] indicates that the particle size distribution for many ground minerals is log normal. The maximum particle volume can be estimated from the mesh size of the sieve that just passes all the sample, but this can cause the sampling error to be seriously overestimated. By assuming that the distribution of particle sizes is the same for all species in a sample, a weighted mean volume, $\bar{V}$, can be calculated from

$$\bar{V} = \sum_{h=1}^{k} g_h \nu_h \tag{7}$$

where

k = the number of groups of different particle size,
ν_h = the volume of the particles of each group, and
g_h = the fraction by weight of the h group.

One major drawback to the use of $\bar{V}$ is that after grinding, different species will not likely show the same particle size distribution due to difference in hardness and brittleness. For rock samples, minerals such as zircon, chromite, and magnetite which are harder than the bulk materials may be concentrated in the larger fractions. Since these coarse particles have the greatest influence on the standard deviation of sampling, such segregation could cause a serious discrepancy between expected and observed sampling errors.

The assumption of spherical particles can also lead to problems. Some species such as micas tend to fragment as flakes or platelets in which case the relationship between volume and particle diameter established for spheres no longer holds. Lastly, we must recognize the tacit assumption that the bulk material is homogeneous with respect to the sampling unit. If this is not the case, the observed sampling error will be larger than predicted because a systematic error due to particle segregation will be superimposed on the random error. Therefore, as we have already suggested, use of a sampling device that eliminates particle segregation is essential.

Experimental Work

Before using Eq 5 to calculate sample sizes required for a given analyte concentration, particle size, and sampling error, it was desired to verify experimentally that the assumptions attendant on the derivation of the equation were valid. Thus, we designed an experiment to compare experimentally measured sampling standard deviations with those predicted by Eq 5 for a relatively ideal system and for one which was less ideal. The matrix material employed was zircon, and the analyte was iron. For the ideal system, spherical particles were prepared by passing angular particles through a large direct current plasma system. The particles melted in the plasma to form spherical droplets which were allowed to free-fall approximately 20 ft during which time they solidified. The less ideal system employed regular angular particles.

Both angular and spherical zircon particles were first washed in alkali to remove free silica and then leached repeatedly in boiling hydrochloric acid until no iron could be detected in the leachate. The iron particles were also given a mild acid wash prior to drying under nonoxidizing conditions.

All four materials were screened to obtain three different size fractions as shown in Table 1. Because of the possibility of internal voids in the particles, actual densities were measured in each case rather than using theoretical values. It was found that the angular particles gave densities close to the theoretical values; but the spheroidized particles had reduced densities, especially the zircon.

The procedure for estimating the mean or weighted mean diameters and volumes of the iron particles shown in Table 1 was as follows. For the spherical and angular −100, +140 iron fractions, several weighed samples were counted microscopically to determine an average particle count per mg. The average spherical particle count was 93 per mg. Using the experimentally measured density of 7.54 g/cm^3, $\bar{V}$ is calculated to be 1.42×10^{-6} cm^3, and the corresponding particle diameter is 139 μm. It can be seen that the average diameter and volume is much closer to the upper boundary of the size distribution because the larger particles contribute much greater sample weight. However, contrary to suggestions in the early literature that the upper particle volume can be used without significant error, we feel that it is much more accurate to employ an average particle volume in making the theoretical calculations. For the −200, +230 fractions, we assumed the same distribution as the −100, +140 since these particles were too small for reasonable counting. At a later date, we anticipate achieving an actual particle size distribution on this fraction. The corresponding average diameters and volumes are shown in Table 1. Finally, in the case of the −325 mesh spherical particles, the weighted average particle diameter of 37 μm and weighted mean volume of 2.73×10^{-8} cm^3 were calculated by obtaining the actual particle size distribution of this fraction with a Coulter Counter. The distribution was integrated using 10 μm intervals according to Eq 7. For the −325 mesh angular iron particles, no distribution was measured due to experimental

TABLE 1—*Particle sizes and volumes for iron.*

U. S. Standard Mesh Sizes	Range of Diameter, μm	Spherical Particles		Angular Particles	
		Average or Weighted Average Diameter, μm	Average or Weighted Average Volume, cm^3	Equivalent Spherical Average or Weighted Average Diameter, μm	Equivalent Spherical Average or Weighted Average Volume, cm^3
−100, +140	149–105	139	1.42×10^{-6}	124	0.99×10^{-6}
−200, +230	74–62	71	1.88×10^{-7}	67	1.55×10^{-7}
−325	44–0	37	2.73×10^{-8}	37[a]	2.73×10^{-8}[a]

[a] Assumed value.

difficulties; so it was assumed to be the same as the spherical particles. Further, distributions were not measured for the zircon; but they should be close to those found for the iron.

Weighed mixtures of iron and zircon of the same size distribution were prepared to give an iron concentration of 3000 ppm. Later studies will consider mixtures of known broad particle size distributions and also where analyte particles have a different distribution than the matrix. Mixtures were placed in a cylindrical container and rotated in an off-axis device. We have no guarantee that homogeneity was achieved, but it should have been approached. As soon as blending was completed, the total sample was split repeatedly in a small particulate Jones type sample riffler. (No small spinning riffler was available.) This operation was continued to produce eight approximately equal weight fractions which were on the order of 100 mg total weight. The actual average weight of the eight fractions depended on the weight of the total mixture which was used at the start of the riffling. Each of the eight fractions was carefully weighed and placed in separate beakers for extraction of iron. Ideally, a larger number of fractions would have been produced; but time limitations dictated the use of eight for each combination.

To deduce the benefit of using the Jones type splitter, each of the three mixtures was also "grab sampled," that is, eight approximately 100 mg samples were removed from the vials by simply scooping with a spatula. Each sample was weighed and treated thereafter in the same manner as the riffled samples.

For each of the three size distributions considered, the eight riffled samples were acid leached, filtered, and made to volume. They were analyzed by a high precision (expanded scale) atomic absorption procedure on two separate occasions using independent calibration curves. The volume of solution was carefully selected to provide an iron concentration giving optimum absorbance values for maximum precision. It should be understood that the duplicate measurements on different occasions provide only an estimate of the actual analytical error and give us no data on any errors associated with the sample preparation step which involves acid leaching, filtration, and dilution. For the system we have used, there is no convenient way to separate the sample preparation error from the sampling error. However, it is reasonable to assume that the sample preparation errors are very small in comparison to the sampling errors in this study.

Results

In all, twelve sets of data were produced, each consisting of eight duplicate determinations of the iron content of 100 mg samples. The agreement of duplicate values was excellent indicating that there was very little difference in the calibration curves used for the two sets of analyses. The

TABLE 2—*Analysis of variance for −200, +230 spherical particles.*

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Quantity Estimated by Mean Squares
Between samples	555 286	7	79 326	$\sigma_A^2 + n\sigma_s^2$
Within samples	895	7	128	σ_A^2
Block	121	1		
Total	556 302	15		

NOTE—
σ_A^2 = "within samples" variance.
σ_s^2 = sampling variance.
n = number of replicate measurements on each sample.

samples were analyzed "in the blind" to prevent any recollection of results from influencing the second set.

Each set of data was analyzed by Analysis of Variance. A typical analysis for the −200, +230 mesh spherical particles is shown in Table 2. Starting at the bottom of the table, the block effect relates to any systematic difference between the calibration curves employed in the two separate sets of analyses. The within sample variation represents the random variability in the duplicate results for each sample of a set. The mean square of 128 provides an estimate of the variance related to the analytical measurement. It must be understood, however, that this estimate does not include the sample preparation variability because of the nature of the analytical scheme employed. The mean square 79 326 estimates the combined variances associated with both analysis and sampling as shown in the table.

The mean squares shown in the analysis of variance table are estimates of the true values. Consequently, the values calculated from these estimates must be designated by the symbol, S, rather than σ to indicate that they are only estimates. The calculation required to get at the estimate of the sampling standard deviation, S_s, is given by

$$S_s = \sqrt{\frac{M_s - S_A^2}{n}} \qquad (8)$$

where

S_s = the estimate of the true sampling standard deviation,
M_s = the estimate of the "between samples" mean square,
S_A^2 = the estimate of the "within samples" mean square, and
n = the number of replicate measurements on each sample.

The calculated sampling standard deviations, converted to percentage values, are summarized in Table 3 along with the expected values calculated from Eq 5. In calculating the theoretical values for the relative

TABLE 3—*Comparison of experimental and theoretical percent relative standard deviations.*

U. S. Standard Mesh Size	Spherical Particles				Angular Particles			
	Riffled		Grab		Riffled		Grab	
	Experimental	Eq 5	Experimental	Eq 5	Experimental	Eq 5	Experimental	Eq 5
−100, +140	14.3	16.6	33.7	15.5	21.9	15.6	24.2	15.7
−200, +230	6.6	6.4	11.8	6.3	9.2	5.6	7.7	6.1
−325	4.5	2.4	5.7	2.4	5.2	2.3	1.3	2.5

standard deviation associated with sampling, actual particle densities and percentage values were employed, and the previously discussed average or weighted average particle volumes, $\bar{V}$, were used.

It can be seen that the theoretical values and the experimental values are in reasonably close agreement for the riffled spherical particles. The experimental overestimation for the −325 particles may reflect some sample preparation error which has not been extracted from the sampling error. On the basis of the data available here, we are not yet prepared to suggest that the theoretical equation underestimates for very fine particles. We hope that later data will shed more light on this question. In any case, it appears that the equation holds quite well for riffled spherical particles in a narrow size range. For "grab" samples, the sampling errors are much larger than predicted by the equation, presumably due to the ease of segregation of spherical particles.

For angular particles, the situation is less clear cut. The riffled samples show a consistently higher sampling variability than predicted by Eq 5. This suggests that particle geometries other than spherical require a correction to prevent underestimation of the sampling variability when using Eq 5. However, for the "grab" samples of angular particles, the agreement between experimental and calculated values is quite good for the two smaller particle size ranges. Possibly some of these discrepancies will be resolved when we have a spinning riffler available for subsampling.

Some preliminary calculations have been made for required particle sizes in various types of synthetic powder standards. Clearly, when small samples are used for analysis, namely, less than 1 mg in spark source mass spectrometry, the synthesis of powder standards is fraught with difficulty. Analyte additives should be of low density where possible. Even then, particle sizes on the order of 0.5 to 5 μm appear to be required if random sampling errors are to be kept below ±5 to 15 percent relative. Of course, these calculations assume that analyte particles retain their identity in the mixture. Grinding undoubtedly produces some smearing and, therefore, reduces this error. Techniques such as homogeneous precipitation from solution may ultimately provide much more satisfactory standards for this type of analysis.

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J. J. Connor[1] *and A. T. Myers*[1]

How to Sample a Mountain*

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ABSTRACT: Techniques of experimental design, based on generalized sampling models, are extremely important for "sampling a mountain," especially because of the possible wide variability in element composition in the samples taken from that "mountain." Current investigations are determining better guidelines in sampling and analytical procedures for minor-element studies in geochemical research. Too often, expensive analytical effort may be wasted owing to lack of proper design in the laboratory by the analyst and in geologic sampling by the geologist. Experimental design techniques are being applied to a wide variety of geologic sampling problems. Analytical procedures, including spectrochemical methods, are expected to change in accordance with the nature of the problem and the geologic sample. An example of sampling for minor-element analysis is given to illustrate types of geologic variance as compared to laboratory variance.

KEY WORDS: sampling, geological surveys, geochemical prospecting, rocks, mountains

In attempting to solve most geochemical field problems, geologists have conventionally tended to collect as many specimens or rocks as time and laboratory facilities permit and to spot sample localities as evenly as possible over the area of interest. Such a sample design implies some rather restrictive assumptions about the natural variability of element composition of the rock body (mountain) being sampled. It assumes both that the material sampled is fairly uniform on a local scale (only one specimen per locality is required to typify the composition of the locality) and that it exhibits important variation in composition on a regional scale (specimens from many parts of the rock body are needed). Either or both of these assumptions can be, and commonly are, false.

If, for example, the rock body is homogeneous in elemental content,

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[1] Geologist and research chemist, respectively, U.S. Geological Survey, Federal Center, Denver, Colo. 80225.

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one specimen taken from anywhere in the body will provide all the geochemical information available. But no real rock body is perfectly homogeneous, and the problem of "how to sample a mountain" is, in reality, one of deciding how many specimens to collect in each sampling locality and how to distribute the sampling localities over the mountain. Any rational decision as to the number of specimens or distribution of sampling localities can only be based on prior knowledge of the natural variability in composition in the rock body. But unless there are megascopic features in the body which permit visual assessment of geochemical variability, one can learn something of the variability only by first collecting some specimens (that is, by sampling). The circularity of this argument is resolved if the sampling process consists of two sequential stages: A first stage of sampling designed to quantify the kinds of compositional variation present in the mountain; the second stage, designed on the results of the first stage, to more accurately define both the average composition and any spatial trends that may exist in this mountain.

A Model of Geochemical Variation

The variation in composition found within any rock body may be a combination of three variations—one between sampling localities, one within sampling localities, and one from laboratory procedures. This view of geochemical variation may be formally stated [*1*][2] as:

$$X_{ijk} = \mu + \alpha_i + \beta_{ij} + \gamma_{ijk} \qquad (1)$$

Here, X_{ijk} represents an analytical value as received from the laboratory, μ represents the grand averaged composition for all potential specimens in the rock body, α_i represents the difference between the average composition of the ith sampling locality and the grand average, β_{ij} represents the difference between the jth specimen from the ith locality and the average of the ith locality, and γ_{ijk} represents the difference between the kth analysis of the jth specimen and the true value for that specimen.

The model in Eq 1 is a specific case (one-way hierarchical) of the analysis of variance. This particular type of analysis was first applied to a problem in field geology by Potter and Olson [*2*] and is discussed at length, also in terms of a geologic problem, by Krumbein and Slack [*3*]. The terms α_i, β_{ij}, and γ_{ijk} are assumed to represent random variables with means of zero and variances of σ_α^2, σ_β^2, and σ_γ^2. Use of the model will provide unbiased estimates of these three variances, as outlined in Table 1.

The observed compositional variation in a suite of specimens may thus be divided into three independent components of variance, one (σ_α^2) which reflects large-scale compositional differences within the rock body, a second (σ_β^2) which reflects small-scale (within-locality) differences,

[2] The italic numbers in brackets refer to the list of references appended to this paper.

TABLE 1—*Analysis of variance for three-level hierarchical design.*[a]

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Mean Square is Estimate of:
1. Among sampling localities	$SS_1 = \frac{1}{bc}\sum_i^a\left(\sum_j^b\sum_k^c X_{ijk}\right)^2 -$ $\frac{1}{abc}\left(\sum_i^a\sum_j^b\sum_k^c X_{ijk}\right)^2$	$a - 1$	$\frac{SS_1}{a-1}$	$\sigma_\gamma^2 + c\sigma_\beta^2 + bc\sigma_\alpha^2$
2. Within sampling localities	$SS_2 = \frac{1}{c}\sum_i^a\sum_j^b\left(\sum_k^c X_{ijk}\right)^2 -$ $\frac{1}{bc}\sum_i^a\left(\sum_j^b\sum_k^c X_{ijk}\right)^2$	$a(b - 1)$	$\frac{SS_2}{a(b-1)}$	$\sigma_\gamma^2 + c\sigma_\beta^2$
3. Between analyses	$SS_3 = \sum_i^a\sum_j^b\sum_k^c (X_{ijk})^2 -$ $\frac{1}{c}\sum_i^a\sum_j^b\left(\sum_k^c X_{ijk}\right)^2$	$ab(c - 1)$	$\frac{SS_3}{ab(c-1)}$	σ_γ^2

[a] Adapted from Krumbein and Slack [*3*]. X_{ijk} is the analytical value of the kth analysis of jth specimen from the ith sampling locality, a is the number of localities, b is the number of specimens per locality and c is the number of analyses of each specimen. The indices i, j, and k increase from 1 to a, 1 to b, and 1 to c, respectively.

and a third (σ_γ^2) which reflects laboratory or "analytical" variation. A major purpose of first-stage sampling is to determine whether large-scale variation exists in important amounts within the rock body. If the estimate of σ_α^2 is large in comparison to the estimate of σ_β^2, an adequate second-stage sample design must include localities spaced over the entire rock body; if σ_α^2 is small, the cost of sampling over the entire rock body may not be justified. If σ_β^2 is large compared to σ_α^2, an adequate estimate of the average composition in any given locality must be based on many specimens. If σ_γ^2 is large with respect to σ_α^2 and σ_β^2, a more precise laboratory method is indicated.

The Problem of Geochemical Error

All geochemical data contain error of various kinds. Error in the statistical sense does not imply a mistake but rather a random deviation from the true, but generally unknown, value [*4*]. If we repeatedly analyze a hand specimen for some particular element, we expect to obtain a slightly different value from each analysis. Such differences are an expression of analytical error; γ_{ijk} in Eq 1 is a random deviation due to analytical error. Similarly, if we repeatedly sample a rock locality and analyze each specimen for that same element, we will obtain different values for each specimen. If the differences observed among specimens tend to be larger on the average than those observed among repeated analyses, we attribute the excess to compositional differences among the specimens themselves. Such differences give rise to sampling error; β_{ij} in Eq 1 is a random deviation due to sampling error.

Under ideal conditions, sampling and analytical errors will be unbiased and will have constant precision (Class 246 of Ref *4*). If either the sampling procedure or the analytical method is biased, the average composition computed for each sampling locality can never approach the true value, regardless of the number of samples collected. If either the sampling method or the analysis contains variable bias, the average composition computed for each sampling locality may diverge from the true value to a different degree in each locality. If either the sampling method or the analysis contains variable precision, the average composition computed for each locality may have different standard errors. The most serious type of error in geochemical data appears to be variable bias [*1*].

In terms of the model in Eq 1, the presence of constant bias will not affect the estimates of the three components of variance. Variable bias in sampling or analysis destroys the additivity of the model and, if severe enough, can result in completely unusable data. Variable precision in sampling and analysis will result in heterogeneous variance which, in moderate amounts, is not considered to be harmful but which nevertheless should be kept to a minimum.

Bias in analysis may be circumvented by the use of analytical procedures of acceptable accuracy. Bias in sampling may be minimized by objectively sampling in such a way that all potentially collectible specimens in all localities have the same chance of entering the suite of specimens. Randomization procedures in selecting sampling sites within each locality can be used to ensure such objectivity. Variable bias and variable precision in analysis may be minimized by analyzing all specimens in the suite in a randomized sequence. Variable bias and variable precision in sampling may be reduced by a rigorous definition of the geologic body to be sampled (it should be reasonably coherent in its composition; if the mountain is composed of lithologically distinct units, each unit should be sampled as a separate study), and by sampling each locality in an objective manner. Variable precision may still persist if the variation is related to the mean level of concentration, as it tends to be in trace-element studies. Under such circumstances, a lognormal transformation of the analytical data prior to data interpretation will commonly reduce variable precision. Miesch [*1*, *4*, *5*] discusses these concepts in detail.

A Geochemical Example

An example will illustrate the ideas outlined above. The geochemical variability of carbonate rocks of Cambrian and Early Ordovician age in southern Missouri has been studied as part of a general geochemical survey of the State's natural environment [*6*]. Although this particular area is not a "mountain," it is nevertheless a large and varied region. For the purpose of this paper we can consider it to be a "mountain." The model of geochemical variation used in Missouri is somewhat more complicated [*7*] than that given in Eq 1, but the measured components of variation may easily be recast into this three-component model.

Four specimens of carbonate rocks were collected in each of twelve sampling localities spread over about 20 000 square miles of outcrop of the unit in southern Missouri and northernmost Arkansas. A sampling locality generally encompasses an area of no more than about five miles in diameter, and two randomly located specimens were collected in each of two random sites in each locality. Some of the specimens were split into two parts in order to estimate the laboratory component of variance, and all were subjected in randomized sequence to a variety of elemental analyses, including emission spectrographic techniques.

Components of variance computed on logarithms of three selected elements are listed in Table 2. A knowledge of variation between localities (large-scale variance) is important for the study of many elements in these rocks, and titanium (Ti) typifies such variation. Over two-thirds of the total logarithmic variance of Ti occurs between localities. This contrasts with vanadium (V) which exhibits less than a fourth of its total logarithmic variance between localities. Both elements were measured by spectrographic techniques and the laboratory variance in each seems to be suffi-

TABLE 2—*Components of logarithmic variance estimated for carbonate rocks of Cambrian and Lower Ordovician age in southern Missouri and northeastern Arkansas*

		Between-locality (large-scale) variance		Within-locality (small-scale) variance		Laboratory variance		
Element	Total $\log_{10}$ variance	Estimate of σ_α^2	Percent of total variance	Estimate of σ_β^2	Percent of total variance	Estimate of σ_γ^2	Percent of total variance	Analytical method
Ti	0.4835	0.3277	68	0.1365	28	0.0193	4	Optical emission
V	0.0529	0.0119	22	0.0337	64	0.0073	14	Do.
Se	0.1183	0.0028	2	0.0307	26	0.0848	72	XRF

ciently small to ensure reliable results. However, a second-stage sample design based on these first-stage results would be quite different for the two elements. For Ti, sampling localities must be spaced over the entire area of outcrop, but only a few specimens need to be taken in each. For V, many samples must be collected within each locality, if the larger scale variation is to be described, inasmuch as the within-locality variance is relatively large. It is conceivable that the sampling requirements for V may be so large as to be financially prohibitive. In contrast to both Ti and V, a geochemical study of selenium (Se) in these rocks should probably be based on a more precise analytical method (if available and feasible) because nearly three fourths of the total observed logarithmic variance appears to be related to laboratory procedures.

An estimate of the number of specimens to collect in a sampling locality during the second stage of sampling may be assessed from the ratio, $\sigma_\alpha^2/(\sigma_\beta^2 + \sigma_\gamma^2)$. Procedures to estimate this number depend in part on the particular goal of the study, but in general, the smaller this ratio, the greater the number of specimens and analyses required. Miesch [*4*], Miesch and Connor [*8*], Garrett [*9*], and Connor *et al.* [*6*] give examples of the use of this ratio.

Conclusion

Mountains and similar geologic features tend to be chemically complex parts of the landscape and attempts to compositionally describe them are best approached through formal experimental designs. This paper urges the use of the hierarchical case of the analysis of variance as an experimental framework for identifying and quantifying scale-related components of geochemical variation. Knowledge of such variation will permit a realistic appraisal of the minimum sampling effort required for describing the geologic feature of interest with any given degree of reliability.

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P. C. Buscemi[1] *and W. D. Washington*[1]

Collection and Handling of Physical Evidence for a Forensic Laboratory

REFERENCE: Buscemi, P. C. and Washington, W. D., "**Collection and Handling of Physical Evidence for a Forensic Laboratory,**" *Sampling, Standards and Homogeneity, ASTM STP 540,* American Society for Testing and Materials, 1973, pp. 37–44.

ABSTRACT: The special considerations which must be given to the collection and handling of physical evidence from the scene of a crime for a forensic laboratory are presented. Specifically covered are the handling of physical evidence from criminal acts which violate those jurisdictions comprising an important segment of the responsibilities of the Bureau of Alcohol, Tobacco and Firearms in the U.S. Treasury Department.

Many of the unique characteristics of this unusual type of sampling are discussed, particularly those aspects differing markedly from the more routine types of chemical sampling. Topics covered in detail include the following: the selection of materials of possible evidential value; the process of collecting and gathering such items of interest; the importance of marking and labeling properly; the packaging of these materials; their preservation; the proper transmission to the forensic laboratory; and the associated legal requirements which must be adhered to throughout this procedure.

KEY WORDS: sampling, investigations, crimes, laboratories, tests

The primary purpose of the Bureau of Alcohol, Tobacco and Firearms (ATF) Forensic Laboratory is to conduct the scientific examination of physical evidence related to violations of those regulations under the jurisdiction of the U. S. Treasury Department. In addition to certain crimes, in violation of the U. S. Tax Laws, the responsibilities of the ATF Forensic Laboratory have increased in the last few years, mainly due to the enactment of two laws. The first was the Gun Control Act of 1968 and the second was the Organized Crime Control Act of 1970, which sets forth regulations on firearms, explosives, incendiaries, grenades, and other related destructive devices.

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[1] Forensic staff chemists, Bureau of Alcohol, Tobacco and Firearms, U.S. Treasury Department, Washington, D.C. 20226.

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The ATF Forensic Laboratory receives a large variety of physical evidence each day. The cases encountered involve mostly bombings, arson, firearms, illicit distilleries, tax frauds, questioned documents, homicides, and narcotic violations.

The job of the forensic scientist is to analyze the physical evidence of rather complex events. Many of the aspects associated with the very sepcialized field of forensic sampling will be discussed, particularly those characteristics which differ markedly from more routine sampling situations. The continuing improvements in the analytical capabilities of forensic laboratories today are providing an ever increasing number of diverse tools to help the law enforcement officer in the fight against crime. The introduction of scientific evidence in the court room continues to grow in importance each year.

The collection and handling of physical evidence associated with a criminal act will be considered under the following sequence of topics:

1. Protecting the scene of a crime.
2. Documentation of the location.
3. Collection of the potential evidence.
4. Preservation of the evidence.
5. Labeling requirements.
6. Chain-of-custody considerations.
7. Letter of transmittal.
8. Collection of reference materials.

Protecting the Scene of a Crime

The importance of sealing off the scene of a crime until all of the physical evidence of interest can be removed from it is the first consideration and can not be overemphasized. Usually, the first police officer called to the scene will initiate action to prevent unauthorized ingress. Private citizens should be aware of the need for protecting and maintaining the location exactly as at the time the crime was committed. Only in those cases where an emergency is present, such as a person's life is in danger, should entry to a crime scene be contemplated by unauthorized persons. The proper protection of the crime scene by private citizens as well as by the first policeman to arrive is the first step in maintaining the value of evidence for the eventual prosecution of a criminal offense. In addition, security must be maintained on any investigative leads. The value of certain findings at the scene of a crime to provide a means of reconstructing the crime and thereby leading to a suspect can be lost if information concerning such evidence is given on newscasts or printed in the local newspapers. The isolation of a crime scene must apply to the flow of information as well as material things. The suspect can be expected to destroy all items related to a crime when he learns the direction the investigation will assume from the physical evidence collected. The protection of the scene of a crime must be continued until the investigative team has exhausted the search for clues.

Documentation of the Location

Two general categories of analytical tests are: destructive and non-destructive tests. As scientists we would quickly conclude that the removal of physical evidence from the scene of a crime is a destructive procedure. The use of photography constitutes an important function in a situation such as this. Within a relatively short period of time the crime site is usually restored to its original condition by maintenance personnel, repairmen, housekeepers, etc.

Before any object appearing to have evidential potential can be handled, certain preliminary steps of documentation must be followed. The position of the object may be recorded by photography, its location specified on a sketch and by recording in a notebook. The notebook should be used to describe minute details of physical evidence to help in the recognition of the object, even though initialled, in the courtroom many months later. at the time of a trial, the availability of clear photographs of the crime scene will be of great value in the court presentation.

Photography is also of great value in the forensic laboratory. A clear photograph will provide a useful exhibit for court presentation of material which will be completely consumed by the chemical tests or whose original appearance will be altered for the examination.

For certain situations, the internal configuration of a sealed package or small items such as blasting caps can be radiographed as well as photographed before destruction of the outer container.

Very often in the case of a bombing, the perpetrator of such a crime is very curious to see how much damage has resulted from his device. A crime photographer would be wise to include shots of the onlookers, as well, in documenting the scene of the bombing incident.

In any crime in which major destruction of property has resulted, such as in acts of bombing, vandalism, arson, etc., an attempt should be made to secure photographs of the location which may have been taken by others before the incident occurred. In addition to photographs, other useful documentation may be provided with any available blueprints, building plans, and maps.

Collection of the Potential Evidence

The collection of physical items of evidential value at the scene of a crime is conducted by individuals having varying degrees of expertise in the field of the police sciences. The variety and complexity of physical evidence present a formidable challenge for the person responsible for this important task.

The forensic scientist very seldom has the opportunity for selecting the physical evidence at the crime scene. In many areas, highly specialized persons, known as scene-of-the-crime evidence technicians, effectively perform this important function as a member of an investigative team. Ideally, the evidence technician must maintain a close working relationship between the investigative officers and the various crime laboratories. He must be thoroughly knowledgeable of the capabilities of the local, state, regional, and national forensic laboratories. The evidence technician, or whoever acts in this capacity, selects those portions of the crime scene which require a more thorough examination in the laboratory. The successful solution of many crimes hinges on the initial collection of this evidence.

Basically, the principle underlying a scientific approach to solving criminal acts depends on the transfer of some substance or object, however microscopic, to the scene of the crime by the perpetrator or vice versa. A speck of paint, jimmy marks, a strand of hair, a chunk of soil, a drop of blood, a footprint, a lipstick smear, while certainly not as unique as a fingerprint, nevertheless, will contribute to the incrimination of the suspect. In many cases, evidence of such transposition can be found to have occurred in both directions and constitutes a very important complement to the body of evidence.

For example, in illicit whisky or moonshine investigations the culprits are seldom found at the clandestine still site, due to an effective lookout. The forensic scientist nevertheless is able to associate the suspect with the still by various means. Chunks of soil on a suspect's boots can be linked to the soil at the still site, by microscopic and chemical means. Hair from the suspect may be compared to hair found at the still. Paint flecks found on branches of trees lining a heavily wooded access road to the still may be linked with a pick-up truck belonging to the suspected individual. The analysis for trace elements in specimens can establish "chemical fingerprints" for comparison purposes and indicate in many cases the common origin of physical evidence.

The scene of a crime should be searched in a systematic manner. The search must be done in an orderly manner so that no portion of it is missed. All items which appear to have any relation to the crime should be collected. Items which do not seem to have been a normal part of the site in its original condition should be considered as clues for the reconstruction of the crime. The help of individuals familar with the area can be useful in providing prior knowledge of many of the items found.

In the case of a bombing involving high explosives, the search should include such items as triggering mechanisms, wire, blasting cap fragments, batteries, parts from clocks, electronic components, etc. Sometimes a source of shrapnel is employed with the bomb; such as nails or other small metal objects. All items which appear to be foreign to the area should be collected for the laboratory.

The laboratory examination of debris from a bombing is based on the fact that, even with high energy explosives, a portion of the explosive contents of the bomb will usually be present at the site of the incident. The search for small particles of the explosive amongst the debris can be a slow tedious process. At the time of a blast, small particles of the explosive can be scattered over a rather large area. Experience has shown certain materials to be good traps for these flying particles. For example, fibrous materials such as insulation and the stuffing in upholstery should be considered for their evidential value. Likewise, in materials such as wood, soil, or asphalt, parts of the destructive device may be embedded.

In many incidents the destructive device is recovered in the unexploded state and constitutes a very bountiful source of clues leading to the perpetrator. Bombers usually think along the lines that this type of crime is ideal since the parcel of evidence, or corpus delecti, will self-destruct beyond recognition. In the majority of cases such an attitude has no sound basis. Even though the evidence may be quite dispersed over a large area after a blast, sufficient fragments of the original bomb can be found to permit a comprehensive conception of the original construction of the destructive device.

In some situations, a mobile laboratory van or just a portable field kit can provide a very rapid evaluation of the physical evidence. A low-powered microscope, coupled with sensitive chemical spot tests can be sufficient for many on-the-scene conclusions, thus saving several days of delay. Spot tests for nitrates, chlorates, sulfur, ammonium ion, and certain explosives have been accomplished at bomb sites successfully. An in-depth examination with highly sophisticated instrumentation and techniques can be reserved for the central laboratory.

One difficult aspect of collecting evidence at the crime scene is the anticipation of what traces the person committing the crime may have carried away from the area. It is important that the evidence technician collects samples of all materials from the scene of a crime which might eventually be found in a suspect's possession at a later time.

Once a suspect has been located, a source of associative evidence becomes available for comparison testing. As can be expected, time is important. A prolonged lapse of time between the crime and the finding of a suspect decreases the amount of useful evidence which can be found. Such pieces of evidence as clothing, blood, skin swabs, fingernail scrappings, hair, examples of handwriting and voiceprints can be of great value for linking a suspect with the crime. A search of the suspect's car, living quarters, and work areas may provide many items of evidential value.

Preservation of the Evidence

The guiding principle related to the preservation of the evidence is to have the contents arrive at the laboratory in exactly the same condition as at the time of packaging. The problem of cross-contamination is always present. Proper packaging will help to preserve the evidence in its pristine condition.

The package must be appropriate for each specimen. Broken pieces of glass and other sharp objects logically should not be placed in plastic bags. Similarly it would be unwise to ship a volatile substance in a permeable container. Certain pieces of physical evidence may require mechanical protection due to the fragile nature of the item or to prevent its surface from contact with other materials.

As is often the case, physical evidence may be a perishable item. Close coordination with the laboratory will be necessary to maintain the integrity of many items of evidential value. In some cases an additive can be used to prevent deterioration of the samples and yet not interfere with any subsequent tests.

After all the items have been selected for transmission to the laboratory a decision must be made on the remaining items considered to be of little potential value. Since it is seldom possible to maintain the scene of a crime until final court deliberations, all remaining evidence having a lower potential value should nevertheless be collected and placed in a secure storage area for possible examination at a later date.

The packaging of items obtained directly from a suspect or his residence for example should not be in the same package as those collected at the scene of the crime for comparison. A cardinal rule in police science is never to allow the suspect to go near the scene of the crime. The value of such evidence as fingerprints, hair and soil, for example, would become worthless in such a situation. In a similar manner the possibility exists for cross-contamination when evidence from both the crime scene and the suspect are in the same package. Extending this concept further, one can rightfully conclude that the crime laboratory itself is a potential source of this type of cross-contamination.

Labeling Requirements

Each package of evidence should be carefully labeled and given a number or letter for identification. Sufficient information must be provided on the label to describe the exact location where the evidence was found. Here again, more complete details may be recorded in the notebook by the evidence technician. Nothing should be left to memory since a long span of time will likely transpire before the presentation in court.

Other pertinent data recorded should include the date and the time the specimen was collected, witnesses to the collection, case number, title of the case, and a brief description of the item.

Chain-of-Custody Considerations

Ever present in the handling of physical evidence is the requirement for maintaining an accurate record in the chain-of-custody. Sufficient records must be kept to assure the court that the integrity of the physical evidence has been maintained from the time the material was collected until the completion of the laboratory examination and the final court presentation.

Sealed packages of evidence should be carried directly to the laboratory or else sent by registered mail. In general, the fewer the number of persons having contact with the evidence, the more acceptable the results will be at the time of the trial. Each change of possession of the evidence must be recorded carefully.

Letter of Transmittal

Whenever physical evidence is sent to a forensic laboratory, a letter of transmittal must also be sent. Included in the letter of transmittal should be information on the crime committed, a brief description of the evidence submitted, as well as the examinations requested of the laboratory. Any information which will aid the laboratory in conducting its examination should also be included in the letter of transmittal.

Collection of Reference Materials

A forensic laboratory must maintain an active reference section of exemplars. The library of such standards must be collected and maintained in many cases long before any crime is committed involving them.

In addition to submitting items of evidential value to a forensic laboratory, samples of related composition must also be collected for control purposes. For example, a transfer of paint between two vehicles very often occurs from the collision of two vehicles in a hit-and-run type accident. Besides sending the paint smeared section to the forensic laboratory, chips of normal paint a short distance away should also be sent as standards for comparison.

Another case which can be cited involves the sampling of soil. The analysis of soil samples several feet away from the violation site will provide a better understanding of variation of the chemical composition of soil in the region of interest.

Conclusion

Associated with each step in the necessity of every phase of this process to be acceptable to the courts. The lack of attention to any of these steps can completely invalidate the laboratory findings and conclusions, regardless of how carefully executed the analysis was conducted.

Except possibly in the case of fingerprints, a single piece of physical evidence is not able to sustain a conviction by itself. Very often there are many items of physical evidence available which added together can be very incriminating to the accused.

There are large differences of opinion with regards to how much material should be collected at the crime scene. At one extreme we find incidents where absolutely nothing is collected; in other cases the site is completely stripped of all items indiscriminately. In the latter case, the large volumes of materials can overtax any forensic laboratory's capabilities. Logically the proper amount of evidence to collect lies within these extremes.

Unless physical evidence is collected and sent to the laboratory, the supportive role of this important wing in law enforcement is lost. In many cases, a confession will be available which will decrease the motivation on the part of an investigator to collect evidence. The confession may not be acceptable to the court, resulting in a very poor case against the defendant. The attitude of the courts in recent years has been to place more importance on the scientific examination of physical evidence.

The dream of any forensic scientist is to analyze physical evidence nondestructively without even breaking the seal on the packet. Certain laboratory procedures have the potential for achieving such an ideal situation. For example, some methods involving X-ray and gamma ray spectrometry can analyze a sample under such a restraint.

While all law enforcement officers should have training in the preservation of the crime scene and the identification and collection of significant physical clue material, skilled and supervised personnel attached to a laboratory with a primary responsibility as evidence technicians on the crime scene search team appears to offer the greatest potential for the most effective use of a forensic laboratory.

J. P. Walters[1] *and S. A. Goldstein*[1]

How and What to Sample in the Analytical Gap

REFERENCE: Walters, J. P. and Goldstein, S. A., **"How and What to Sample in the Analytical Gap,"** *Sampling, Standards and Homogeneity, ASTM STP 540*, American Society for Testing and Materials, 1973, pp. 45–71.

ABSTRACT: The possibility of obtaining greater optimization of spectrochemical techniques by selectively isolating radiation from the analytical spark gap is discussed. Instrumental factors required to achieve positional stability of the spark necessary for these techniques are discussed in terms of the chemical reactions controlling spark formation. Using simple optical systems capable of viewing the spark differentially, emission profiles of several metallic and sparking-gas species have been recorded. The heterogeneous spatial and temporal structure in these profiles has been employed to group the spectral lines into classes according to when and where they appear in the discharge. Suggestions are made as to how the spark may be viewed to isolate lines of one class from those of other classes, thereby reducing background and line interferences and enhancing signal-to-noise ratios.

KEY WORDS: spark emission spectroscopy, spectrochemical analysis, time resolved spectroscopy, sampling

Sampling selected regions in the discharge (analytical) gap for purposes of enhanced sensitivity is a common practice when a direct current arc is the power source. The "cathode layer" technique [*1*][2] is well developed (for example, Ref *2*) and much of the theory associated with sample transport through the cathode space charge has been explored [*3*]. Still, in spite of the analytical benefits associated with this experimental approach, its use generally has been associated with arc-type systems.

The concept of spatial isolation of selected regions of the analytical gap for optimized spectrochemistry has yet to be put on a working basis

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[1] Professor and research assistant, respectively, Dept. of Chemistry, University of Wisconsin, Madison, Wis. 53706. Dr. Goldstein is now with Ames Laboratory USAEC, Iowa State University, Ames, Iowa.

[2] The italic numbers in brackets refer to the list of references appended to this paper.

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for spark discharges. Here, the wandering of the discharge over the electrode surface and the relatively small dimensions of the analytical gap combine to make spatial isolation techniques somewhat academic. The simplicity and ruggedness that are necessary in apparatus intended for heavy industrial use is not easily recognized when this discharge is considered a target for spatial isolation methodology.

Yet, of all the discharges, the spark most needs to be used with spatial isolation for analytical purposes. It is highly heterogeneous in all of its dimensions, and much of the radiation detected in an integrated experiment is not of direct analytical value (often, as with line interferences, certain spectra are detrimental to sensitive analytical work). Since the technique has not achieved widespread use, the relationship between background and line radiation, ion and neutral spectra, and plasma and electrode vapor lines has not been recognized as almost completely spatial, and consequently capable of being separated on a spatial basis.

The principal difficulty involved in utilizing the spatial heterogeneity of the spark discharge has been, and to a large degree still is, the wander (positional instability) of the discharge. Until the spark can be made to stand still on a dimensional scale comparable to that of its smallest diameter, the benefits of separation of line from background, of interfering plasma lines, and of multiple stages of ionization will be only marginally realized.

Fortunately, the discharge can be stabilized, even with conventional apparatus, to a degree sufficient to allow many of the previous advantages to be available on a routine basis. This paper will discuss some of the processes that allow the discharge to be stabilized and what techniques can be used to observe the resulting system. Following that, general criteria will be set for observing selected discharge regions to provide improved spectrochemical results.

Instrumentation for Stabilization

Since the main function of the spark (or excitation) source is to form the discharge and deliver current to it to sample the electrodes, it is prudent to retain the best features of present sources in any apparatus that is intended to produce a stable spark. The delivery of current to the formed spark via capacitor discharge is one such feature. The circuitry involved is simple, the currents attainable high, and the problems associated with shaping the resulting discharge waveform uncomplicated. The formation aspects of the spark also may be readily controlled with a capacitor-discharge type source if attention is paid to some few details. Thus, in the first approximation, it is not necessary to completely rework such sources as the air-interrupter [*4*], rotary-gap [*5*], or pulse-triggered [*6*] types to stabilize the spark. While it is true that sources may be designed

[*7*] that can produce highly stable sparks [*8*], the "conventional" source is sufficient to begin relatively sophisticated experiments.

The key to generating a positionally-stable spark lies in recognizing that the discharge forms and accepts current at atmospheric pressure, where large numbers of low-energy collisions will control its pathway. Directed ion movement over substantial distances is not involved. Rather, high-frequency, longitudinal, wave-like "movement" of regions of charge dominates (the analogy to water waves or falling stacks of dominoes is appropriate). With this in mind, it follows that the channel or core of the discharge is quite mobile, and the space charges at the electrodes may be fixed in position while the core snakes about under various influences. Conversely, the discharge core may be firmly fixed, perhaps in a straight line directed along the interelectrode axis, while one or both of the space charges move about the electrode surfaces. Since the cathode space charge (or spot) is most important from a spectrochemical viewpoint (in that it is from the cathode that the highest sample erosion is observed), the conditions that would cause the movement of this region over the electrode surface are most critical to control.

The first, and most obvious, instrumental technique to stabilize the cathode space charge region is not to allow the current to rapidly reverse direction during the lifetime of each spark as occurs in the conventional high-voltage, air-interrupter source (that is, an "oscillatory, high-voltage" spark source). If this happens, the space charge must form and reform with every other polarity change, and the probability is high that it will wander substantially in the process. On the other hand, there are concurrent disadvantages to generating a long, overdamped unidirectional discharge, not the least of which is the heavy heating and erosion of the cathode and destruction of what should be a reference surface for movement of electrode material into the gap. In achieving a compromise to these two extremes, a source has been developed that provides what we call a pulsed-unidirectional spark. This simple circuit, which may be added to any existing source with only a few modifications, is remarkably effective alone in stabilizing the wander of the spark. The circuitry and waveforms have been described before [*9*], as have several key experiments concerning the "excitation" produced [*10*]. It is, in summary, the pulsating (about 100 kHz) unidirectional current that is important.

An additional consideration that would appear to be obvious is that the gas through which the spark will form and accept current must be introduced in a laminar manner. However, the subtle aspect is that, at atmospheric pressure, the gas may well be considered "chemically" active in forming the spark. The combination of these two considerations is singularly effective in stabilizing the spark. The "chemical" aspect of the discharge gas is seen if a simple model is visualized for the excitation of a gas, for example, argon. We picture an electron equilibrium (microscopically reversible) as active:

$$\mathrm{Ar} + e^- \rightleftharpoons \mathrm{Ar}^* \rightleftharpoons \mathrm{Ar} + h\nu$$

The excited Ar* simply is an intermediate for collisional or radiative de-excitation. However, if the number of collisions, say with an electron, is sufficiently high, and the lifetime of Ar* sufficiently long, then another process may enter the picture:

$$\begin{array}{rcl} \mathrm{Ar} + e^- \rightleftharpoons & \mathrm{Ar}^* & \rightleftharpoons \mathrm{Ar} + h\nu \\ & +e^- & \\ & \uparrow\!\downarrow & \\ & \mathrm{Ar}^+ & \end{array}$$

Here, the Ar* becomes a metastable "reactant" that can lead to ionization of Ar by relatively low energy electrons. Continuing the reasoning, suppose that in addition to the electrons, another reactant were present that could collisionally deactivate the Ar*, for example, nitrogen gas. Then there would be a four-part balanced equilibrium active, one part of which would be the ionization of Ar:

$$\begin{array}{rcl} & \mathrm{Ar} + \mathrm{N}_2^* & \\ \#4 & \uparrow\!\downarrow & \\ & \mathrm{N}_2 & \\ \#1 & + & \#3 \\ \mathrm{Ar} + e^- \rightleftharpoons & \mathrm{Ar}^* & \rightleftharpoons \mathrm{Ar} + h\nu \\ & +e^- & \\ \#2 & \uparrow\!\downarrow & \\ & \mathrm{Ar}^+ & \end{array}$$

In this case, if N_2 gas were added to the system, equilibrium *#4* would be shifted to the product side, and equilibrium *#2* to the reactant side, decreasing the ionization. These processes are quite well known (for example, Ref *11*) and are observed in many classes of electrical discharges. However, at atmospheric pressure, where the concentration of the pivot species Ar* may become relatively high due to the high collision frequency, they also may serve the unique role of discharge stabilization.

For example, we may envision some type of gas delivery device that would deliver a thin beam of argon gas from the anode to the cathode electrode in a spark gap. If this beam were introduced through an air (or nitrogen) environment in a laminar manner, a "wall" or boundary would exist between the argon and nitrogen. In the argon core, equilibria *#1* and *#4* would combine to favor ionization, and at the boundary, equilibrium *#1* and *#4* would combine to "quench" the ionization. In other words, the spark would form and follow the argon beam. Via careful adjustment of the argon flow rate, the spark could be stabilized in space between the two electrodes. Just such behavior has been observed in our laboratory [*8*], as well as by others [*12*]. The degree to which the laminarity of the gas must be maintained (namely, the flow rate consideration) is indicated in Fig. 1.

While the above visualization is necessarily simplified compared to the multiple competitive equilibria that may occur in the spark, it nonetheless accompanies well the experimental facts that the introduction of a laminar beam of a gas such as argon into an electrode gap, when coupled with a pulsed-unidirectional current waveform, will provide a discharge of

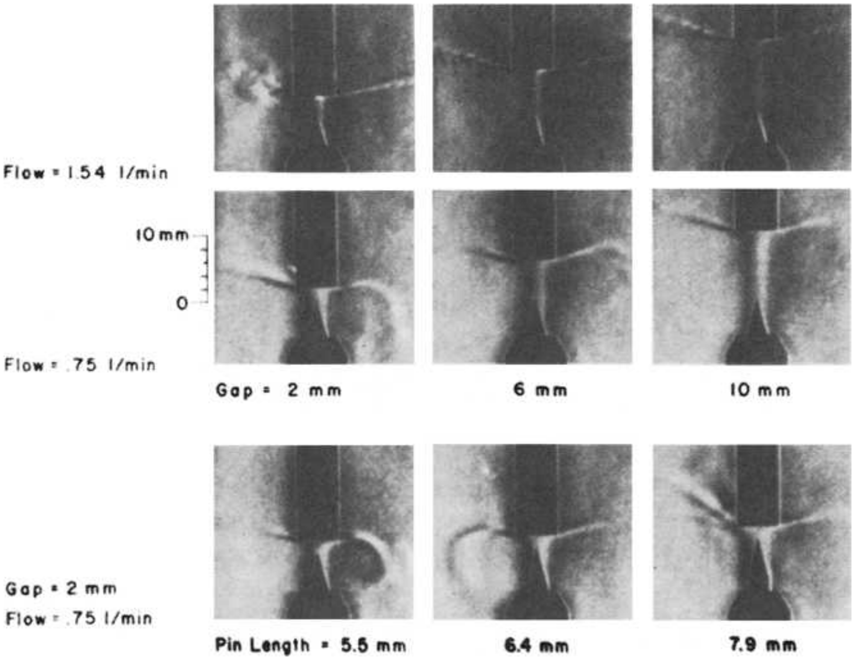


FIG. 1—*Gas flow regimes for argon required to produce a stable discharge. Upper Photographs: Laminar gas flow as a function of flow rate and gap spacing. Pin length constant for each photograph. Lower Photographs: Laminar gas flow as a function of pin length above the jet orifice. Center row of pictures shows sufficient laminar flow for stability. Top and bottom rows are unacceptable. Lower electrode shown in Fig. 2.*

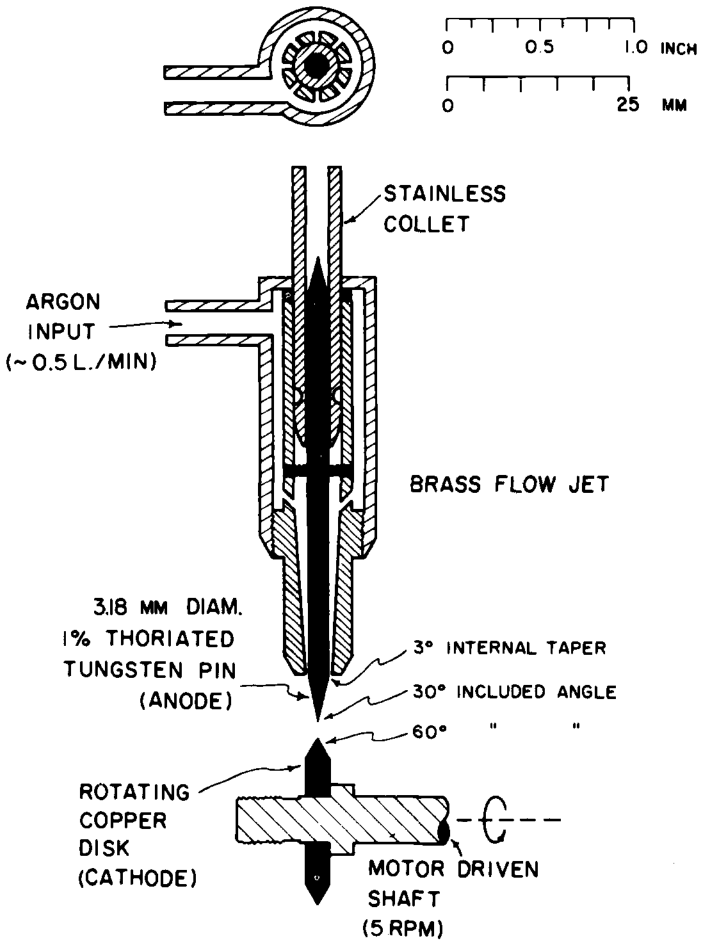
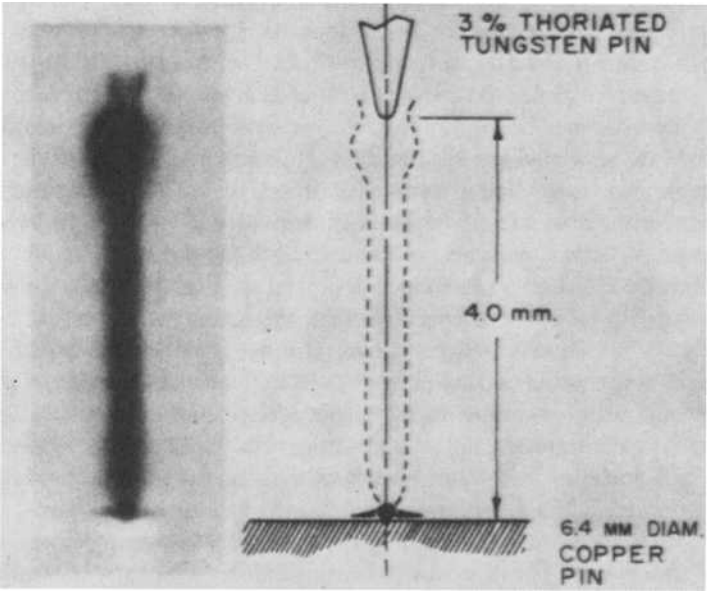


FIG. 2—*Electrode system for production of a stable discharge.*

remarkable stability. In Fig. 2 we show a device that has been used for gas introduction to a beveled rotating disk electrode for our research work with stable sparks, and several other types of electrodes have been shown in Ref *8*.

It is unfortunate that highly irregular current transients are found in the majority of commercial air-interrupter spark sources, largely due to the coaxial cables used to couple to the spark stand. They may cause polarity reversals during the first few instants of current conduction and deteriorate the stability from what may be observed in a transient-free research source. For example, Fig. 3 shows a stop-motion photograph of the spark formed in this source [7] just after "ignition" and immediately before current conduction or "capacitor discharge" begins. The firmly-



ARGON SPARKING GAS
SPARK REPETITION RATE – 2000/SEC.
PHOTOGRAPHIC EXPOSURE – 360 SEC.
EXPOSURE (SHUTTER) TIME – 0.005 μSEC.
DELAY TIME ~ 0.03 μSEC. AFTER IGNITION

FIG. 3—*Framing camera photograph of the first formation of a stable spark discharge in argon. Source and parameters described in Ref 8.*

anchored cathode spot is apparent. With this stability, we have found it possible to effectively write one's name on a lathe-machined electrode simply by moving the electrode beneath the spark. With a conventional source, modified to produce a pulsed-unidirectional current waveform, such dramatic stability is not obtained. However, the discharge wander is sufficiently reduced, using apparatus similar to that shown in Fig. 2, that regular spark tracks about 2 mm wide can be placed over selected electrode regions by rotating the electrode, and the discharge may be viewed with spatial discrimination of unwanted regions.

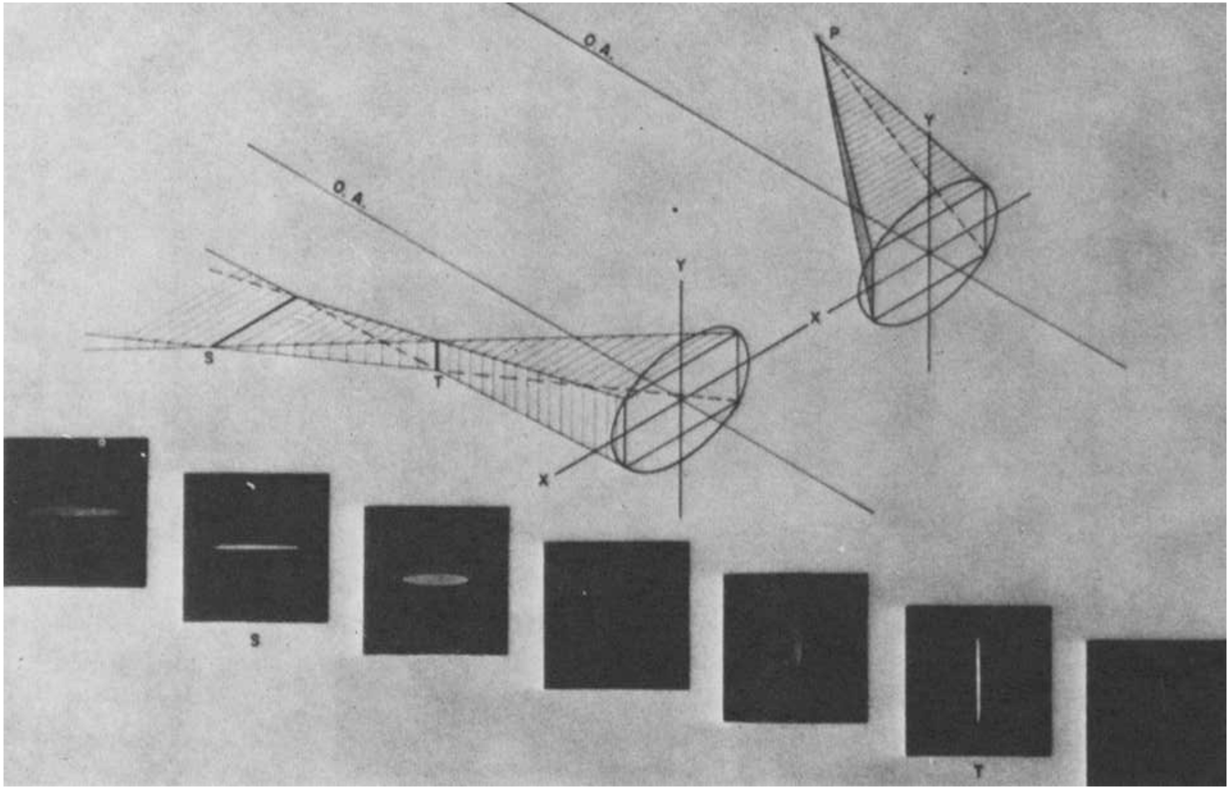
Instrumentation for Viewing the Discharge

At first glance, it would appear that a simple quartz lens would provide sufficient imaging properties to allow spatial discrimination of a stabilized discharge. In fact, but for one drawback, this is true, and many of our developmental experiments are done with this single, simple optic and a slit or mask. Results of these experiments have been presented [*13*] and will soon appear in the open literature.

However, chromatic aberration is an annoyance in lens systems used for this application, requiring a limitation over the range of wavelengths that may be used in an "exactly" discriminated experiment, and we favor mirror optics for definitive work. Unless the special expense of a catadioptric system can be met, most mirror systems used for imaging will be worked off-axis, and the resulting astigmatism and coma will deteriorate the image. However, using pairs of mirrors in a "Z" configuration has long been known to cancel coma [*14*], and sets of pairs of mirrors may be stacked to either enhance or cancel the astigmatism (one application of enhanced astigmatism has been reported in Fig. 1 of Ref *15* to allow reliable viewing of a wandering discharge for time-resolved study).

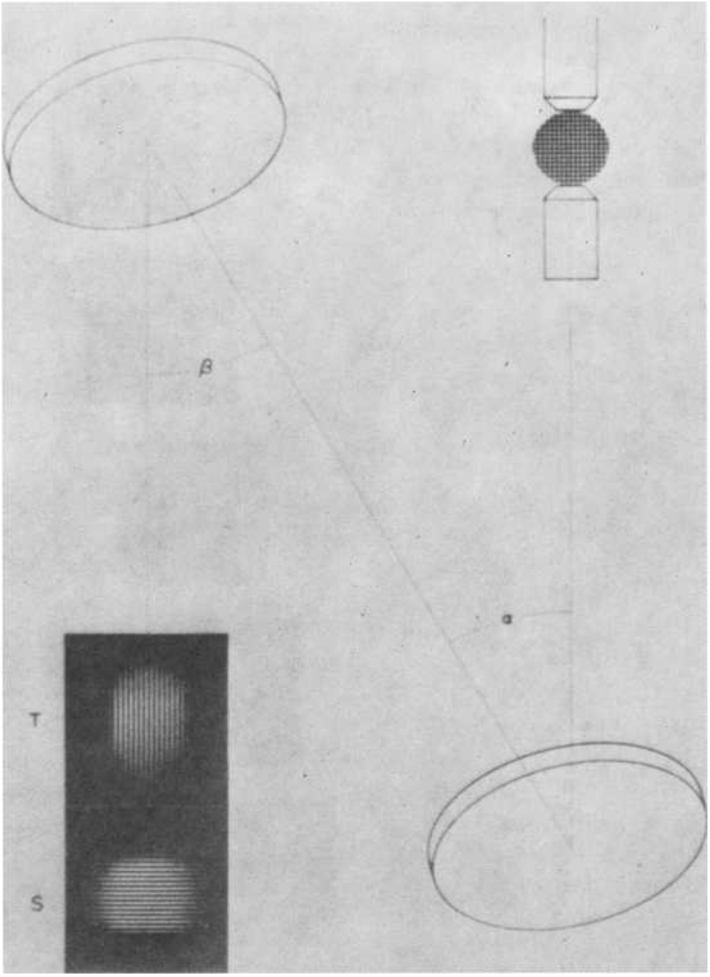
In Fig. 4 we show photographs of the astigmatism produced from a point light source imaged by a pair of parabolic mirrors. This type of image transfer can prove valuable in an analytical problem, since it is possible to place a discriminating slit at the tangential focus of the system (T in Fig. 4) and pass the radiation from a row of points in this discharge into a spectrometer. If the discriminating slit is the entrance slit of the spectrometer proper, the off axis angles of the Z configuration may be adjusted to average the row of points and give the decided advantage of uniform slit illumination while still accomplishing spatial discrimination (at least in one dimension). An example is shown in Fig. 5, where a screen of about 0.05 mm hole size was placed at the source position, and the off-axis angles α and β adjusted to give a clear separation of the sagittal and tangential focal planes (S and T in Fig. 4). In the tangential focal plane, points equally removed from but parallel to the interelectrode axis are averaged. By placing a narrow slit parallel to the interelectrode axis, all but one column of points in the source may be vignetted from view. Similarly, in the sagittal focal plane, rows of points perpendicular to the spark axis are averaged, and regions away from the electrode surface may be viewed (example, Refs *8* and *16*).

If 2 two-mirror systems are combined such that images of one serve as objects for the other, the astigmatism from one system may be enhanced or cancelled by the other system. An example is shown in Fig. 6, where mirrors M_1 and M_2 (over-and-under) are at 90 deg to mirrors M_3 and M_4 (side-by-side). In fact, mirrors M_3 and M_4 may consist of a system of mirrors such as those in an Ebert or Czerny-Turner spectrometer and associated external mirrors also in the same plane. In this case, one set of external mirrors may be adjusted to cancel or add to the astigmatism of the entire system. Figure 7 shows a "cancelled" result, where four mirrors were associated with a Czerny-Turner spectrometer and rotating-mirror, time-resolving optics, and another two arranged as M_1 and M_2 (Fig. 6) to provide sufficient separation of the focal planes to cancel the astigmatism of the four. For Fig. 7, a screen with 0.05 mm holes and wires was placed at the nominal source position (0 mm), five millimeters ahead (+5 mm),



S = sagital image
T = tangential image

FIG. 4—*Astigmatism produced in transfer of a single point source* (P) *by a parabolic mirror. Mirror indicated schematically in two parts for clarity: upper diagram is input, lower is output.*



Grid dimension = 0.05 mm
S = sagittal image
T = tangential image

FIG. 5—*Astigmatism produced in transfer of a grid of point sources by a pair of parabolic mirrors set in a "Z" configuration.*

and five millimeters behind (−5 mm). The screen was back-illuminated by an iron hollow cathode, and the spectra shown obtained with a 1.0-m Jarrell-Ash Czerny-Turner spectrometer used for the time-resolved experiments in progress at the time. The spatial resolution is evident.

The important point is not, however, unique arrangements of mirrors. The examples shown here are used for experimental convenience in our research applications. In some cases, off-axis angles may be kept sufficiently small (for example, 2 to 3 deg) that both the astigmatism and coma from a single concave mirror are minor. Rather, what is important is that the relative dimensions shown in Fig. 7 for the transferred image of rows and columns in the discharge represent well the level of spatial resolution we have observed to be important in the spark.

The imaging systems used for practical work may fall in either of two classes. The first is the "blocking" class, where radiation from all regions of the discharge other than a preselected few is passed and used for analysis. The second is the "passing" class, where a particular region of the discharge is passed to the exclusion of others. It has been our experience (for example, Ref *13*) that blocking experiments are useful for discrimination against background and interfering plasma or channel lines, while passing experiments allow the selection of particular classes of spectral lines (for example, highly-excited ion lines) of the electrode material to the relative exclusion of other classes. Dimensions as small as 0.05 mm or as large as a millimeter or two may be involved in either case, and the specification of a particular window size will depend entirely on the application sought, the chemical nature of the electrode, the sparking gas spectrum, and the positional stability of the entire system.

Thus, it is clear that, with respect to specifying the "how to sample" part of this paper, we are writing ahead of our time. It is, however, equally clear that the spatially-isolated or resolved experiment, when put to practical use, will require at least as much development and standardization as the present ASTM "suggested" class of methods [*17*], if not more, and the imaging systems involved must lend themselves to such standardization. Whether this proves a liability or asset remains to be seen.

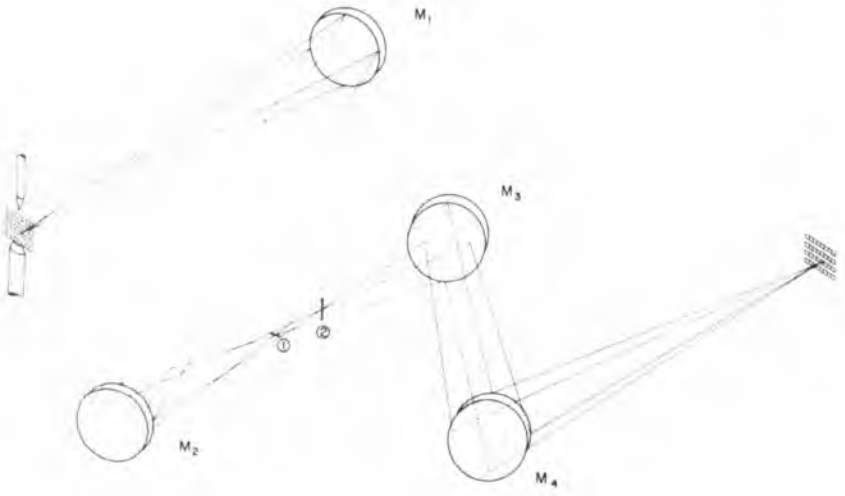
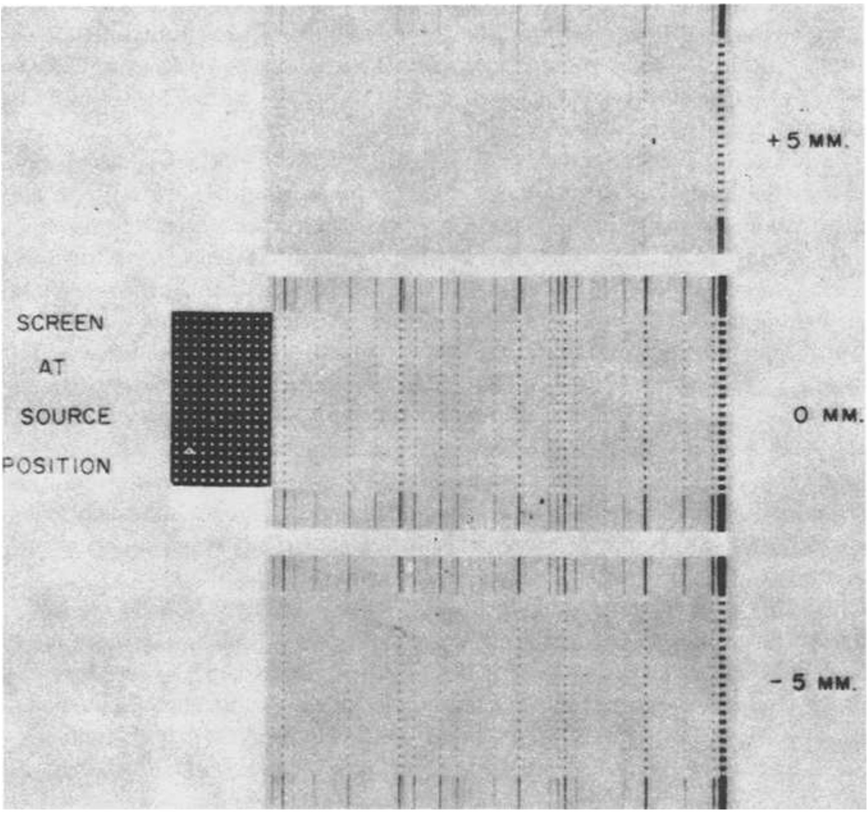


FIG. 6—*Arrangement of four parabolic mirrors for transfer of a grid of point sources with controlled astigmatism.*



Screen Dimension = 0.05 mm

FIG. 7—*Image fidelity observed with an optical system equivalent to that in Fig. 6. Spectrograph—JACO 1.0 m Czerny-Turner "0 mm" indicates grid at proper position for highest fidelity image transfer.*

What to View

The most remarkable single characteristic of the spark discharge is its ability to sample as wide a variety of electrodes as is encountered today (for example, Ref *17*). It is, however, this same ability that leads to its high spatial heterogeneity, and concurrently either the problem or opportunity of selecting what to observe in the gap. The two-fold nature of the discharge, for example, a separate channel and electrode vapor plume, is well known, with descriptions of the two systems dating back to 1901 [*18*]. Recently, one of us reported on how "excitation" in the classical sense may be primarily due to the relative interaction of these two systems [*10*]. Our current feeling is that the single most important point to emphasize, or reemphasize, about this discharge is that it consists of (at least) two systems, one the current-dependent "channel" and the other the thermally-expanding cloud (or plume or jet) of electrode vapor. When this is realized on a working basis, a large measure of order is introduced into the kinds of radiation observed from the spark, and the problem of deciding what to view becomes more logical, if not simpler.

An example of these two systems as they interact with each other is shown in Fig. 8. On the left is the pulsed-unidirectional current sustaining the discharge, showing a first peak at about 200 A at 3 μs. In the center is shown a time-swept, "radial slice" taken from the spark at a distance of 0.50 mm away from the copper cathode surface. Such data are readily obtained by placing an isolating slit of 0.05 mm width at Focus 1 in the optical system shown in Fig. 6, then spinning mirror M_4 about a horizontal axis such that a single row of points from a region of the discharge is swept up the figure. The radial slice is then a fully resolved cross-sectional view of any row of points perpendicular to the interelectrode axis. At the right are shown selected spectral lines, radially-resolved, photographed at preselected times after the discharge is formed. It is evident that the argon, or plasma, lines are associated with the darkened central portion of the time-swept image. Of note is that it is this portion whose radial excursion from the central spark axis appears to follow the current, expanding as the current increases and contracting as the current decreases. In contrast are the neutral copper lines from the electrode vapor that is filling the gap with increasing time. They are observed to expand outward from the central interelectrode axis, and decay from these wing regions, rather than contracting back in as the current decreases.

In our first observations of these two systems [*19*], emphasis was placed on the reversible aspect of the "channel" lines. That emphasis must now be expanded to point out that the darkened regions shown in the center of Fig. 8 do not contain only the spectral lines of the channel species. Additionally, they contain spectra from the electrode vapor as it moves through and interacts with the channel species. This is a genuinely mixed system of two (or more) components, and the unique spectra that are observed will depend both upon the channel size (a function of the instantaneous current amplitude) and the position and velocity of the moving cloud of electrode vapor.

The order and regularity associated with these two systems can be observed most easily in the electrode vapor spectrum recorded as a function of time and distance from the parent cathode. For simplicity, the radial dimension may be integrated, for example, each row of points outward from the central spark axis are averaged with an astigmatic optical system and the position of the row progressively moved away from the parent cathode surface in a stepwise manner. Such time-resolved spatially-isolated spectra are shown in Fig. 9 for two copper lines observed in a low-current, unidirectional spark [*8*].

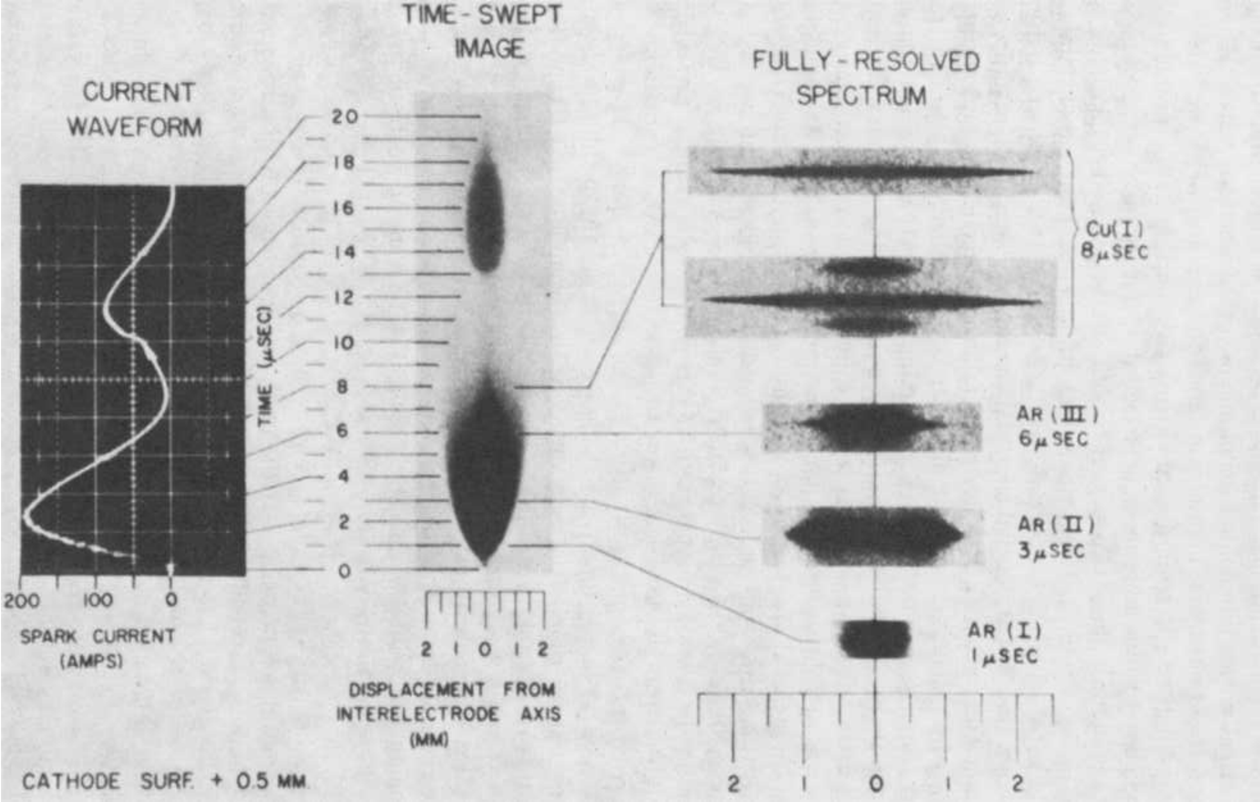
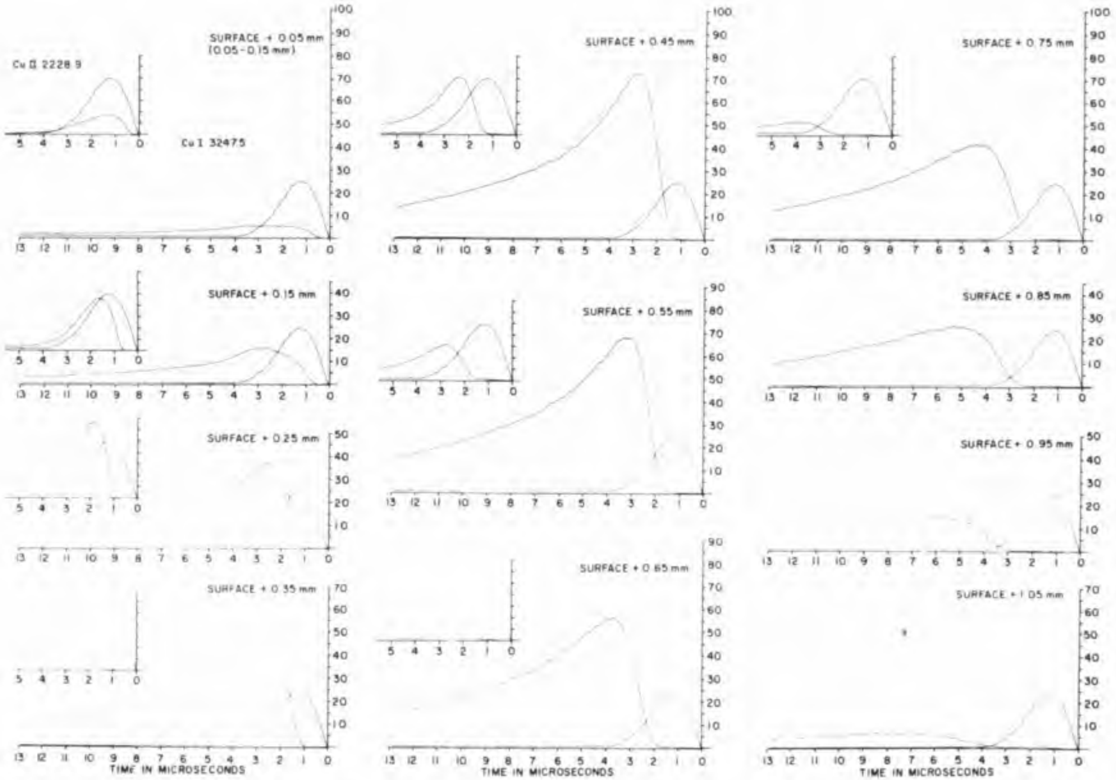


FIG. 8—*General procedure for obtaining fully-resolved spectra.*



Abscissa = time in μs Ordinate = current in amp

FIG. 9—*Time-resolved, photoelectrically detected spectra from a stable spark discharge in argon. Discharge current pulse shown in lower right in all insets. Spark source and parameters described in Ref* 8.

In the upper left corner of each frame of Fig. 9 is an inset showing the intensity of the 2228.9 Å Cu II line recorded with the current waveform. The main part of each frame shows the intensity of the 3247.5 A Cu I resonance line recorded with the current waveform. The labeled ordinate is current in amperes, intensities are relative, and the total electrode separation was 2.0 mm (complete discharge parameters are given in Ref *8*). While each photoelectric tracing shows interesting structure (for example, the double exponential decay of the 3247 line at 0.35 mm displacement), three overall features deserve special mention.

The first feature is the progressively increasing delay in time prior to detectable emission in both lines as distance away from the cathode is increased. Analysis of many lines has indicated that this delay is associated with the time required for the vapor cloud originating at the cathode to move into the observation window. Regardless of the current waveform, this delay will be present, giving at least one "what to view" criterion. If the analytical gap is spatially segregated and regions away from the immediate cathode surface viewed, the radiation detected will contain information from the cathode only part of the time the spark is carrying current.

The second feature concerns the intensity of the emitted radiation relative to the amplitude of the current pulse. If, for example, the 3247 line is observed between 0.25 and 0.75 mm from the cathode surface (as would be the case with a "pass" window 1/2 mm high set 90 deg to the spark axis), there will be emission of substantial intensity after the discharge current has terminated. However, if the same window was set with its lower edge 1.05 mm from the cathode surface, the 3247 line would be detected at significantly lower intensity. In fact, it would be difficult to detect at all, the reason being that the discharge current would have dropped to a low value (or zero) prior to the time material from the cathode reached the region being observed. This gives rise to the interesting, if not useful, observation that it is possible to adjust the position of a spatially discriminating window such that radiation from the electrode vapor simply is not detected in a time-integrated experiment.

The third feature to be noted requires more careful inspection of the data. If the time behavior of the Cu II line is compared to that of the Cu I line, it will be evident that the II line leads, or feeds into, the I line. Since these tracings have been recorded photoelectrically, the intensities are both linear and reliable, and the fact that the end of the decay of the II line corresponds well to the onset of the decay of the I line may be taken to indicate that the bulk of the signal detected in a time integrated measurement of the 3247 line would come from the relaxation of more highly excited, and ionized, parent species. In an earlier series of experiments [*16*] this was reported for many additional lines of both copper and aluminum. More recent work has indicated that the rate of this relaxation, while undoubtedly fundamental in origin, shows the form in Fig. 9 due to both the velocity of the cathode electrode vapor and the amplitude of the current. Thus, in the practical experiment, it should be possible to choose spatial regions of the discharge for observation of the radiation of, say, a neutral atom spectrum to the exclusion of the first ion spectrum (or the first ion to the exclusion of the neutral), aiding in the reduction, if not elimination, of some line interferences.

The above observations, while illustrated from time-resolved data, do not presuppose that practical analytical advantages will require time-gated methods of detection. It is true that with the current state-of-the-art in gating circuitry at a refined level, the problems of time sampling a photomultiplier pose nowhere near the challenge they once did (for example, Ref *20*), and where this approach proves advantageous, it is only logical to apply it. However, since the time separation of line intensities such as

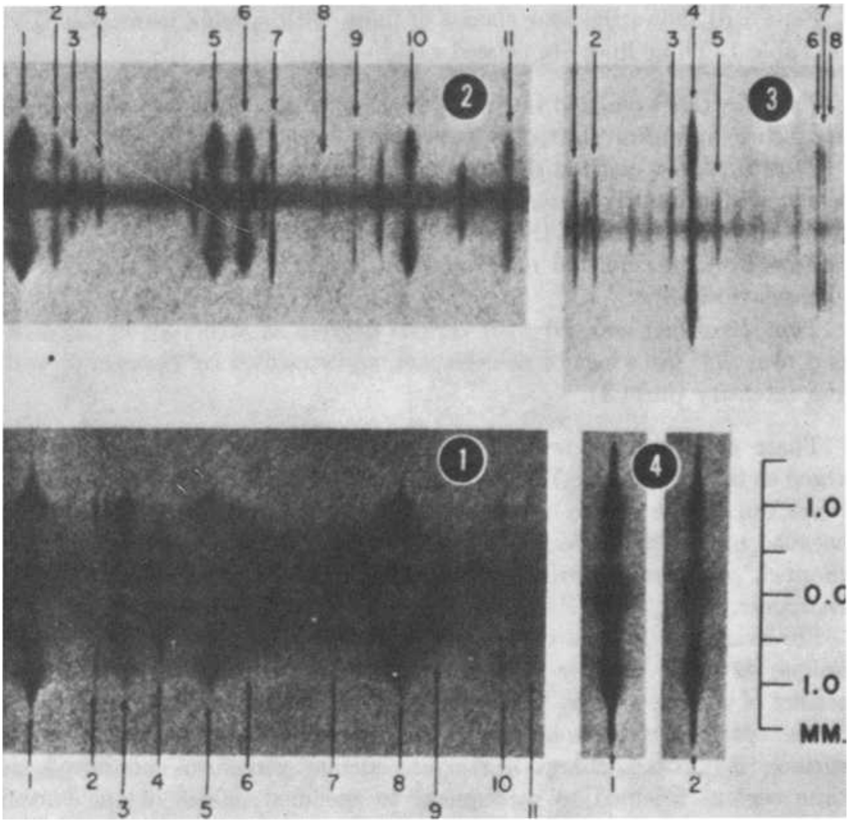


FIG. 10—*Fully-resolved spectra to illustrate standard line structure. Numbered lines identified in Table 1.*

shown in Fig. 9 arises due to the movement of electrode vapor, time becomes equated to distance by velocity. Thus, it is probable that what could be gained by time gating also could be gained by spatial discrimination; the latter being substantially easier in routine use.

Fully Resolved Spectra

Complete insight into the "what to view" problem comes more readily when spectra from the discharge are resolved in time, by wavelength, and three dimensionally in space. In previous work, such "fully resolved" spectra were point plotted, after computer correction for the thickness of the source in the radial direction, for aluminum sparked in nitrogen [*19*]. However, the detail of such plots is hardly inspiring for selecting optimum view regions for practical analysis, and rather than belabor the point, we have chosen to summarize photographically four typical line patterns that will be observed at selected times in a fully resolved experiment.

Figure 10 shows the four classes of lines, with specific transitions given in Table 1. These lines are classed as:

Type 1—Lines emitted in the near wings of the discharge channel that are diffuse and often shifted in wavelength (inset 1).

Type 2—Lines emitted throughout the channel but heaviest in the near wings and primarily observed in connection with a heavy background down the exact center of the channel (inset 2).

Type 3—Lines emitted most strongly in the far wings of the discharge channel (inset 3).

Type 4— Lines emitted with various degrees of structure in the center and near and far wings of the channel, accompanied by changes in width and intensity (inset 4).

These classes cover several metals, although all are associated with argon as the plasma gas. These line types also may occur at several separate times during the course of a single discharge. Again, the structure exists because of the movement of the electrode vapor relative to the spark channel, and this may be shown most graphically in a fully resolved experiment.

For example, the two silver resonance lines (inset 4 in Fig. 10) have a unique structure. The experiment that shows the origin of this structure consist of three steps: (*a*) A window, of small width, is placed perpendicular to the spark interelectrode axis at a measured distance from the cathode surface. (*b*) The discharge is started, current waveform monitored, and time regions selected to correspond to specified values of the current. (*c*) Wavelength dispersed spectra are taken at each time interval for a specified distance, the distance changed, and the same spectra taken at the same time intervals.

TABLE 1—*Line identification for Fig. 10.*

Line Number	Species	Wavelength, Å
Inset 1—Photographed 3.5 μs after discharge initiation; 0.05 mm off the cathode.[a]		
1	Cu I	3273.96
2	Cu I	3279.82
3	Ar II Cu I [b]	3281.70 3282.71 [b]
4	Ar III	3285.87
5	Cu I	3290.54
6	Ar II Ar II [b]	3293.64 3293.92 [b]
7	Ar III	3301.87
8	Ar II Cu I [b]	3307.23 3307.95 [b]
9	Ar III	3311.25
10	Cu I	3317.22
11	Cu I	3319.68
Inset 2—Photographed 2.5 μs after discharge initiation; at the cathode surface.[a]		
1	Au II	2802.06
2	Au II	2805.21
3	Ar III	2807
4	Ar IV	2809.44
5	Au II	2819.80
6	Au II Au II [b]	2822.55 2823.17 [b]
7	Au II	2825.45
8	Ar IV	2830.25
9	Au II	2833.02
10	Au II	2837.87
11	Au II	2846.96
Inset 3—Photographed 3.5 μs after discharge initiation; at the cathode surface.[a]		
1	Au III	2665.16
2	Au III	2666.99
3	Ar III	2674
4	Au I	2675.95
5	Ar III	2678.38
6	Au II	2687.63
7	Au II	2688.16
8	Au I	2688.72
Inset 4—Photographed 6.0 μs after discharge initiation; at the cathode surface.[a]		
1	Ag I	3280.68
2	Ag I	3382.89

[a] Observation window width = 0.05 mm. Current wave-form as shown in Fig. 8.

[b] Lines too close for separate identification.

In this experiment, fully resolved spectra will be obtained before, during, and after the time the electrode vapor cloud passes a particular discharge region, and the microscopic excitation processes accompanying the movement of the vapor will be registered by the resulting spectral changes.

Selected spectral regions for the above "front-crossing" experiment are shown in Fig. 11 for a silver disc sparked in argon. Four distances were selected and spectra were recorded at six times, all corresponding to a current waveform such as that shown in Fig. 8. The two resonance lines of silver are marked, along with a millimeter scale to indicate the radial dimension of the discharge at any particular time and axial displacement of the viewing window.

There is one remarkable feature of the spectra shown in Fig. 11 that may be observed by stopping the time and increasing the distance away from the cathode surface. For example, if the viewing time is stopped at 1.0 μs, a well-developed and intense spectrum containing the Ag resonance lines, several radially contracted and broadened Ar II lines, and a heavy background is observed at the cathode surface. However, when the viewing window is advanced to a distance of 0.4 mm from the cathode surface, only the two silver resonance lines are observed at any measurable intensity, superimposed on a light continuum. When the observation window is advanced further, to a distance 0.75 mm from the cathode, only a faint continuum is observed. A careful search over approximately 1000 Å (from 2500 to 3500 Å), in the exact regions where the Ar II spectrum would radiate most strongly, confirms this observation, namely, that no radiation other than a faint continuum is detected.

However, when the front of the electrode vapor plume enters and passes the observation window, the plasma and electrode vapor spectra simultaneously appear, with developing radial structure. This can be seen by simply moving the time gate to increasing time at a fixed displacement of the observation window from the cathode. We feel these photographs illustrate with singular clarity the fact that the radial structure of the electrode and plasma lines depends upon the movement of electrode vapor through the gap and its subsequent interaction with the spark channel. Figure 11 may be considered a picture of an excitation process in action.

The spatial structure of electrode vapor lines will follow other processes in conjunction with its movement away from the cathode. Level cascading, recombination, collisions of the second kind, and combinations of these processes will be unique for different energy levels within a stage of ionization, and for different stages of ionization. However, most of the processes may be classed as "relaxation phenomena" whereby the lower energy species follow the higher (see Fig. 9). Since the electrode vapor velocity is thermal (see Fig. 15 of Ref *10*) and relatively slow, the relaxation processes will combine with the movement to produce shells or layers of unique spectral composition about the central spark axis. It is the presence

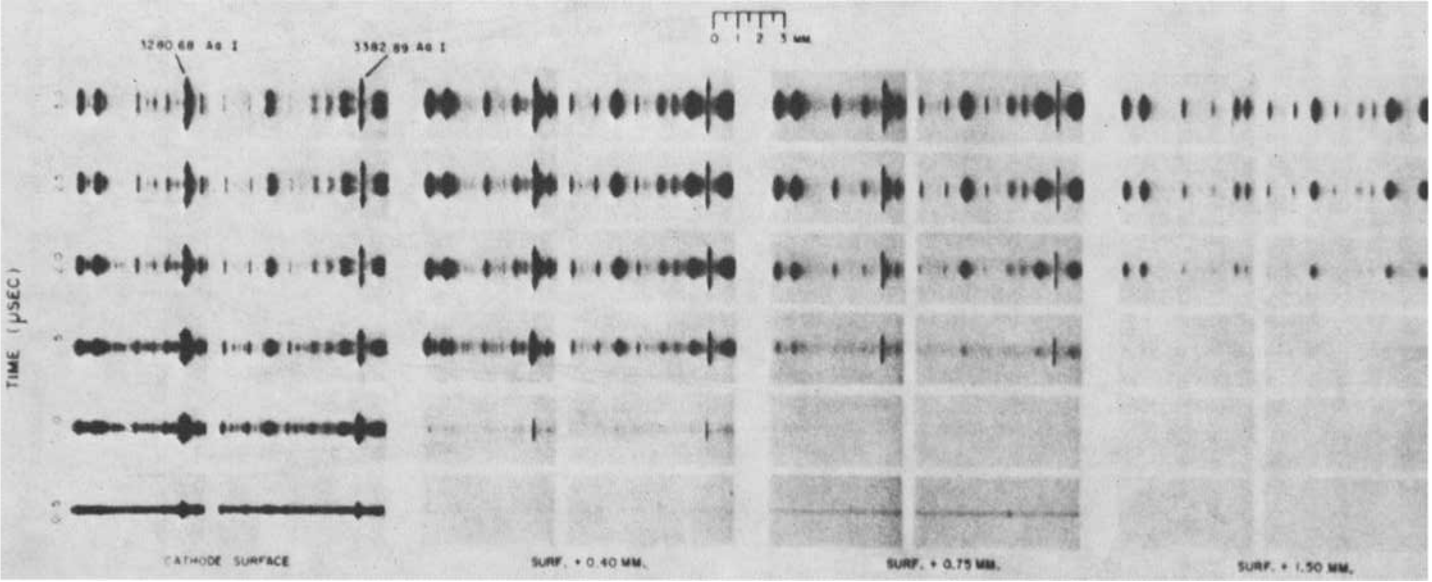


FIG. 11—*Fully-resolved spectra to illustrate formation of differing line structures. Silver disc sparked in argon. Electrodes as in Fig. 2. Current waveform as in Fig. 8. Spark source described in Ref* 9. *Central spark axis follows the horizontal centerline of the spectra.*

and stability of these shells that ultimately answers the "what to sample" question for spectrochemical purposes. While complete generalization may be premature, some operating concepts may be introduced with reference to copper sparked in argon as a specific example.

Figure 12 shows line densities (2-log percent T) for key lines in the copper spectrum. The data have not been radially inverted [*19*], so they represent what would be detected at the focal plane of a direct reading spectrometer in a spatially isolated experiment. Reference to Fig. 10 will

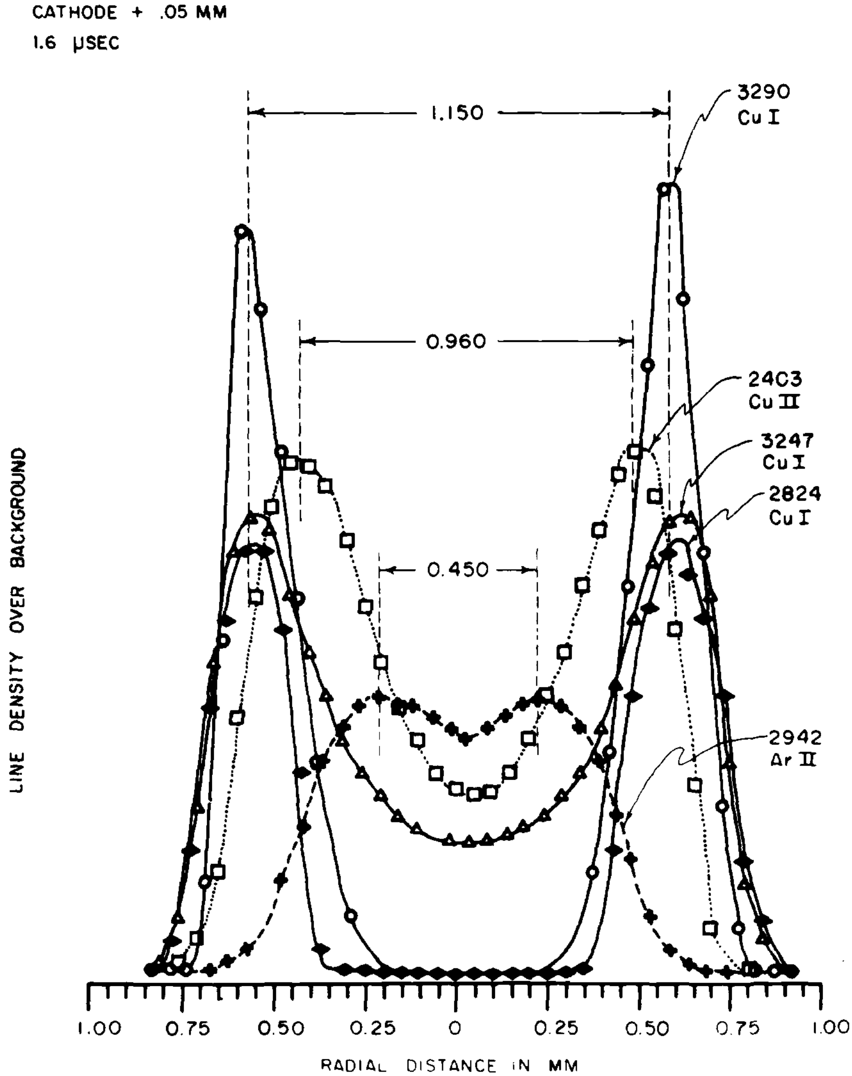


FIG. 12—*Line profiles for characterization of radial structure of the spark.*

provide perspective on the original form of the spectrogram. It has been our experience that the argon lines are most tightly contracted about the discharge core, with the innermost lines coming from the highest stages of ionization (Ar III < Ar II < Ar I in radial excursion for any fixed value of the current and cathode displacement). Typically, this is true for the background also, the central core of the discharge showing the highest background intensity with the wings being less cluttered. Some obvious exceptions to this are shown in inset 1 of Fig. 10.

The radial structure of the electrode vapor lines is markedly dependent on the time and current, the latter being a secondary interaction effect. In Fig. 12, the more highly ionized the electrode species, the closer to the discharge channel their intensity maxima. In the case of the neutral lines, it generally follows that the higher above the ground state their upper levels, the closer to the central axis their maxima. However, the autoionizing levels in neutral copper as well as aluminum [*19*] may deviate from this rule depending on when they are observed in the discharge lifetime. Further, as has been indicated for the silver resonance lines in Fig. 10, multiple maxima may exist, one peak being in the channel proper and the other in the far wings of the discharge. However, with increasing time, the lower energy neutral lines will move farther into the wings, and spatial shells favoring the lowest energy transitions will form away from the background rich channel.

Practical Application

As mentioned in the beginning of the paper, practical application of spatial discrimination implies a positionally-stable discharge. The apparatus shown in Fig. 2, coupled with a spark source capable of generating a pulsed-unidirectional current waveform, will produce sufficient stability to allow detection of fully resolved spectra. However, applications will arise in which a disk electrode is not the most convenient sample form. We have explored other sample geometries and found various degrees of stability, some that are undesirable for basic research but none that are unacceptable for realizing practical improvements over present, totally-integrated methodology.

For example, Fig. 13 shows time-swept images of radial slices of the discharge at four distances from the cathode surface for four different electrode geometries. The electrodes are all copper, with one covered with a ceramic cap to restrict the electrode area the discharge can strike. Comparison of the time-swept images verifies that the rotating beveled disk provides the highest stability, as evidenced by the crispness of the bright sampling spot at the immediate cathode surface. However, good stability also is observed from a pointed stationary electrode, and the wander associated with capped and flat electrodes typically is not more than two to three times the diameter of the cathode spot (about 0.10 mm).

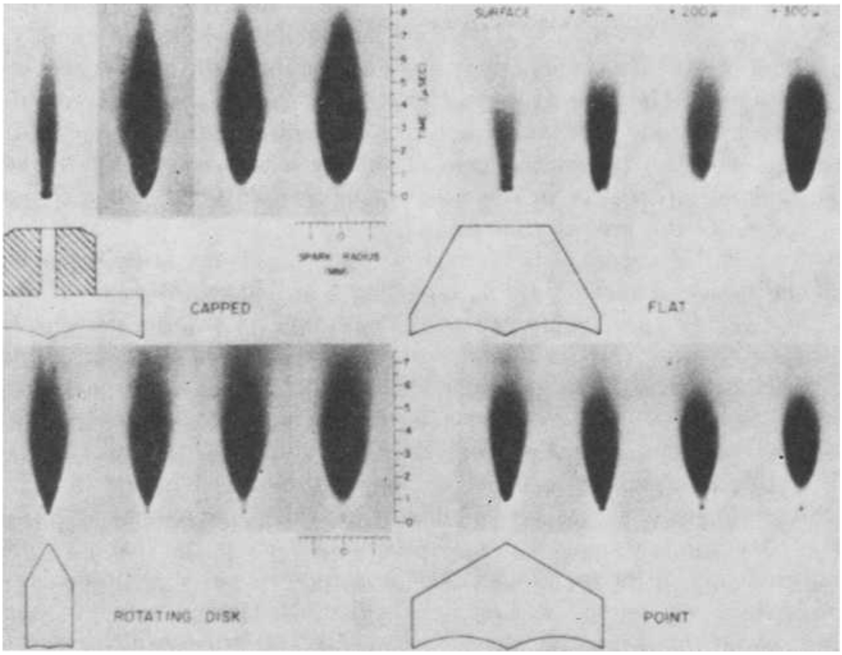


FIG. 13—*Time-swept images of a 0.05 mm window placed perpendicular to central spark axis for electrode geometries indicated. Copper electrodes sparked in argon. Current waveform as in Fig.* 8.

The spectral consequences of a lack of stability such as shown in Fig. 13 are indicated in Fig. 14. Here, a progressive change from a sharply pointed disk through a flat disk, and capped pin was made (all copper), and fully resolved spectra were then recorded at four times and two distances from the electrode surface. Appropriate lines are indicated by small arrows. These spectra are different, but more in degree than in kind. One of the more pronounced differences is that for some electrode geometries, the lines are radially unsymmetrical (skewed). In these cases, a blocking approach for spatial discrimination would provide better reproducibility than passing a selected region. In the same vein, whatever electrode geometry is chosen should be standardized, and surface roughness held to some repeatable value. However, for all the various shapes, the general trends established in Fig. 12 are preserved.

The different spectra associated with different electrode geometries arise from a perfectly logical cause that forms the final working requirement for a spatially discriminated experiment. When the surface of an electrode becomes badly pitted, or when ridges are present, the cathode vapor cloud cannot expand uniformly about the spark channel, and the wings of the discharge do not develop fully. The many small thermal explosions com-

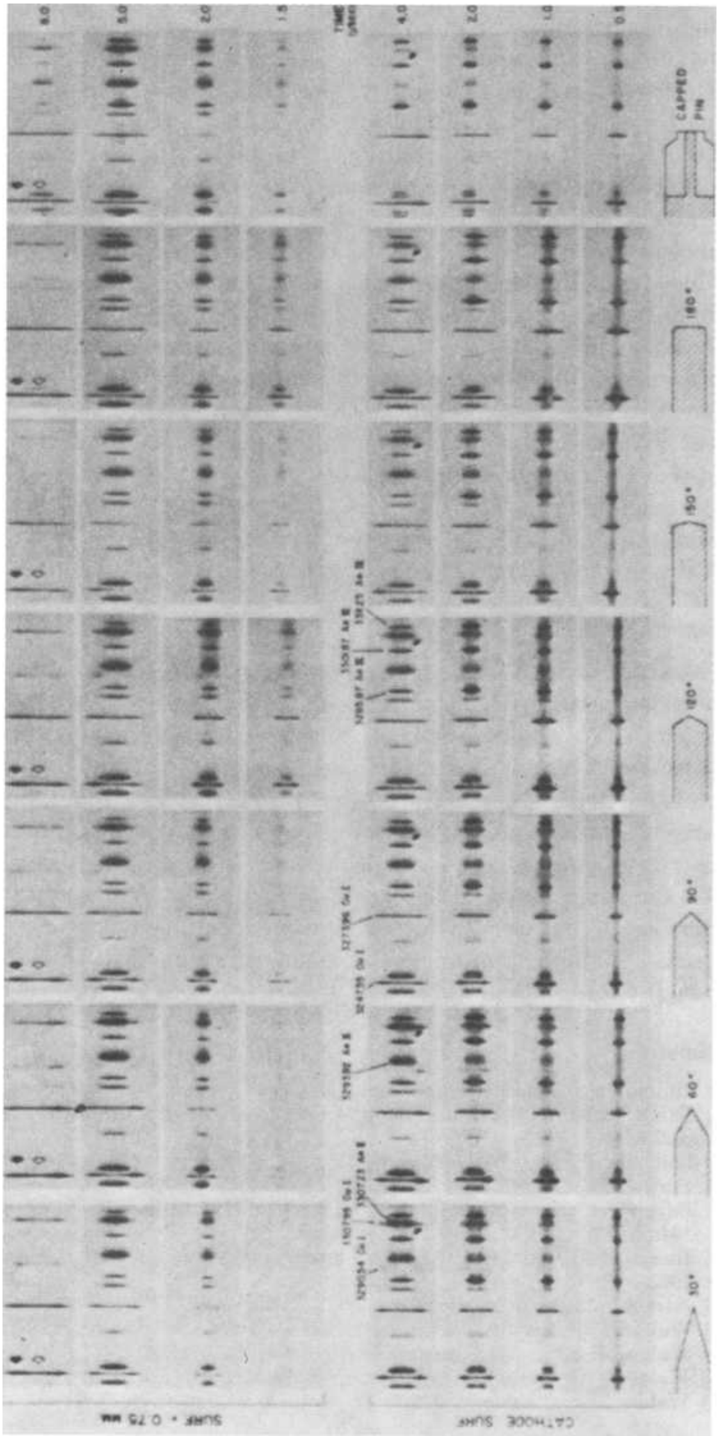


FIG. 14—*Fully resolved spectra for copper electrodes of various geometries sparked in argon.*

prising the expanding vapor envelope are partially occluded at the electrode surface proper, and while the channel regions receive, and interact with, the electrode vapor, its overall trajectory is constrained, favoring more the pathways along the interelectrode axis than those radially outward into the wings. One ready solution is to rotate the electrode at a rate such that its surface does not become badly pitted, an expedient that not only allows full development of the discharge wings with consequent enhancement of the neutral electrode spectrum, but also assures that the stability of the discharge does not lead to a nonrepresentative analysis of the bulk sample electrode.

The ideas introduced in this paper are being tested in our laboratory with a series of blocking experiments on aluminum alloys. The project is sufficiently extensive to preclude inclusion here. The point we wish to make is that with a stabilized discharge, the "what to view" question can be discussed for individual lines, classes of spectra, or types of radiation (for example, background) at length. We hope that such discussion will become an ASTM activity, since neither the potential of nor the problems with the spark discharge have been exhausted.

Acknowledgments

The authors would like to acknowledge Russell Riley, Robert Lang, Robert Schmelzer, and Kenneth Spielman for their extensive contributions in apparatus fabrication. The assistance of Jimmy Hosch in obtaining the data for Fig. 1 is appreciated. Financial support from the National Science Foundation under Grants GP-5073, GP-7796, and GP-13975, the Wisconsin Alumni Research Foundation, the American Oil Corporation, the Ethyl Corporation, and the Graduate School and College of Letters and Science of the University is appreciated.

Portions of the work reported here were completed by Mr. Goldstein in partial fulfillment of the requirements for the Doctor of Philosophy degree in Chemistry.

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W. R. Kennedy[1]

Problems in Manufacture of National Bureau of Standards Cast Metal Standard Reference Materials

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REFERENCE: Kennedy, W. R., **"Problems in Manufacture of National Bureau of Standards Cast Metal Standard Reference Materials,"** *Sampling, Standards and Homogeneity, ASTM STP 540*, American Society for Testing and Materials, 1973, pp. 72–87.

ABSTRACT: A description is given of problems arising during manufacture of standard reference material castings for the National Bureau of Standards. Cast iron, steel, blast furnace compositions, ductile iron, and high temperature alloys are discussed. Techniques to effect sound structure and integrity in the end-product are given.

KEY WORDS: sampling, standards, quality control, cast iron, manufacturing

In April of 1965, a contract with National Bureau of Standards to produce ductile cast iron standard reference materials (SRM) was started, which eventually also evolved into a complex project involving cast steels, blast furnace irons, high temperature alloys, and combination production of solid cast samples and cylinders to produce chemical chips. As each of these projects presented compositional as well as operational problems, it is the purpose of this paper to describe some of these problems and the way we attempted to solve them to assure integrity in the product.

The Ductile Irons

(*SRM 1140, 1141 and 1142*)

The foremost industrial process for production of ductile iron is by inoculation of a suitable base metal composition with a magnesium-containing product to promote nodularization. Two other feasible inoculants, but too expensive for commercial consideration, are rare earths (chiefly cerium)

[1] Spectroscopist, American Cast Iron Pipe Co., Birmingham, Ala. 35202.

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and yttrium. Moreover, when ductile iron is produced with magnesium addition, rare earth additions are commonly used as scavengers in lesser amounts to counteract the detrimental effects of some tramp elements which are normally present.

Three chill cast compositions for ductile iron compositions were planned which would give us a white structure by casting on the National Bureau of Standards' water cooled copper block.[2] In addition, the compositions were such that if these materials were to have been slow-cooled or annealed from the chill-cast state, they would retain their ductile structure. In other words, any of the three would represent truly ductile iron structure by balancing the three separate inoculant compositions, one chiefly cerium ductile, one chiefly magnesium ductile, and one chiefly yttrium ductile. Among the three compositions, aim values were set to produce a range for calibration of each of the elements.

This was not a unilateral decision. A committee was formed from members of the Ductile Iron Society and consisted of Ford Motor Company, International Nickel Company, U.S. Pipe and Foundry Company, and American Cast Iron Pipe Company. Together we determined the initial aim compositions for all the elements shown in Table 1. As a committee we also agreed to supply the necessary analytical data to help characterize

TABLE 1—*Proposed ductile SRM compositions—April 1966* (*weight percent*).

	SRM 1	SRM 2	SRM 3
C	2.8	3.2	3.4
S	0.02	0.008	0.005
P	0.008	0.06	0.16
Si	1.5	2.0	3.4
Mn	0.7	0.5	0.15
Cr	0.01	0.15	0.05
Mo	0.01	0.05	0.02
Ni	1.5	0.5	0.05
Cu	0.03	0.1	1.0
V, Ti	0.03	0.01	0.005
Sn	0.005	0.12	0.02
Pb	0.006	0.001	0.003
Al	0.005	0.01	0.08
As	0.08	0.02	0.005
B	0.01	0.05	0.005
Ce	0.005	0.12	0.02
Mg	0.02	0.05	0.15
Y	0.25	0.06	0.01

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[2] Michaelis, R. E. and Wyman, L. L., preparation of National Bureau of Standards White Cast Iron Spectrochemical Standards, National Bureau of Standards Miscellaneous Publication 260-1 (1964).

the material for certification after it was processed by the National Bureau of Standards.

The National Bureau of Standards supplied the necessary documentation on their water-cooled copper mold[2] as well as a movie produced by the Naval Research Foundry[3] showing the preparation of SRMs 1174 and 1175. A select crew was chosen in our special products division and National Bureau of Standards personnel came to assist with the first casts by showing techniques and methods of assembly of cores, basin, and ceramic stoppers on the copper mold.

Our first cast, we shall call a dry run, was really a comedy of errors and not unexpected in many new endeavors. The first cores used were supplied by the National Bureau of Standards, had been in storage several years, and were what our crew called "rotten." Not only did cores break, but stoppers broke, our iron was cold, we had the wrong composition, wrong weight, and wrong timing—just about everything was wrong! While we didn't know it at the time, we were to have a year of experience before it

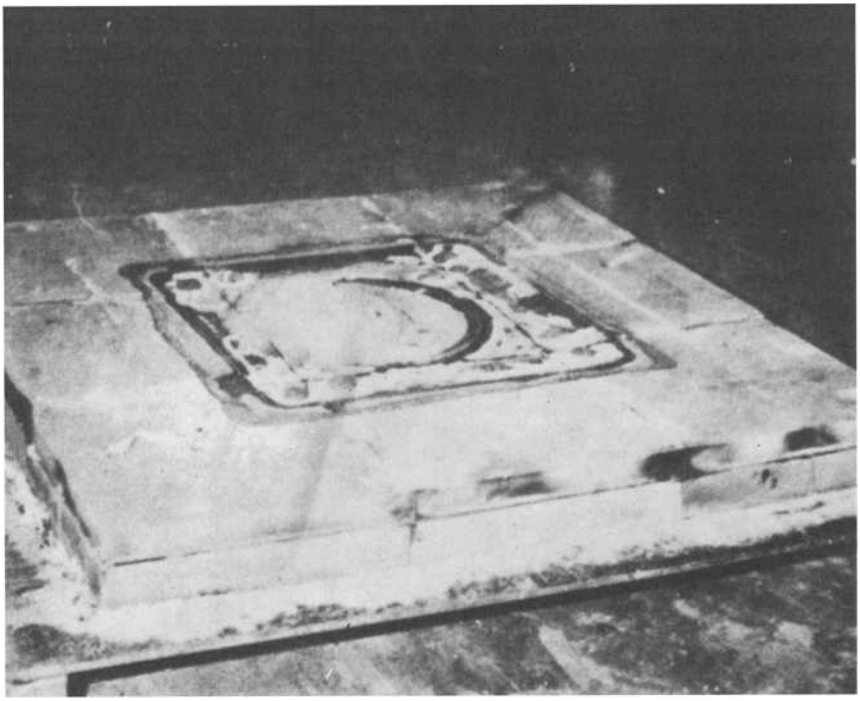

FIG. 1—*Core integrity maintained after casting 576 samples.*

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[3] Naval Research Laboratory film, preparation of White Cast Iron Standards, 16 mm color, sound, 15½ min (1965). Available from National Bureau of Standards.

FIG. 2—*Complete 64 sample block showing shrinkage tendency at extreme ends.*

was over. The program was begun in April 1965 and casting began in May 1966 and was completed in June 1967.

We ultimately developed a sand mix to form strong cores which would retain their shape throughout the cast. Figure 1 shows one of our later casts after removal of the pouring basin, just after it had been slid off the copper mold. Core integrity is evident when compared to our first ones where cores cracked and disintegrated from the heat causing loss of metal and consequent loss in sample recovery.

Our initial operations were based on 350 lb of metal per cast, but early in the program we noticed some shrinkage in iron samples formed at the end of runners farthest from where metal entered the core. Figure 2 shows an entire block of samples still intact except where samples fell off at these extreme ends. Figure 3 shows a rough diagram of the same block with samples taken from five places within the block. Figure 4 shows the runner side of another block which we modified to permit faster iron-running. Figure 5 is a rough diagram of this layout showing typical sample fractures.

This was an improvement, but the modification did not entirely eliminate the shrinkage. The early patterns from National Bureau of Standards had a triangular shaped runner which is more easily seen in Fig. 6. We ultimately changed the runner to a rectangular cross section and widened it also. Figure 7 shows a casting, rejected, in which a comparison can be seen between the two runner systems. Had this heat been hot enough, we would have obtained 100 percent sample recovery; however, it can be seen that the wider runner system has significantly more useful samples than the narrow runner system. Any modifications to the cores call for an increase in the volume of metal needed to fill the cavities. Since the tundish[2] was always almost empty at the end of the cast, we felt that 500 lb heats would give a better hydrostatic head than those with 350 lb and we went to this weight rather early. Shrinkage of metal is a problem which plagued us with steel and will be discussed later.

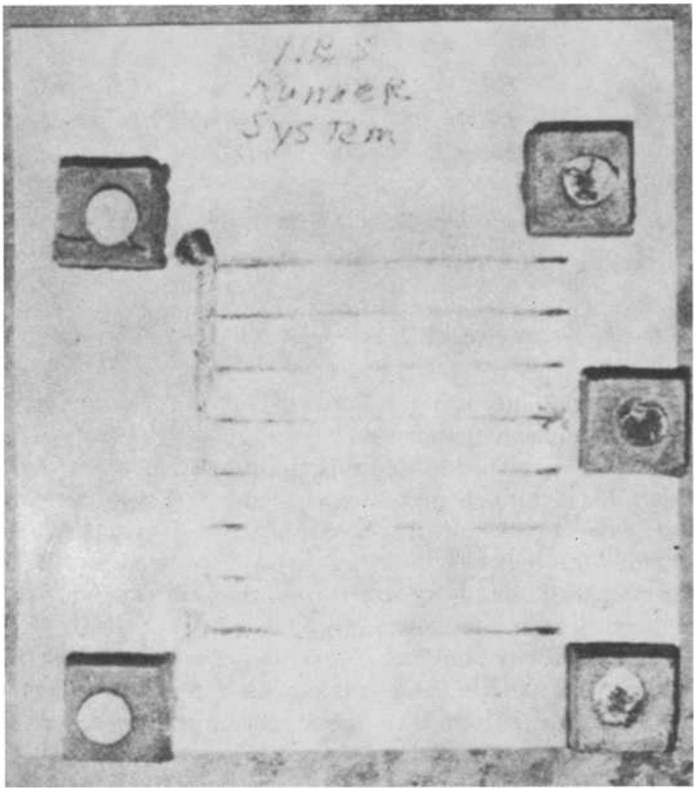

FIG. 3—*Sketch of NBS Runner System with typical samples from various locations.*

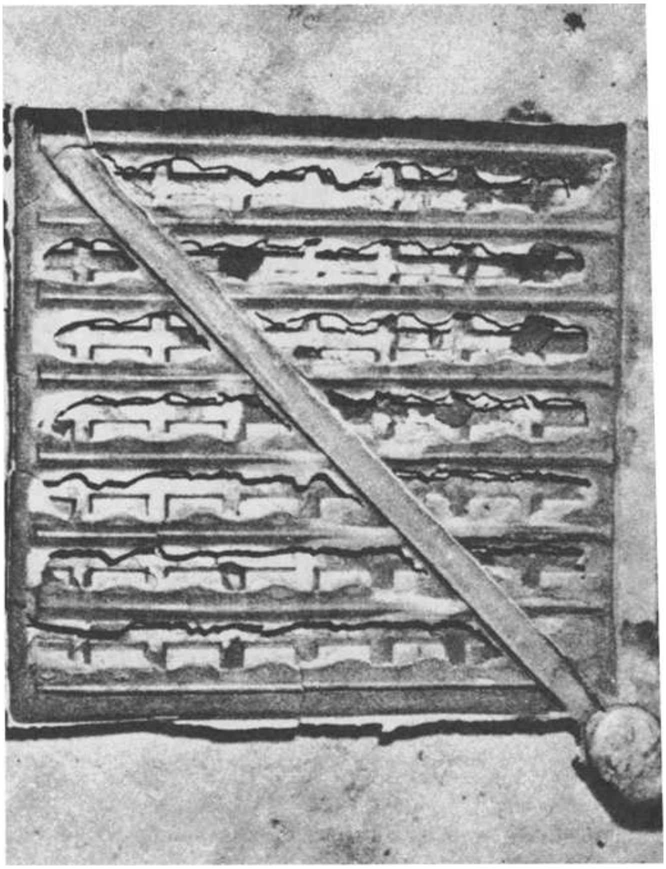

FIG. 4—*Upper side of casting modified to permit faster core fill.*

It was disheartening to ship apparently good castings to the National Bureau of Standards only to learn that the first compositions, high in yttrium, were so segregated that they were unusable as standards. We obtained additional yttrium, remade the heats in duplicate, and later learned that these, too, were unacceptable. Evidently, we know little about making the yttrium addition without encountering inclusions from its oxide.

With the help of the Ductile Iron Society committee, we decided to go without the yttrium and Table 2 shows the outcome with respect to the ductile forming elements. SRM 1140 is basically a cerium ductile, SRM 1142 is basically a magnesium ductile, while SRM 1141 is essentially a combination ductile of all three ductile forming elements (magnesium, yttrium, and cerium). Ultimately, we cast eleven ductile iron heats before we had six good ones.

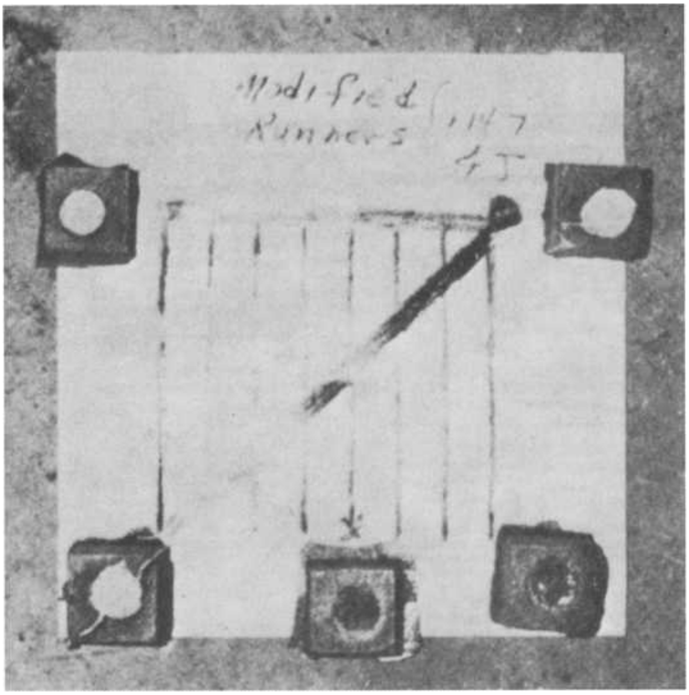

FIG. 5—*Sketch of modified casting with samples from various locations.*

Samples received at the National Bureau of Standards were cleaned, processed, and given a stress relief. Representative samples were selected, ground down to certified thickness, notched and returned to the American Cast Iron Pipe Company. Figure 8 shows a notched sample about to be

TABLE 2—*NBS ductile irons, ductile forming elements, aim and final composition—April 1966 (weight percent).*

	Standard			
	1	2	3	1[a]
Mg Aim	0.02	0.05	0.15	0.02
Final	0.02	0.044	0.10	0.019
Ce Aim	0.005	0.12	0.02	0.12
Final	0.002	(0.05)	(0.015)	(0.09)
Y Aim	0.25	0.06	0.01	0.00
Final	0.20	0.04	0.01	<0.002
NBS SRM	[b]	1141	1142	1140

[a] Revised October 1966.

[b] Four heats made and discarded due to yttrium inclusions.

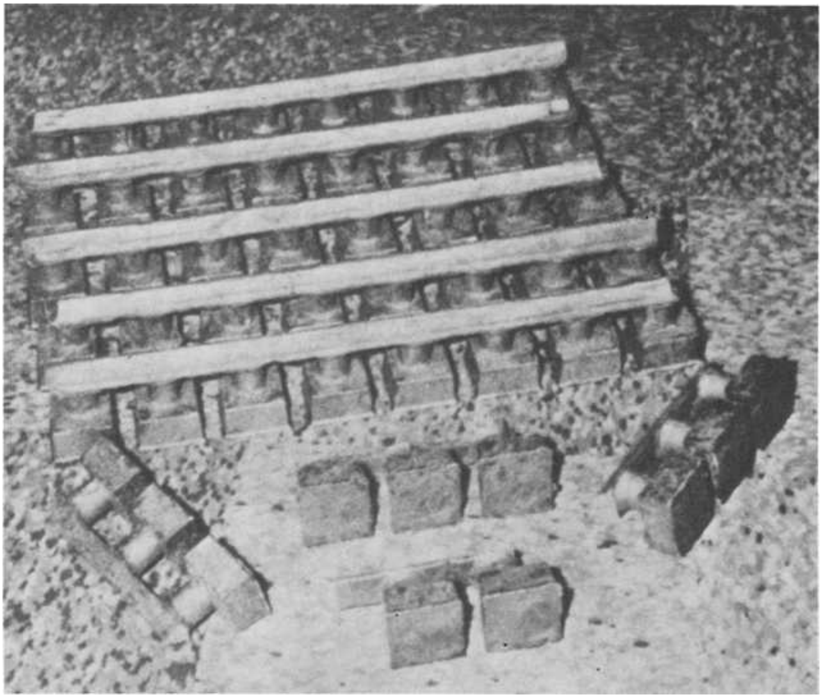

FIG. 6—*Casting showing runners, ingates and samples.*

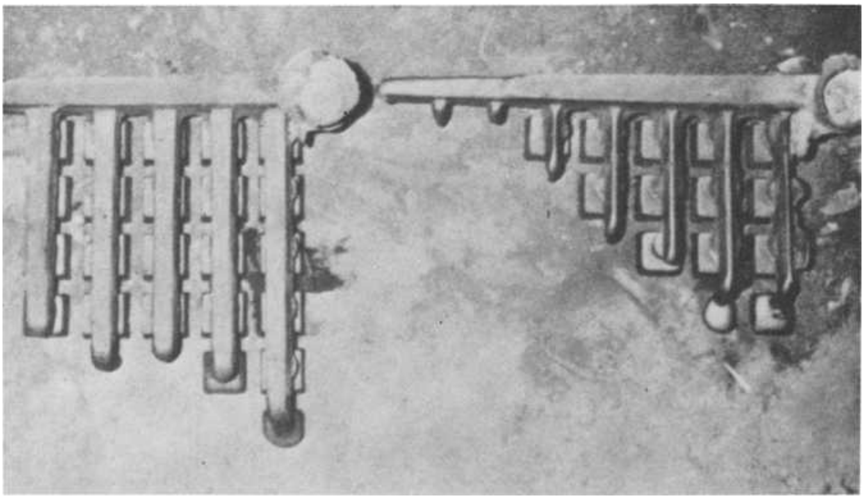

FIG. 7—*Castings from 342a comparing yield from modified runner to old runner system.*

dropped into a tool steel mortar for crushing with a pneumatically driven hammer. Crushing all the samples to pass a 20 mesh sieve without contamination took several weeks because it was done when routine work would not interfere. After completely crushing each lot, it was bottled and returned to the National Bureau of Standards as shown in Fig. 9. This material was allocated to chemists for obtaining analytical data.

Because of a mix-up in signals, the Ductile Iron Society committee did not participate in the ductile iron analytical program as planned. There was much disappointment, and frustration of one of the cooperators brought the statement, "And we have been practicing for this opportunity for forty years." Nevertheless, where the committee was denied participation in this aspect of the ductile irons, it was called on to do the analytical work on SRM 1143, 1144, 1147, 1148, and 1149 which had chemical chip

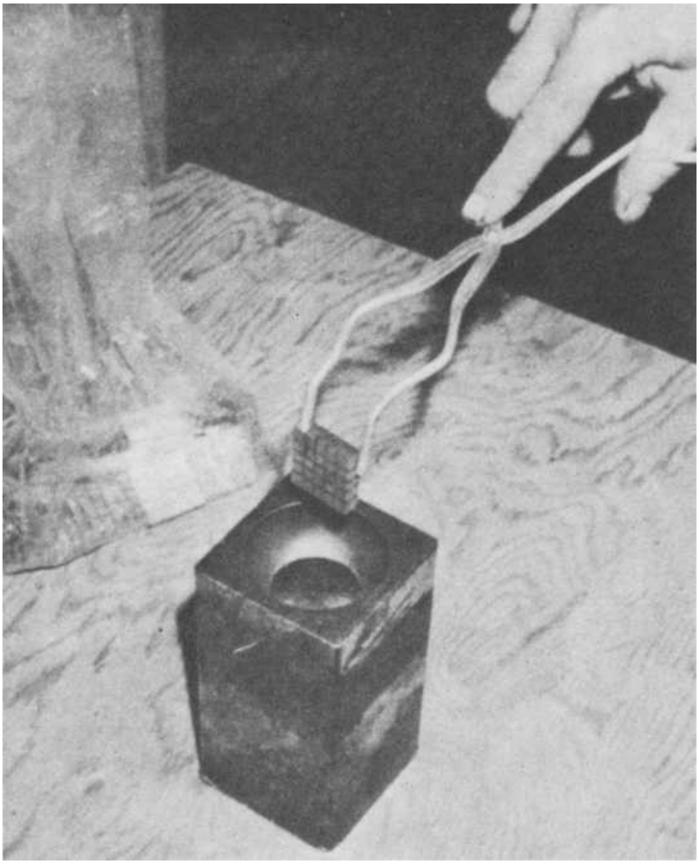

FIG. 8—*Notched sample prior to crushing.*

FIG. 9—*Crushed and bottled samples as returned to National Bureau of Standards.*

counterparts. The time from the receipt of the crushed samples to provisional certificate was approximately four months, including homogeneity testing at General Motors. The National Bureau of Standards' records show these were the first metal standards to proceed to provisional certificate without any National Bureau of Standards' results and in record time. I found the analytical aspect in production of these standards to be the most rewarding and the least fraught with problems, contrary to others' past experience. The reason for this has to be the high caliber of the chemists who performed the work.

The Blast Furnace Irons

SRM 1143 and 1144

The physical and chemical requirements for the blast furnace irons were stringent: carbon at 4 to 4.6 percent, all with a carbon equivalent at about 4.8 percent. The irons were requested to be all white with no greater than 0.01 percent free graphite. Such graphite-free material had never been produced before. As it occurs in the basic oxygen furnace or holding ladle, blast furnace iron temperature is usually around 2600° F, at which temperature it can hold only about 4.1 percent carbon. Being saturated with carbon, excess free graphite forms on the surface what is known as "kish." This defies any attempt at sampling to obtain a graphite-free sample. We tried a composition of high carbon and low silicon, adding tellurium to the heat when tapping. This was unsuccessful and the heat was rejected. An interesting thing about this heat was the way samples sparkled. Inspection showed glassy particles on the surface which resembled diamonds. We felt like all the necessary conditions for formation of diamonds were there; high temperature, pressure, and high carbon. For weeks our menu was steak for lunch and we told everyone we had made diamonds. We had almost convinced ourselves, until much later when we sent a sample to the General Electric artificial diamond experts who identified the material as alpha quartz. It would have been fun to inform National Bureau of Standards it had rejected a diamond-studded heat!

About this time, a seemingly inconsequential thing happened which caused the loss of many heats, some of which were not replaced including two duplicate blast furnace iron compositions. The supply of colloidal graphite, known as Aqua-Dag, ran out. This material, highly diluted with alcohol, was painted on the copper block and allowed to dry before cores were assembled on it. Its action was as an insulator and prevented the molten metal from fusing to the copper block. The reorder was not Aqua-Dag, but an oil-dag which would never completely dry on the block, but left a slightly greasy feel. In addition to the four blast furnace heats, two high temperature alloy heats were lost due to gas from this source. The gas holes were so small and were so far from the surface that they were not detected until much later in the processing at National Bureau of Standards; much too late to correct the fault. Figure 10 shows some of these regularly shaped gas holes in one of the blast furnace irons rejected.

After our failure to produce a blast furnace iron with white structure by pouring onto tellurium, we felt that if we got the metal hot enough to retain the carbon in solution, we could inoculate with tellurium in the furnace. Once the inoculation was effected, we could lower the temperature and pour with no fear of free-graphite formation because all the carbon would be tied up as carbide. Our first attempt at this was successful, and with only one plunge with tellurium. We rigged a ceramic cylinder onto an L-shaped pipe handle and retained tellurium pellets inside with glass rope. Small holes in the wall of the cylinder allowed the tellurium to escape into the metal and react. Witnessing a tellurium plunge is an unforgettable experience. After relative quiet for 2 s or so, the floor shakes, the furnace jumps, metal flies in all directions for about 15 s; then quiet! The first cast was beautiful: everything was white iron, even the small amount of metal left in the tundish. The metal was exceptionally brittle and fractures in the

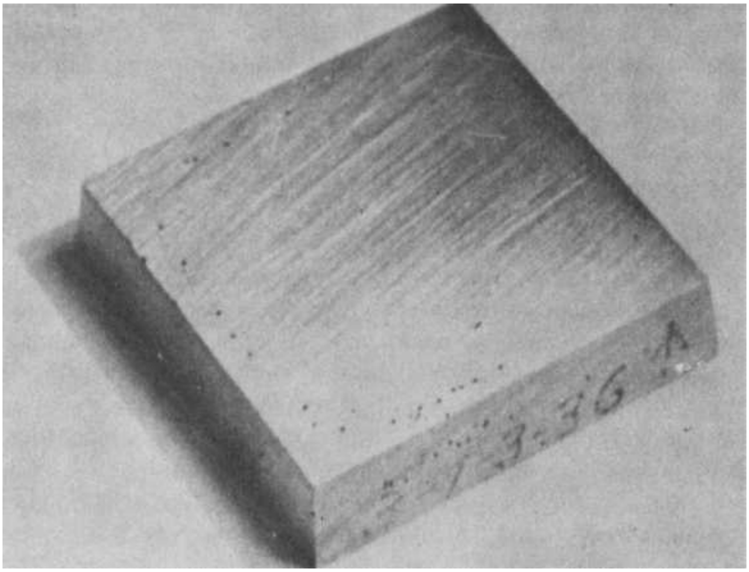

FIG. 10—*Gas holes in rejected blast furnace sample.*

sample ingates showed beautiful varicolored iron carbide (Fe_3C) crystal platelets, which metallurgists call spiking.

Our second attempt at the blast furnace iron was unsuccessful. Someone had redesigned the ceramic cylinder and the tellurium just didn't do the job. We cast the heat and everything was gray (one reason may have been that we had 5 percent carbon). The largest material cost in production of these heats is the cores and their assembly onto the copper block. As we could not afford to continue losing heats we took a two week break to perfect our practice on a small 50-lb induction furnace. During this period we tried various methods of introduction of tellurium, but ended up with the original design and plunging methods. We did bring a binocular microscope into play, though, which helped. After tellurium treatment, a chill cast sample was taken and broken in half. Viewing the fractured specimen under the microscope, if the tellurium had not been effective, the free graphite was visible and a second treatment was made, or a third if needed, until it was successful. During this two week period, we produced 50 lb lots of every composition required by the project, all free from graphite. We found that once the carbon was tied up by the inoculation, we could cast metal on the ground and it would be white—no copper block needed! We cast 4 by 8 by 4 in. keel blocks in sand which were white throughout and had a 60 HRC.

Back to the production floor, we were prepared with the binocular microscope and enough inoculant and cylinders to treat three times if necessary. Treating temperatures varied from 2800 to 2950° F and each tellurium addition amounted to 0.08 percent. The remaining compositions were completed with no further complications except we were not aware that some of our perfect casts were being ruined by the oil-dag.

The Cast Steels and High Temperature Alloys

SRM 1138, 1139, 1206-2, 1207-1, 1207-2, 1208-1, and 1208-2

From the shrinkage we had seen in the iron materials, we knew that the steels and high temperature alloys would be worse. Patterns were constructed to widen runners and ingates and to increase the volume and hydrostatic head of the tundish. Now we were up to 1000 lb heats and metal costs were higher. With the high temperature alloys, there was almost no way to eliminate shrinkage; but by doubling the sample thickness, shrinkage was made to form in the portion of the sample to be discarded. Figure 11 gives an idea of the scope of the problem. We tried many small heats of similar compositions in lots of 64 samples at a time before we finally settled on the double-thickness sample approach.

It is sad, too, that some of these heats were ruined by the oil-dag. One Wasaploy was ruined by a practice which, until then, had been considered innocent. The Waspaloy molten material is almost indescribable. It sticks to everything like glue. About one fifth of the heat never comes out of the furnace when it is tapped. Another fifth sticks to the transfer ladle and another fifth remains in the tundish when the stoppers are pulled. Almost

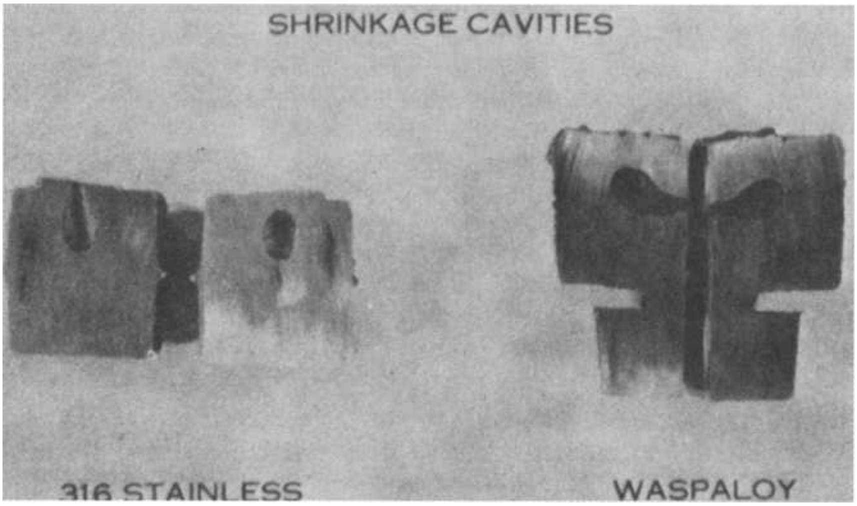

FIG. 11—*Shrinkage cavities in high temperature alloys confined to unused portion of samples.*

twice the amount needed has to be melted. After one of our Waspaloy heats, the furnace needed to be chipped out and patched for the next day. Immediately after we tapped, the furnace helper filled the furnace with water to cool it. The Waspaloy duplicate made the next day in the same furnace was scrapped due to hydrogen gas porosity.

The Combination Chemical Spectrographic SRMs

SRM 1147-4J, 1148-5L, and 1149-6G

Ever since the early 1920s, the American Cast Iron Pipe Company has provided cast iron cylinders to the National Bureau of Standards specification. From these cylinders chemical chip SRMs are produced by machining. It was our idea that it would be nice, with access to the copper mold, to produce chemical and spectrographic solids from the same metal. A laboratory having access to both forms of the same metal can stave off many disagreements between chemist and spectrochemist.

While our crew now had experience with casting the solid samples, the cylinder casts were rather new to them and six cylinders were required where we had provided only two in the past. These heats were prepared in an electric furnace whereas our previous donations to the National Bureau of Standards had been regular cupola iron. Metal was prepared in 5000 lb lots and tapped at 2700° F into a teapot ladle. Seven hundred pounds of this were removed to pour the spectrometer solid samples while the remainder was poured into an open ladle and allowed to cool to about 2450° F before pouring the cylinders. On our first cast, we got the spectrometric solids, but poured directly from the teapot ladle into the cylinder molds. The metal which had to be hot for the solids cast was much too hot for the sand rammed cylinder molds. As a result all cylinders were rejected because of a condition of burn-in where sand fuses deeply into the metal surface. The heat, including metal for the solids, was remade later.

In qualification of the cylinders for composition, we poured ten chill-cast specimens before and ten after casting the cylinders. We made four direct reader analyses on each of the ten before and after specimens. Subjecting the means of before and after results to Student's "t" test for each element gave some idea of the homogeniety of the metal at the beginning and end of the pour. The larger the "t" value, the more probable that there was a significant difference for these elements. Table 3 shows typical data on another chemical cylinder we provided earlier for SRM 82B. The tabulated critical "t" for this set of data is about 2.50, so it can be seen that there are no significant differences in the elements shown. In all the tests we made, there were a few elements like titanium and manganese for which the "t" value exceeded the critical "t," but in no case were these metallurgically significant. Note how well our before and after means of May 1965 agreed with the National Bureau of Standards certification of April 1966. We re-

TABLE 3—*Typical direct reader assurance test for metal before and after casting NBS cylinders, 11 May 1966.*

	Si	Mn	Cr	Ni	Cu	V	Ti	P
Average before—4 sparkings on each of 9 samples								
Percent	2.024	0.740	0.332	1.200	0.0366	0.023	0.0244	0.0204
1 Sigma	0.0203	0.0081	0.005	0.0086	0.001	0.0006	0.0005	0.00154
C.V.	1.00	1.09	1.51	0.72	3.27	2.61	2.05	7.55
Average after—4 sparkings on each of 10 samples								
Percent	2.020	0.738	0.330	1.202	0.031	0.023	0.0242	0.0202
1 Sigma	0.0411	0.0068	0.0042	0.0098	0.0008	0.0006	0.00045	0.00153
C.V.	2.03	0.92	1.27	0.82	2.58	2.61	1.86	7.57
Student's "t" on before and after means								
	0.27	0.55	0.79	0.50	0.98	0	1.05	0.40
NBS Certification—82B, April 1966								
Percent	2.10	0.745	0.333	1.22	0.038	0.027	0.027	0.025

gret that in making SRM 342a the cast was tapped too cold to pour the spectrometrics completely (see Fig. 7), but the cylinders were acceptable.

Conclusion

I feel that inherently, photoelectric spectrometers will obtain better repeatability on rolled steels because in working the metal, the grain size is reduced and inclusions are broken up and dispersed. With cast iron, what you see is what you get and many elements will not approach the instrument repeatability achievable with more homogenious samples. However, I feel these cast iron SRMs meet a real need in the industry.

Considering that some of the casts had never been done before, I believe the American Cast Iron Pipe Company provided the National Bureau of Standards with integrity in these SRMs. This publication provided an excellent place to explain some of the problems encountered and certainly, I have gained an appreciation of the sampling problem as viewed by the National Bureau of Standards.

Acknowledgments

I would like to acknowledge the aid and assistance of National Bureau of Standards personnel R. E. Michaelis and the late Clarence Gifford; S. F. Carter of American Cast Iron Pipe Company, under whose direction the project was completed, and the following from the Ductile Iron Society who formed our committee: C. M. Davis and C. H. Allbright of International Nickel Company, F. R. Bryan of Ford Motor Company, Charles Gaskill of United States Pipe and Foundry Company, and R. N. Smith of American Cast Iron Pipe Company.

J. C. Cline[1]

Problems in Sampling Ferroalloys with Emphasis on Ferrosilicon

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REFERENCE: J. C. Cline, **"Problems in Sampling Ferroalloys with Emphasis on Ferrosilicon,"** *Sampling, Standards and Homogeneity, ASTM STP 540*, American Society for Testing and Materials, 1973, pp. 88–95.

ABSTRACT: This discussion is limited to the problems involved in obtaining a representative sample for chemical analysis of silicon alloys and L. C. Fe Cr alloys. The problems of segregation of elements within a product are discussed and comparative analysis as taken at the furnace, shipment preparation, and spot checks after preparation are given. The problems of taking samples by the customer and the related problem of processing them is also covered.

Results of segregation studies and the significance of the lack of homogeneity within a given heat and also within a lot or composite of several heats are discussed. Supporting data shows that a proper sample can only be taken at one phase in the production—customer usage process.

KEY WORDS: sampling, ferroalloys, ferrosilicon, castings, segregation inhomogeneity

While this paper covers sampling ferroalloys in general, predominant interest currently centers around problems of sampling ferrosilicon. For this reason it will be used as an example, and in order to appreciate the extent of the sampling problem of this material, it is helpful to review its manufacture.

Manufacturing Procedures for Ferroalloys

Most ferroalloys are produced in an open submerged arc furnace. Ferrosilicon is the product of the reduction of silicon dioxide or quartzite with steel scrap melted in such a furnace and tapped into a ladle. The melt is poured into a mold, in castings weighing approximately 4 to 10 tons, and taken to a cast rack for cooling. After cooling, it is broken into large lumps and stored in a bulk pile. Depending on the end use of the product, it is taken from the bulk pile, sized to various specifications as required, and

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[1] Chief chemist, Interlake Inc., Beverly, Ohio 45715.

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packaged for final shipment. Shipments may be in bulk, pallet boxes, steel drums, or in a customer's own containers. Many of the difficulties in sampling ferrosilicon, basically equal parts of iron and silicon, arise because of its manner of production and processing. Casting temperature and inherent nonhomogeneity are two contributing factors.

Metallurgical Structures of Ferrosilicon

Commercial ferrosilicon has segregation, the degree of which will vary depending upon its temperature when cast and the depth of the mold into which it is cast. An excellent presentation dealing with the metallurgical structures of ferrosilicon, including the segregation with regards to layer thickness, has been made by J. A. Dehuff et al of the Air Reduction Laboratories, Murray Hill, N.J.[2]

Figure 1 (a copy of Dehuff's Fig. 5) shows that as the thickness of the

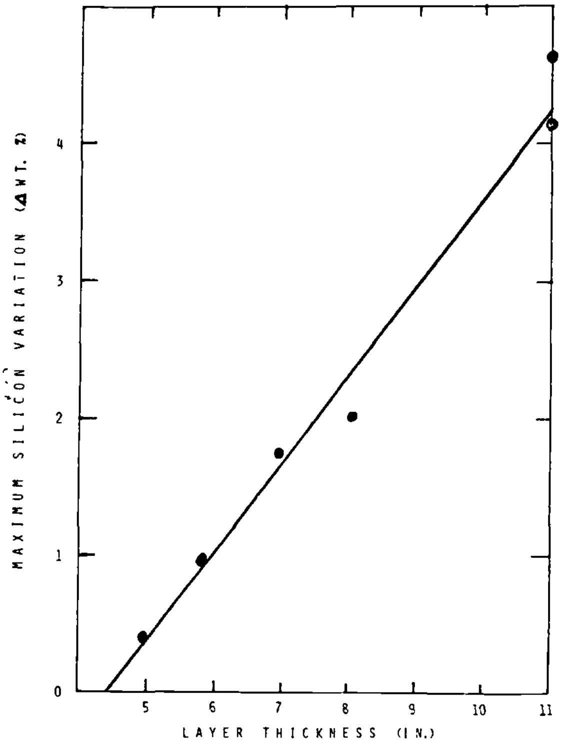

FIG. 1—*Influence of cast thickness on Silicon Segregation in Commercial 50 percent ferrosilicon (from Dehuff, et al).*

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[2] Dehuff, J. A., Coppolecchia, V. D., and Lesnewich, A. in *Proceedings*, The Electric Furnace, AIME, American Institute of Mining and Metallurgical Engineers, Vol. 27, 1969, p. 169.

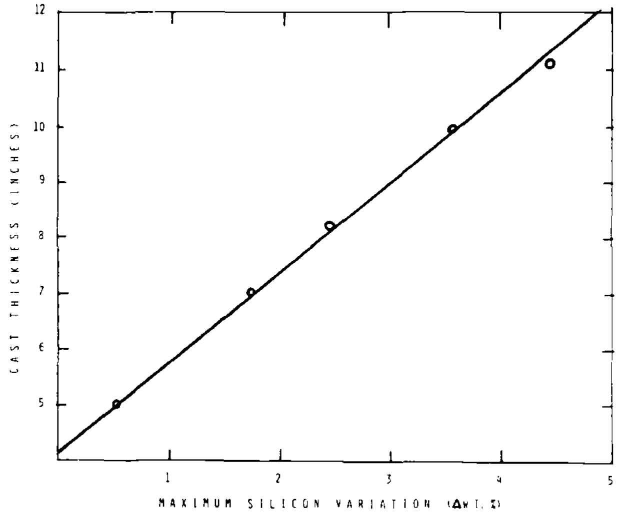

FIG. 2—*50 percent ferrosilicon. Effect of cast thickness on Silicon Segregation (Beverly Plant).*

cast increased the silicon variation increased. Note that at the 6-in. thickness cast, approximately 1 percent maximum silicon deviation occurs whereas at the 8-in. thickness there is approximately a 2½ percent deviation.

Figure 2 is a graph prepared independently at the Globe Metallurgical Laboratory of Interlake, and the data is remarkably similar. At the 8-in. thickness there is a 2½ percent deviation; at the 6-in. thickness there is a 1 percent deviation, and at the 11-in. thickness there is approximately 4½ percent silicon deviation. The greatest silicon deviation found within a cast occurs in a vertical direction.

TABLE 1—*Silicon segregation of an 8-in. casting of 50 percent ferrosilicon.*

	Percent Silicon				
Location	Edge	Between	Center	Average	Maximum Deviation
Top (2 in.)	50.00	49.20	49.40	49.53	0.80
Middle (4 in.)	49.50	49.60	49.40	49.50	0.20
Bottom (2 in.)	47.50	47.40	47.80	47.56	0.40
Average	49.00	48.73	48.87		
Maximum deviation	2.50	1.80	1.60		
Weighted average		48.87			
Cast crushed to 1 in. and sampled		48.75			

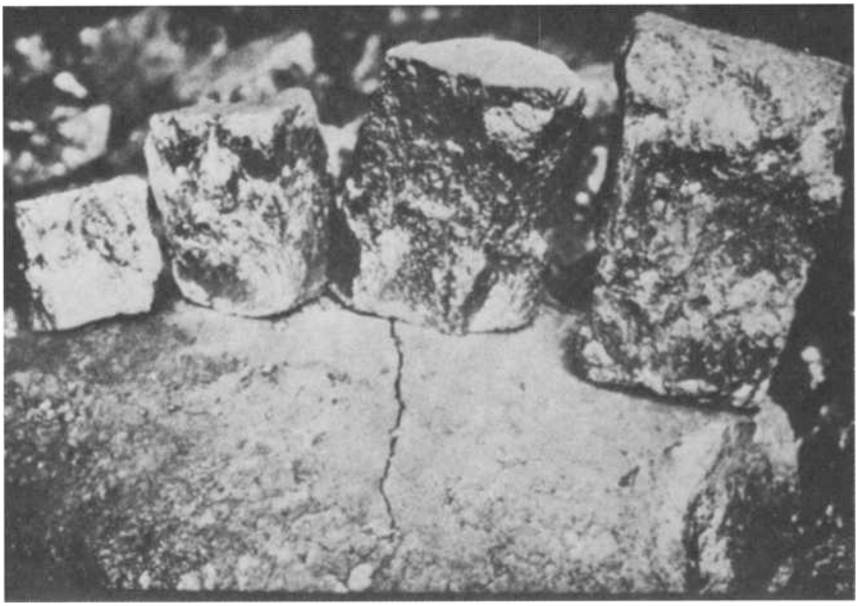

FIG. 3—*Cross sections from 4, 6, 8, and 11-in. thickness casts.*

Figure 3 shows a photograph of the cross sections broken from castings. These cross sections were taken from the castings away from the edge and toward the center. We have taken three of these cross sections from one casting, and have identified these as the outside edge, the between area, and the center area of the cross section.

Table 1 relates the data from this 8-in. casting. Note that the maximum deviation occurs at the edge of the cast, with 50 percent silicon at the top of the casting cross section and 47.5 percent silicon at the bottom. Moving inside, some segregation occurs from the inside to the outside (0.80 percent silicon maximum). However, there is more pronounced segregation from top to bottom, 2½ percent silicon, 1.8 percent silicon, and 1.6 percent silicon. The weighted average analysis is 48.87 percent silicon.

Sampling Procedure

Taking the entire casting, not just the cross section, crushing it 1 in. by down, and taking a representative sample, analysis of 48.75 percent silicon is obtained, which agrees with the previous weighted average. Results from one cross section from the vertical center of the casting shows 48.87 or 48.73 percent silicon in between. This leads us to believe that a cross section taken at the outside edge leads to high silicon results, and indeed, this has been our experience in taking samples at our Beverly Plant. The edge must be avoided because of the high silicon segregation which is not

TABLE 2—*Deviation between during-preparation sample and top-of-container after-preparation sample.*

	50 Percent ferrosilicon sampling study			
Size	Pounds Shipped	During Preparation	Across Top of Container	Deviation
75 lb by 4 in.	111 880	48.10	48.60	0.05
75 lb by 4 in.	36 000	48.70	48.10	0.60
7 in. by 4 in.	41 140	49.05	49.75	0.70
⅜ in. by 12 meter	30 710	48.15	48.20	0.05
5 in. by 3 in.	41 400	48.60	48.65	0.05
6 in. by 3 in.	123 780	47.80	48.40	0.60
4½ in. by 2 in.	109 400	48.35	48.20	0.15
75 lb by D	45 000	49.05	48.65	0.60
	Average	48.48	48.57	0.41

representative of the entire casting in question. Notice that the casting segregates with the iron going to the bottom of the cast, and the silicon rising to the top. Therefore, segregation is chiefly in a vertical direction and very little occurs horizontally. The segregation of individual castings from a heat is only one problem in taking a representative sample of ferrosilicon.

Another problem, mentioned earlier, is that these heats weigh from 8000 to 20 000 lb. A normal shipment lot of ferrosilicon, consisting of many individual castings, will weigh from 20 000 to 120 000 lb. On occasion, shipments have been made in excess of one million lb. At the Beverly Plant the standard practice for sampling these shipment lots is to take a representative sample *during* the final preparation of the shipment lot. A large drum of crushed material is taken for the sample.

Table 2 shows data of samples taken during a typical final preparation and also an equal amount of sample taken across the top of the container boxes, *after* the material was prepared. The sample taken during preparation analyzed 48.1 percent silicon. The sample taken across the top of the container analyzed 48.6 percent. This gives a deviation of 0.5 percent silicon. Deviations occur from +0.7 percent to −0.6 percent, with an average deviation of 0.41 percent silicon (without regard to sign). These are representative samples taken to the best of our ability, and represent typical results to be expected from good sampling of shipment lots.

Selection of the Sample

A recent sample from a 100 000 lb, 3 in. by ½ in. lot was prepared during final preparation and analyzed as 48.30 percent silicon. An additional sample, taken across the top of containers of this shipment analyzed

48.55 percent. Table 3 shows that the material used in preparing this shipment varied from 50 to 47.30 percent with an average casting analysis of 48.42 percent silicon. In studying this data, the question of segregation and the inhomogeneity of castings arose. From this shipment, which contained 24 pallet boxes, one small piece from each box, called "grab samples," was taken. These samples, which were approximately 1 in. in size, were analyzed individually. This represents the problem that can arise in trying to make an analysis based upon a small "grab sample." These small pieces varied in composition from 45.8 to 52.5 percent silicon, or a total range of 6.7 percent silicon. The average deviation is ±1.81 percent silicon. These pieces (although not valid data because they were small, biased samples) averaged 49.49 percent silicon, which exceeds 1 percent of the shipment lot analysis.

Samples taken in a similar fashion on a lot of 109 400 lb show similar

TABLE 3—*Percent silicon deviations within a 100 000 lb 3 in. by ½ in. lot.*

	Individual Heats		Small Pieces—(grab)	
	Casting Analysis	Deviation from Lot Analysis	Individual Pieces	Deviation from Lot Analysis
	48.90	+0.60	51.20	2.90
	47.40	−0.90	48.80	0.50
	48.60	+0.30	45.80	2.50
			50.90	2.60
	48.00	−0.30	50.30	2.00
	48.20	−0.10	46.70	1.60
	47.30	−1.00	50.80	2.50
	47.90	−0.40	48.30	0.00
	49.80	+1.50	46.20	2.10
			50.50	2.20
	49.10	+0.80	52.40	4.10
	48.30		48.60	0.30
	48.80	+0.50	46.90	1.40
	48.20	−0.10	50.90	2.60
	48.70	+0.40	49.40	1.10
	50.00	+1.70	48.90	0.60
			50.20	1.90
	48.00	−0.30	50.60	2.30
	47.80	−0.50	48.50	0.20
	48.20	−0.10	50.30	2.00
			48.60	0.30
			52.50	4.20
			50.60	2.30
			49.80	1.50
Average	48.42	0.59	49.49	1.81

Sampled during-preparation (lot) 48.30
Sampled across-top-of-containers 48.55

TABLE 4—*Percent silicon deviations within a 109 400 lb 4½ in. by 2 in. lot.*

	Individual Heats		Small Pieces—(grab)	
	Casting Analysis	Deviation from Lot Analysis	Individual Pieces	Deviation from Lot Analysis
	48.00	−0.35	48.20	0.15
	49.40	+1.05	51.60	3.25
	48.10	−0.25	46.50	1.85
	49.60	+1.25	50.00	1.65
	48.60	+0.25	48.30	0.05
	49.60	+1.25	49.20	0.85
	48.60	+0.25	47.00	1.35
	47.00	−0.75	48.50	0.15
	47.60	−1.35	47.60	0.75
	47.20	−1.15	46.80	1.55
	48.60	+0.25	49.20	0.85
	47.20	−1.15	50.10	1.75
	49.20	+0.85	47.20	1.15
	50.20	+1.85	46.00	2.35
	48.20	−0.15	49.60	1.25
	46.40	−1.95	47.50	0.85
	49.40	+1.05	48.60	0.25
Average	48.41	0.89	48.35	1.18

Sampled during-preparation (lot) 48.35
Sampled across-top-of-containers 48.20

data (see Table 4), with less bias. This time random, small pieces were taken, trying not to limit sample size to the 1-in. size. Range within this shipment lot goes from 49.6 to 46.4 percent silicon, with an average deviation of 0.89 percent. The data on the left are of the castings that went into making up this shipment lot. The individual "grab" pieces here range from 46 to 51.6 percent silicon with a maximum range of 5.6 percent silicon, and an average deviation of 1.18 percent silicon. It is coincidental that the average analysis of these pieces (48.35 percent) is the same analysis as the lot. It is not recommended to consider these valid samples, because they were small pieces and, statistically, not enough of them to give a reliable, representative sample. The data in Table 4 show variations of the same magnitude as that in Table 3, but not as wide a range.

The data presented here show that the problem of segregation of ferrosilicon must be recognized before any of the other problems can be solved. It is the writer's opinion that the best time to sample this material is while it is still in cast form; taking a complete cross section from each of the castings going into the shipment lot. Nevertheless, many times it is desirable to sample material after the casting has lost its individual identity.

In this case, in order for a sample to be representative, it must be a large, unbiased sample taken during the final preparation of a shipment and prepared with proper equipment. On occasion, the customer or the supplier desires to make a spot check of a shipment lot of material. When this is necessary, it is highly recommended that a large sample be taken to get representation. Under no circumstances should one take one or two small pieces from a shipment lot and expect them to yield meaningful data. (It is interesting to note that The American Society for Testing and Materials (ASTM) recommends that 1 percent of the shipment lot be taken as a sample. On a 600 ton barge, they would require a 12 000 lb sample. This standard practice is currently under study by a task group considering possible revision of this recommendation.) A particular caution in obtaining a representative sample would be to avoid selecting obviously shiny or unusual pieces. Do try to get an unbiased sample.

Regardless of the origin of the sample it must be crushed, preferably to less than ¼ in., quartered, and approximately 500 g of sample pulverized to −100 mesh. This should be riffeled out to about a 100-g laboratory sample for analysis. Special care should be taken during preparation to prevent contaminating the sample from the crushing or pulverizing equipment. *All* of the material must pass through the sieve and none may be discarded. Typical sample preparation equipment necessary to properly process samples of ferroalloys includes, crushers, dividers or riffels, pulverizing equipment, and sieves, all of which are commercially available.

Problems can arise, and do, from the fact that many of the users of ferroalloys are inexperienced in the sampling of these materials. In one particular instance the writer received a complaint from one of our customers that they could not arrive at the lot analysis on which the material had been shipped. They complained the carbon content was high and silicon content was low by a magnitude in the range of 10 percent. Where the lot was shipped at 50 percent silicon, our customer was getting 38 to 40 percent silicon. Discussing the problem with their chief chemist, it was apparent his analytical procedure was adequate. This left the sampling procedures that were being followed to be discussed. The sample had been taken from each of the boxes that were shipped and a 60-mesh sample had been taken to the laboratory for analysis. While 60 mesh is not quite adequate for the fusion technique they used, it would suffice if special precautions were taken in the fusion of the material. (ASTM recommends a 100-mesh sample). We called in the sampler prior to going into the mill to take a joint sample which we agreed would be representative and upon which we would base a settlement of the shipment. The sampler was asked how he took the previous sample. He said he took some samples from each pallet box of the shipment. When asked how he pulverized the material, he said no crusher was available which would handle this material. The sample taken, simply was passed through a 12-in., 60-mesh sieve, screening the 60 mesh out. This material was taken to the laboratory for an analysis. Right away it was apparent that what he had taken was a sample of the dust of the fines that had been generated during transit, which is always low in silicon and does not represent the actual material. Having heard what had happened, the chief chemist agreed that there was really no basis for their complaint, but we would still take a joint sample and prepare it properly. This sample was analyzed within the normal variations that would be expected in a shipment lot. This case history represents one of the largest problems which occurs in the supplier-user relationship. The discrepancy in chemical analysis occurs because many of the users will base their analysis on one small pulverized piece, maybe 1 to 2 in. in size. If nothing else is gained from this presentation, it should be apparent that one small piece does not represent one large shipment lot.

Conclusions

This paper points out some of the problems in sampling ferroalloys. Considerable data was accumulated for this study, some of which is presented herein. However, it is difficult to draw conclusions on exactly how to sample ferrosilicon from the data. A definite statement might be: "A sufficiently large sample must be taken; that it should represent the material that has been produced and is being consumed; and that it must be properly processed."

In March 1972, as a delegate from ASTM Committee A-9 on Ferroalloys and Alloying Additives, the writer attended a meeting of ISOTC132 held in Moscow, on "Sampling and Chemical Analysis of Ferroalloys." At this meeting a task group was set up, with the USSR serving as task group leader, to "Establish Standard Practices for Sampling Ferroalloys." Hopefully, a "How To" recommendation with regard to sampling ferrosilicon will be forthcoming from this task group.

Clyde W. Moore[1] *and C. David Maars*[1]

Sampling and On-Stream X-Ray Control of Portland Cement Raw Mix Slurry

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REFERENCE: Moore, Clyde W. and Maars, C. David, "**Sampling and On-Stream X-Ray Control of Portland Cement Raw Mix Slurry,**" *Sampling, Standards and Homogeneity, ASTM STP 540,* American Society for Testing and Materials, 1973, pp. 97–109.

ABSTRACT: The trend in the cement industry toward large grinding mills, kilns, and kiln feed storage facilities has emphasized the need for continuous on-stream control of the chemical composition of the raw mix. This paper describes a sampling and control system in which the chemical composition of the solids in a continuous sample of flowing slurry is monitored by X-ray emission techniques. The chemical composition is used by a raw mill blending and control program to adjust feed rates of the raw material streams entering the raw grinding mill. A more uniform product in terms of certain chemical and physical properties of the cement has resulted from the combined performance of the X-ray sampling and control system, the kiln, and the finished cement grinding system.

KEY WORDS: portland cements, X-rays, raw mix, computers, slurries, chemical tests, physical tests, grinding mills, kilns, sampling, on-stream control

In the early part of the 19th century an English bricklayer named Joseph Aspdin first made portland cement by burning powdered limestone and clay in his kitchen stove. He took out a patent in 1824 on a hydraulic cement which he referred to as portland cement because it resembled natural stone obtained from the Isle of Portland off the British coast. Portland cement grew in popularity in Europe after about 1850, but it was not until the 1870s that it was first manufactured in the United States in the Lehigh Valley of Pennsylvania.

Today the raw materials used in the manufacture of portland cement are frequently the same as those used by Joseph Aspdin, but the manufacturing process is infinitely more complex. Performance specifications for the product require close control over many separate, continuous operations

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[1] Manager, Central Research Laboratory, Houston, Tex. and assistant plant manager, Production and Quality Control, Greencastle, Ind., respectively, Lone Star Industries, Inc., Greenwich, Conn. 06830.

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by frequent chemical and physical tests in plant laboratories. In order to meet the more exacting specifications, the list of possible raw materials frequently used has grown to include limestone, shells, chalk, clay, shale, blast furnace slag, slate, silica sand, and iron ore.

Two or more of these raw materials are prepared for burning by one of two different processes. In the wet process the crushed raw materials, properly proportioned, are ground with enough water to form a slurry with fluid characteristics which can be pumped and fed to the kilns. In the dry process the materials are ground, mixed, and introduced into the kiln in the dry state. Otherwise the two processes are quite similar.

The words "properly proportioned" constitute the key connection between these manufacturing processes and the general subjects: sampling, standards and homogeniety.

Traditionally, preparation of the raw materials in a cement plant has been by batch process even though the kilns operate continuously. In both the wet and dry processes, basins or silos are filled with the ground raw mix, sampled, analyzed, and then blended to the desired chemical specifications. Control is exercised over one or more of the four major elements, calcium, silicon, aluminum, and iron, depending on the number of degrees of freedom allowed by the choice of available raw materials.

In the mid-1950s X-ray emission had been developed to the extent that elements of atomic number down to and including silicon and aluminum could be analyzed. This provided a more rapid method of chemical analysis and opened the door to the possibility of automated control over the proportioning of raw materials. By 1961 X-ray analyzers receiving a continuous sample of dry powder were in operation in cement plants. One such installation was described by Hoffman and Pastorious [*1*].[2] Work was also being done on the direct analysis of slurries. One application of slurry analysis was reported by Abelmann and Smallbone [*2*]. This, and other progress in the field, prompted the German writer Lahl to write in 1965 that "The latest developments in the cement industry show that advanced automation of raw meal preparation is inconceivable without *X*-ray fluorescence analysis" [*3*].

Concurrently with the development of automated chemical control, kiln systems grew in size, and product uniformity received ever-increasing emphasis. Both of these developments made it increasingly important that the feed to the kiln be uniform in all respects. The performance of a cement kiln is adversely affected by input material nonuniformity, not only of chemical composition but also of physical properties. The many advantages to be achieved through automation of cement plants of large capacity have been summarized in the British publication *Cement Technology* [*4*].

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

The trend toward larger kiln systems in modern cement plants was accompanied by a trend toward one or two large processing units as compared to several smaller ones in older plants. As a result, in a wet process plant, when the raw mix leaves the grinding circuit and is stored in one or two large slurry basins there is little major homogenization or blending to be achieved, as contrasted to the batch blending referred to previously. Therefore, it is essential to keep the raw mix being pumped to the holding basins or silos at or very near the desired composition to eliminate the need for corrections in the holding basins.

Two approaches may be taken toward control of the physical and chemical properties of the raw mix. Both are widely used today in modern plants. They are feed forward control and feed backward control.

Feed forward control signifies that information is fed to some device such as a computer which uses this information to control some part of the process forward of the point where the information or data are gathered. In this type of control, the raw materials, which comprise the feed to the raw mill, are thoroughly analyzed and carefully blended, stacked or piled so that the withdrawal from each raw material pile will have a uniform composition the same as the information entered in the computer. The computer then proportions the raw material feed streams to obtain the desired raw mix composition leaving the raw mill system. Such a system can be initiated by a systematic analysis of the quarry, such as has been described by LeBel, Proner, and Guy [*5*].

Feed backward control signifies that data are collected at some point in the process and fed to a control device which uses these data to control some part of the process preceding the point where the data were taken. The raw mill system output is sampled and analyzed in this type of control in a cement plant. The analyses are made available to a computer which uses this information to adjust the raw material feed streams to obtain the desired chemical composition.

Laboratory Investigation

With this background, a research project was initiated by Lone Star Industries in 1965 at Lake Charles, La. to outline a feed backward control system to be installed in a one-kiln plant of 4 000 000 bbl (752 000 tons) per year capacity to be built near Greencastle, Ind. The new plant was to be a wet process plant replacing an existing plant with four kilns producing an average of 2 230 000 bbl (419 000 tons) per year. Start-up in mid-1969 was anticipated. The objectives of the project were:

1. Determine the accuracy achievable by X-ray emission with continuous sample of flowing slurry.

2. Determine whether the interelement effects and particle size effects were tolerable with the specific limestone, clay, shale, and iron ore anticipated for use at the plant.

3. Determine the precision achievable.
4. Determine what measures would be required to control the water content of the slurry.
5. Outline a mode of operation for the control laboratory.

Equipment

A laboratory X-ray spectrograph with six goniometers and associated detection equipment was fitted with a removable slurry flow cell pivoted in such a way that either the slurry or a standard reference sample, within a helium atmosphere, could be exposed at will to the primary X-ray beam. A closed cycle circulating system composed of a reservoir, a constant head tank, pumps, and mixers permitted the slurry to be adjusted in composition and water content and circulated continuously around the cycle.

Procedure

At a fixed water content of 50 or 55 percent, a minimum volume of slurry was mixed in the reservoir using weighed portions of raw materials from the proposed new plant site. These samples of limestone, clay, shale, and iron ore had previously been ground to a representative particle size, blended, sampled, and analyzed by both X-ray emission and wet chemistry. The slurry was pumped to the constant head tank at a rate sufficient to give an overflow which was returned to the reservoir. The slurry flowed by gravity from the head tank through the slurry cell past a thin Mylar window (0.00025 in.) where it was exposed to the X-ray beam and then returned to the reservoir. The head tank was adjusted in height to give a flow rate through the cell in the range of 1 to 2 gal per min.

Details of X-ray production and measurement have been reported by many authors and are not repeated here (see Ref *6* for instance). Table 1 shows the analytical lines used and the detector arrays for both the laboratory investigation and the plant operation.

TABLE 1—*Analytical lines and detector arrays.*

Element	Analytical Line, Å	Analyzing Crystal[a]	Detector
Al	K_α 8.338	EDDT	Gas Flow
Ca	K_α 3.359	EDDT	Gas Flow
Fe	K_α 1.937	LiF	Scintillation[b]
Si	K_α 7.126	EDDT	Gas Flow

[a] EDDT = ethylenediamine d-tartrate, LiF = lithium fluoride.

[b] In the instrumentation selected for the plant operation, a gas flow detector was used for the determination of iron.

When slurry circulation was stable, as indicated by the characteristic X-ray intensity from silicon, aluminum, iron, and calcium, intensity measurements were made simultaneously for all four elements for a fixed time of 100 or 200 s. The standard reference sample was then rotated into position under the primary X-ray beam and intensity measurements were made for an equal time. The reference standard used in the laboratory investigation and later at the plant is the same as that described by Moore for the analysis of portland cement by X-ray [7]. The X-ray intensity of each element in the slurry was divided by the corresponding intensity from the standard reference sample. For a fixed water content the concentration of the element in the slurry was found to be a linear function of this ratio of intensities.

Changes in concentration were made by adding to the reservoir a weighed portion of one of the raw materials along with the appropriate amount of water. In this way, the concentration of each of the four elements could be varied in desired increments over the normal range used in portland cement raw mix without requiring more analytical work than the four raw material samples used in the particular test run.

Results of the Laboratory Investigation

Typical values for accuracy determined in a single test are shown in Table 2. The interelement and mineralogical effects of the four raw materials are reflected in the data on accuracy. It was concluded that these data were sufficiently promising to proceed with the intended application.

X-ray intensities varied with water content of the slurry. An effort was made to correct for variations in water content by monitoring the X-ray emission from a ring of zirconium metal mounted a fixed distance below the Mylar window. This technique was abandoned. Another method of correcting for variations in water content has been reported by Abelmann

TABLE 2—*Data on accuracy achieved in laboratory project.*[a]

Oxide of Element	Average Concentration Percent	Standard Deviation	Coefficient of Variation
Al_2O_3	3.1	0.16	5.2
CaO	44.0	0.38	0.86
Fe_2O_3	1.7	0.08	4.7
SiO_2	14.0	0.59	4.2

[a] Data for Table 2 supplied through the courtesy of J. P. Rodgers, X-ray engineer, Lone Star Industries, Inc. (Presently assistant plant manager, Lone Star Industries, Inc., Chesapeake, Va.)

and Smallbone [2]. It was clear, however, that slurry from the raw grinding mills containing about 34 percent water would have to be diluted to at least 50 percent water and perhaps to 55 percent water to assure proper flow through the instrument. Therefore, a sampling system was designed for the new plant which would dilute the slurry sample to a fixed water content.

Tests indicated that the Mylar windows were safe for at least 8 h of continuous operation. Beyond that the abrasive effects of the slurry, along with X-ray damage, increased the probability of rupture of the Mylar. Changing the window after each 8-h shift provided a convenient schedule. At that time some mechanism to establish the calibration curve is required. The routine worked out under plant operating conditions is described later in this paper.

Plant Raw Mix Control

The new plant began operation in mid-June 1969. As originally planned, it was a wet process plant with one kiln and one raw grinding mill. The mill is 13 ft in diameter and 47 ft long. Driven by a 3000-hp motor, the mill has two compartments, the first contains 112 tons of 15-ft-long steel rods, and the second contains 152 tons of steel balls. The combination of raw materials was changed to limestone, two sources of shale, and sand. It is fed to the mill at a rate near 170 tons of dry solids per hour. Water is added to give a slurry of 34 percent water. After grinding and screening, the slurry is transferred to two slurry basins near the feed end of the kiln.

The plant is highly automated, having a third generation direct digital computer (DDC) for process control. The raw mill output is controlled by the computer which receives data from the X-ray spectrometer and

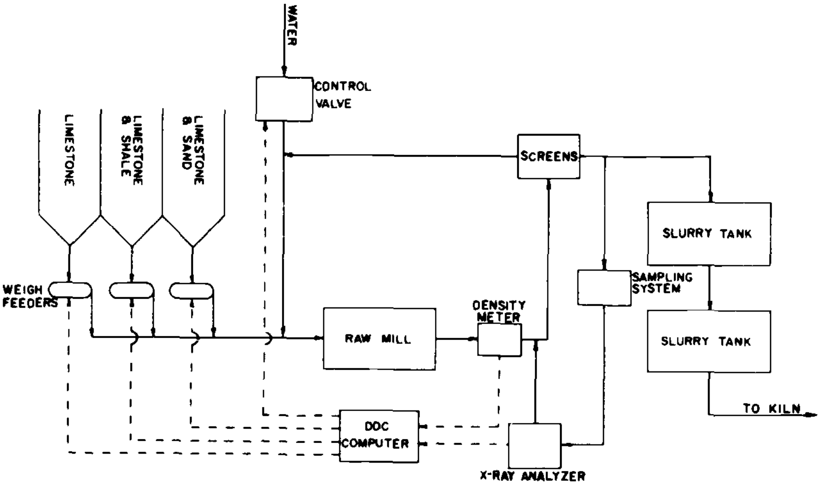

FIG. 1—*Raw mill system.*

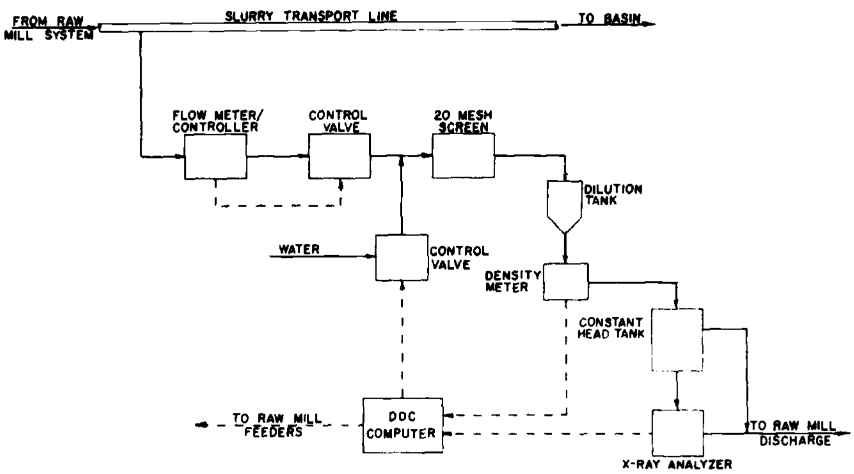

FIG. 2—*Slurry sampling system.*

calculates chemical composition of the raw mill output. A new slurry analysis is made available for the raw mill control program every 250 s. A schematic of the control system is shown in Fig. 1.

The key to good control is the ability to obtain a representative sample.

X-Ray Sampling System

The slurry is sampled as it leaves the raw mill system on its way to the slurry homogenization area as shown in Fig. 2. The sample is taken from the slurry transport line. The size of the sample is equivalent to approximately 2.5 percent of the raw mill output. The flow of the slurry sample to the sampling system is controlled by a flow meter/controller. The control signal is sent from the flow meter/controller to a hydraulic activated modulating valve which maintains the slurry flow at set-point.

Water is added to the slurry at a rate controlled by the computer to give 50 percent water. A feed-back signal from the density gage described below is used in the control. A small vibrating 20-mesh screen of 30 in. in diameter removes any scale or large particles of raw mix which may have bypassed the screens in the raw grinding circuits. It then moves into a 50 gal mixing tank.

The agitator in the mixing tank thoroughly mixes the slurry. The mixing tank is also the reservoir for the pumps which transport the slurry to the X-ray analyzer constant-head tank in the X-ray room. The mixing tank is operated with a constant overflow to ensure a constant and uniform feed to the transport pumps.

The X-ray slurry sample passes through a radiation density gauge as it leaves the mixing tank. The signal from the density gauge is sent to the computer to be used to control the moisture content of the X-ray slurry sample.

The pumps which transport the slurry from the mixing tank to the constant-head tank for the X-ray analyzer are electrically-controlled, air-operated diaphragm pumps. There are two of these pumps operating in parallel during normal operation. The system is designed so that enough slurry can be transported by one pump to supply the X-ray analyzer if one of the pumps fails.

The slurry sample is received in the X-ray room in the constant-head tank. The slurry flows by gravity to the X-ray from the bottom of the tank. This slurry rejoins the overflow from the head tank and flows to a holding tank for another electrically-controlled, air-operated diaphragm pump, which returns the sample to the raw mill system.

X-Ray Analyzer

The slurry analyzer selected for plant operation is an X-ray spectrometer having five channels capable of analyzing for four elements simultaneously

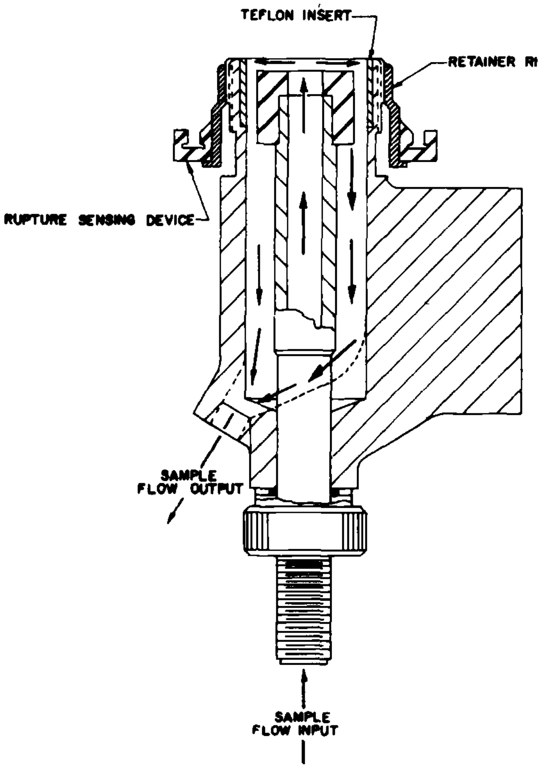

FIG. 3—*Sectional diagram of the flow cell. (Provided through the courtesy of Philips Electronic Instruments.)*

with one spare channel. The spare is frequently used to give a duplicate analysis for one of the four elements. The analyses are performed in a helium atmosphere to favor the elements of low atomic number specifically silicon and aluminum.

The slurry sample is presented to the X-ray analyzer on a continuous basis. The slurry flows through a slurry cell which is identical to that used in the laboratory investigation. Figure 3 shows a schematic diagram of the cell. The direction of flow is upward through the center of the cell, mushrooming against a 0.00025 in. Mylar window; leaving the cell through an annular space around the center of the cell to return to the raw mill discharge sump. The instrument automatically cycles the slurry cell and then the reference standard into position for analysis and then repeats the cycle. Figure 4 is a photograph of the upper surface of the flow cell and the reference standard retracted from the instrument. In this position the Mylar window can be changed without removing the cell from its mount.

The analyzing technique used is an "intensity ratio" technique which was just described. The "intensity ratio" is used to establish calibration curves for the element. The calibration curves are linear. Therefore, the concentration of calcium oxide (CaO), for example, may be represented as

$$\text{percent CaO} = m\left(\frac{I_{ca}\ \text{(slurry)}}{I_{ca}\ \text{(reference)}}\right) + b$$

where

m = slope of the line,
I_{ca} = calcium intensity (counts), and
b = intercept on the y-axis.

The X-ray analyzer is interfaced with the DDC computer. The data sent from the X-ray analyzer are the elemental characteristic X-ray intensities for both the slurry and the reference standard. The computer performs the calculations to transform the intensities to oxide percents.

The constants m and b, in the calibration curves are manual inputs into the computer X-ray program. The ability to change these constants is utilized to update the calibration curves after each slurry cell Mylar window change. The calibration curves are updated as soon after each window change as possible because the thickness of the Mylar and the curvature of the window affect the calibration curves. Also, updating the calibration curves nullifies, to some extent, the effects of the change in particle size distribution and mineralogy in the slurry due to the changes in screening and feed stream proportions.

The analysis computed by the X-ray program is made available for the raw mill control program.

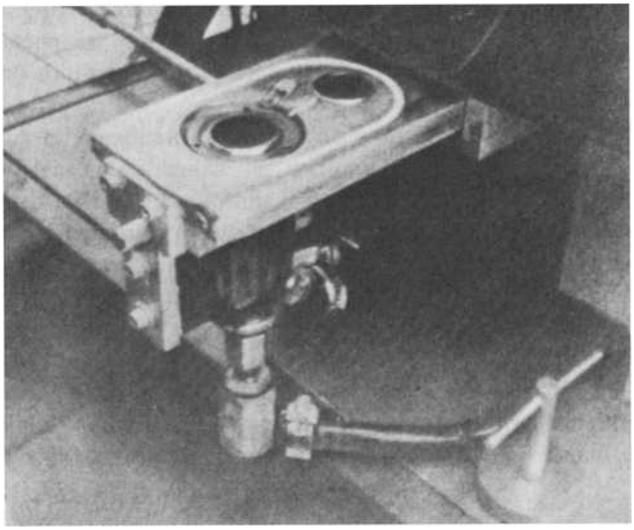

FIG. 4—*Slurry cell* (left) *and reference standard* (right) *withdrawn from the X-ray spectrometer. The tool at lower right is used to change the Mylar window without removing the cell from its mount.*

Raw Mill Blending and Control Program (RMB)

The primary objective of the RMB is to have the chemical composition of the slurry in the slurry basins at the desired composition when the slurry basin is full. The RMB accomplishes this by maintaining the chemical composition of the slurry in the basin as near the set-points as possible at all times by changing the feed stream proportions continuously or as necessary.

The control constants used to make adjustments in the feeder ratios are proportional gain, integral action gain, and second integral action gain. The proportional gain and integral action gain are the control constants which determine the rate at which the immediate raw mill output is moved to the set-points. The second integral action gain is the control action which determines the rate at which the slurry in the slurry basin being filled is moved towards the set-points. The computer controls weigh feeders in the field which input the proper amount of feed from each feed stream to the raw mill.

The RMB is also capable of using a manual input analysis of the raw mill slurry to control the raw mill output. The only basic difference is the length of time between available analyses for raw mill control.

Raw Mill Control—Physical Properties—The water content is controlled by a program which proportions the process water input to the raw mill with the feed to the mill. This program receives a signal from a nuclear slurry density meter which it uses to accomplish its objective (see Fig. 1).

The fineness of the slurry is governed by screens. The oversize particles are returned to the mill and the material passing through the screens is pumped to the slurry basin. The pressure on the inlet side of the screens is controlled within a narrow range to obtain as uniform fineness as possible.

Homogenization—The slurry is pumped from the raw mill system to the first of two slurry tanks. A stream splitter distributes the incoming stream across the diameter of the basin. The slurry is pumped from the bottom of the first basin into the top of the second, and from the bottom of the second basin to the kiln.

The slurry tanks are 100 ft in diameter and 42 ft high, and each holds approximately 12 000 tons of raw materials solids when full. The agitation is a combination of mechanical action, air lifters, and air bubblers.

Results

Of course, "The proof of the pudding is in the eating." The results of this sophisticated sampling, control, and homogenization of the feed to the rotary cement kiln at Greencastle are the uniformity of both the clinker coming from the kiln and the physical properties of the cement produced. The following is an indication of this, using the C_3S[3] and Silica Ratio[4] as indicators. These data represent composite samples collected on eight consecutive days of operation (see Table 3).

These data plus data on the precision of the slurry analysis shown in Table 4 indicate the reliability of the system. Ball and Burke point out

TABLE 3—*Data on uniformity of the portland cement clinker produced.*

Day	C_3S, %	Silica Ratio
1	59.9	2.89
2	64.2	2.88
3	62.2	2.95
4	63.7	2.90
5	60.7	2.89
6	63.1	2.92
7	61.8	2.91
8	61.7	2.88
Average	62.2	2.90
Standard deviation	1.4	0.02
Holding point	62.0	2.90

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[3] Cement chemists use the following shorthand for the oxides present in the manufacture of Portland cement: C = CaO, S = SiO_2, A = Al_2O_3, and F = Fe_2O_3. See ASTM Specification for Portland Cement (C 150-73) for method of calculating C_3S (tricalcium silicate) from the oxide analysis.

[4] Silica Ratio = $S/(A + F)$. This provides an index of burnability for the material.

TABLE 4—*Data on precision of slurry analysis in plant operation.*

Oxide of Element	Average Concentration	Single Operator-Day Precision (1S)	Single Operator-Day Coefficient of Variation
Al_2O_3	3.50	0.08	2.3
CaO	44.00	0.15	0.34
Fe_2O_3	1.50	0.01	0.67
SiO_2	13.70	0.23	1.68

that the accumulated standard deviations due to sampling error, error intrinsic in technique, instrumental error, and chemical error is about 0.32 percent CaO in the raw mix of a wet process plant [*8*]. This, coupled with variations in the ash content of the coal which is used as fuel, can more than account for the variation in C_3S and Silica Ratio shown here.

Compressive strength, as measured by ASTM Test for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. (50-mm) Cube Specimens) (C 109–73), is one of the most important physical properties of portland cement. In a recent statistical study of compressive strength of Type I cements produced at Greencastle and ten other Lone Star plants, only one had a lower coefficient of variation at ages of 7 days and 28 days. In addition, a comparison of compressive strength data between the new plant and the old plant at Greencastle showed the new plant with a lower coefficient of variation at ages of 7 days and 28 days and an equivalent one at 3 days. The raw mix control system shares the credit for this improvement in uniformity along with the kiln performance and the performance of the cement grinding circuit.

Conclusions

It is clear that the intrinsic problems of a large kiln system and the more rigid specifications and applications of portland cement demand that the raw mix being fed to the system be uniform. At the present time there is no analytical system other than X-ray suitable for closed-loop automatic control.

The control system described in this paper has proved adequate for the requirements. However, it is not free of problems. The need to analyze a check sample each shift when the Mylar window of the slurry cell is changed requires attention from laboratory personnel which would preferably be directed to other tasks. In addition, some of the mineralogical effects and effects of particle size changes are still present. These are more prominent in some raw materials than others. The latter problems are not a function of the instrumentation but are inherent in the physics of

X-ray emission. This can be eliminated at present only by more complex sample preparation techniques which are more difficult to automate.

In spite of these difficulties, X-ray emission plays a prominent role in present day cement manufacture. The difficulties are partly alleviated by the speed of the analyses and the fact that the averages over a period of time tend to converge acceptably close to the mythical "true value." While the authors agree with the German writer, Lahl, they will welcome a system which will operate totally unattended while providing data equal to or better than that just described.

Acknowledgments

The authors wish to thank the management of Lone Star Industries, Inc. for permission to publish this account. We also gratefully acknowledge the work of J. P. Rodgers who conducted many of the experiments on slurry analysis during the laboratory investigation at Lake Charles, La. Finally, we thank Philips Electronic Instruments for providing graphical information on the slurry cell.

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C. B. Jenkins[1] *and G. C. Soth*[1]

Sampling and Analysis for an Oxygen Steel Shop

REFERENCE: Jenkins, C. B. and Soth, G. C., **"Sampling and Analysis for an Oxygen Steel Shop,"** *Sampling, Standards and Homogeneity, ASTM STP 540*, American Society for Testing and Materials, 1973, pp. 110–122.

ABSTRACT: Preliminary and final samples from the basic oxygen steel shop are analyzed for a variety of elements to control the steelmaking process and determine the chemical analysis of the final product. Faster and more accurate methods of sampling and analysis are being sought to minimize the time required to produce a heat of steel. Rapid sampling and analysis of slag and bath oxygen content are needed to improve control over the oxygen steelmaking process.

KEY WORDS: sampling, basic oxygen steel making, carbon analysis, spectographs, quality control

The operation of a basic oxygen steelmaking furnace requires the sampling of the steel and the slag from the furnace prior to the tapping of the heat. This sampling is done to determine if the carbon content of the steel has been reduced sufficiently by oxidation and that phosphorus and sulfur levels have been lowered to required levels by proper slagging action. Some other residual elements are determined also, to permit calculation of proper amounts of additions needed to produce the desired grade of steel. The steel is sampled after it is made in order to verify the chemical analysis and to assure that this analysis meets the requirements for the product being made.

Sampling of Preliminary Steel Samples

After the heat of steel has been blown with oxygen for a period of time to reduce the carbon content, the oxygen lance is withdrawn from the furnace. The furnace is then tipped to allow a sampling tool to be inserted into the

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[1] Supervisor, spectrography and chief chemist, respectively, Kaiser Steel Corp., Fontana, Calif. 92335.

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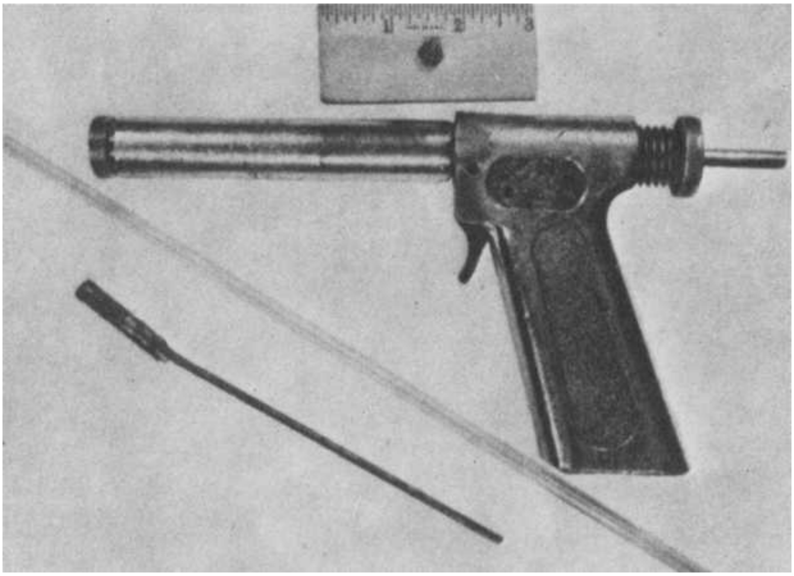
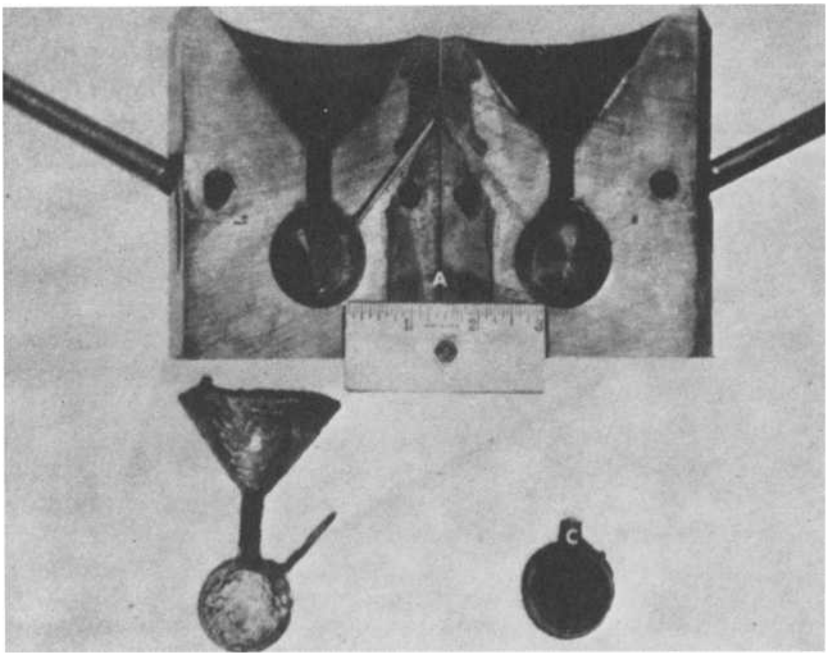


FIG. 1—(top) *Sampling gun,* (center) *glass sampling tube,* (bottom) *and wire sample.*

steel. This tool is 15 ft long, weighs 50 lb and has a cup on one end capable of holding 10 lb of steel. At Kaiser this tool is called a spoon. The spoon is coated with slag, then inserted through the slag layer into the steel and a volume of steel is removed from the furnace. The steel in the spoon is "killed" by inserting aluminum wire into the steel until all sparking has ceased. This is done to remove entrapped oxygen from the steel and to prevent pinholes and voids in the samples which are subsequently taken from the spoon of steel.

Two types of preliminary samples are used at Kaiser Steel for analyzing the steel in the furnace prior to tapping the heat. One of these is the wire sample shown in Fig. 1. After the steel in the spoon has been killed as just described, a sample is taken with the sampling gun shown in Fig. 1. The steel is drawn into the glass tube attached to the sampling gun. The sample is water quenched, breaking the glass and cooling the sample. The resulting wire is 5 mm in diameter and up to 140 mm long. This wire sample is inspected visually for voids, pits, or slag inclusions. At Kaiser, if the sample is of satisfactory quality, it is cut into 1 g pieces on a dual bladed cut-off saw. These pieces are inspected again for soundness.

The other type of preliminary test is a poured test. After the wire sample has been taken from the spoon, the remaining steel in the spoon is poured into a cast iron mold (Fig. 2a). After perhaps 30 s for the steel to solidify, this mold is separated and the sample is removed and water quenched. The riser, or upper portion (Fig. 2*b*) of the sample, is cut off



(*a*) Preliminary sample book mold.
(*b*) Preliminary slug sample with riser.
(*c*) Preliminary slug sample prepared for spectrographic analysis.

FIG. 2—*Preliminary slug samples and mold.*

and discarded. This riser is used as a reservoir of steel during the cooling of the test to ensure that the lower portion of the test is solid and free from pits or voids. At Kaiser this poured test is called a slug sample. The slug sample is sent to the chemical laboratory for analysis via a pneumatic tube system. At the laboratory this sample is surfaced on a wet grinder until enough material is removed to provide a suitable surface for analysis on a vacuum spectrometer. The sample is dried with a stream of compressed air and finish-ground on a belt sander using 50× grit aluminum oxide belts.

Analysis of Preliminary Steel Samples

Two of the wire pieces are run on separate combustion carbon analyzers in the usual manner and the results are compared. The results should agree within ±0.01 percent at a usual level of around 0.1 percent carbon. The carbon results are recorded and reported to the melter over a speaker system. A third wire piece is analyzed for sulfur using an RF induction furnace interfaced to a specific conductance cell. The fourth wire piece is run in the same manner for a sulfur check analysis. The results are recorded and reported to the melter over a speaker system.

The slug sample is analyzed on a vacuum spectrometer for nineteen elements. This analysis requires 35 s. Results are given in weight percent on a console printer and a punched card. The spectrometer operator reports the analyses for the chemical elements of interest via the speaker system directly to the melter in the oxygen shop. The punched card data are transmitted via a telegraphic card reader over a teletype system directly to the oxygen shop to provide a hard copy of the analysis. Manganese, phosphorus, tin, and copper are reported verbally on all heats. These elements, along with the carbon and the sulfur results obtained from the wire sample, are needed to calculate the amounts of materials to be added to the steel to produce the desired finished product. Chromium, nickel, and molybdenum are reported verbally to the melter at the oxygen shop for heats with stringent maximum concentrations for these elements. The total time required from taking the sample from the furnace to transmitting the analysis from the laboratory to the oxygen shop is approximately 5 min. Satisfactory chemical analyses may be obtained on the vacuum spectrometer for carbon and sulfur below certain levels. However, the time element involved in taking the sample and delivery to the laboratory by pneumatic tube is greater than that for combustion analyses on the shop floor.

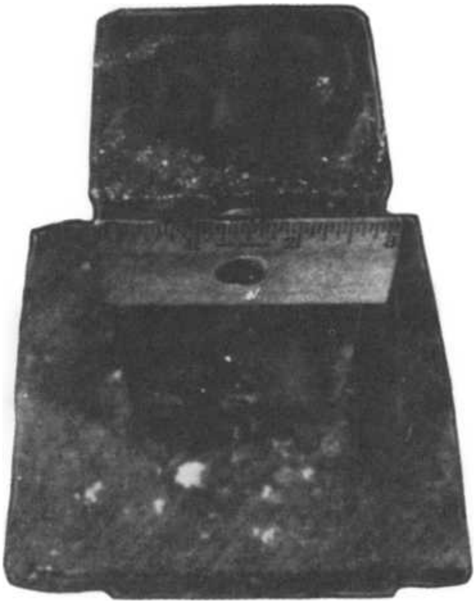


FIG. 3—*Cast iron mold for final poured test.*

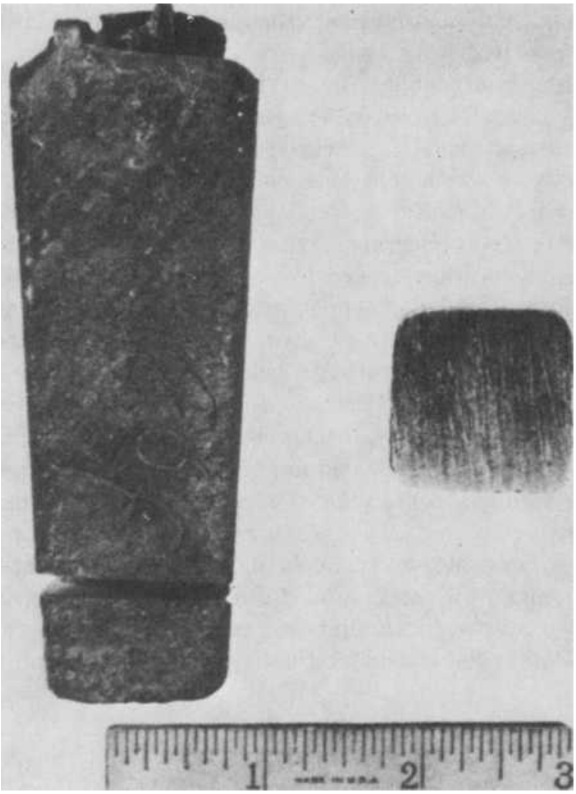


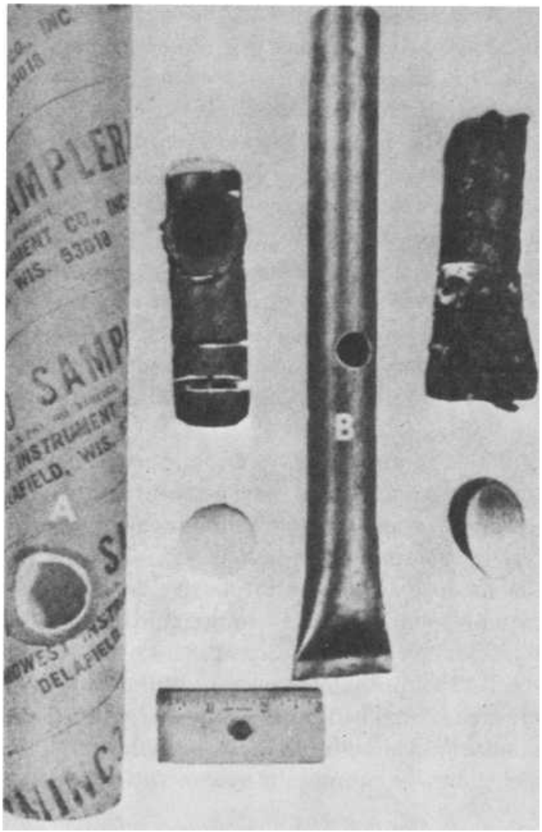
FIG. 4—*Final poured test. Sliced test showing identification number* (left). *Bottom portion of test prepared for spectrographic analysis* (right).

Sampling for Final Heat Analysis

Samples are obtained from the stream of steel from the ladle as the heat is being poured into the ingot molds. These samples are used to obtain the chemical analysis of the steel after the addition of the various alloying constituents used to make the desired grade of steel.

The stream of molten steel from the ladle is throttled down and a spoon similar to the one used for taking preliminary samples is used to take a sample of steel from the ladel stream. A pre-weighed amount of aluminum wire is placed in the spoon prior to taking the sample from the stream of steel from the ladle. Again, the function of the aluminum wire is to deoxidize the steel and provide a solid test, free of pits or voids, for spectrographic analysis. These samples are taken at the first, middle, and last part of the pouring of a heat of steel from the ladle. The steel sample is poured from the spoon into a cast iron mold shown in Fig. 3. After the test has solidified it is removed from the mold by inverting the mold and tapping the mold to free the test. The test is then water quenched and stamped with an identification number. After all the tests for the particular heat have been taken, they are shipped via pneumatic tube to the sample preparation room at the chemical laboratory. The samples are sliced on a cut-off saw and the lower 1/2-in. piece is surfaced on a belt sander using a 50X grit aluminum oxide belt. The test is shown before and after slicing in Fig. 4. The large upper portion of the test may be drilled for use in combustion carbon and sulfur analyses where necessary or desired.

Dip tests are taken on heats with aim manganese of 1 percent or higher. Research has shown that some manganese oxidizes out of the spoon and poured test, resulting in low results for manganese on poured tests. It has been found that manganese results on dip test samples agree closely with results for manganese on check samples from the finished product into



(*a*) Ceramic dip test.
(*b*) Crimped pipe dip test.

FIG. 5—*Dip tests and resulting samples.*

which the steel is fabricated. Aluminum wire for deoxidation of the sample is added to the dip test sampler before the sampler is immersed in the molten steel in the ingot mold. Figure 5 shows two types of dip testers and the resulting tests obtained. These tests are stamped with identification numbers and sent to the sample preparation room in the laboratory via pneumatic tube. The resulting sample slices are analyzed on a vacuum spectrometer for weight percent concentration of nineteen elements. Drillings also may be obtained from these dip tests for use in combustion carbon and sulfur analyses when desired.

Discussion

Over 90 percent of the preliminary slug samples are acceptable for analysis by a vacuum spectrometer. Only one analysis is made on the preliminary slug samples on the vacuum spectrometer. In the past, two analyses were performed on each slug sample and the results were averaged to arrive at the final analysis. A study showed an average variation of only 2.5 percent of the amount present for two analyses on a given slug sample for the elements listed previously. Because this variation is small, it was decided that only one analysis per sample was necessary. This results in a minimum time savings of 35 s per heat of steel and a cost savings of $25 per heat. Attention to sample quality, appearance of the burn from the vacuum spectrometer, and level of internal standard iron voltage is required to produce satisfactory results with only one analysis per sample.

The major defect in preliminary slug samples are quench cracks resulting from a high concentration of carbon. No analytical work is carried out on a sample exhibiting cracks. No research is being done on preliminary samples since sample quality and analytical results are considered satisfactory.

The quality of final poured tests is not as good as preliminary test quality with only 75 percent of the tests acceptable for spectrographic analysis. Several major types of defects in the tests prevent them from being analyzed on a vacuum spectrometer. The aluminum wire can be washed out of the spoon by the stream of steel from the ladle, resulting in voids in the sample which make it impossible to analyze the sample spectrographically. The level of aluminum in the test is believed by many to be best between 0.125 and 0.250 percent. Aluminum levels greater than 0.250 percent may cause small areas of undissolved aluminum to appear in the samples, resulting in unreliable spectrographic results. Some people in the industry feel that high aluminum concentration in the test enhances carbon results.

The major problem experienced on these tests is the occurrence of small pinholes in the burn area. The pinholes are usually visible only after the test has been analyzed spectrographically. The causes of these pinholes have not been determined. Work is presently underway to improve the

TABLE 1—*Zirconium results on dip tests.*

Test Type	Percent Zirconium	Percent Relative Standard Deviation[a]
Crimped pipe dip test	0.105	±10.9
Ceramic mold dip test	0.094	± 5.2

[a] The percent relative standard deviation is based on the average of 21 determinations.

sample quality of these final slug tests. Book molds which are used to obtain preliminary tests are being tried for final tests. These tests are water quenched within 60 s after pouring and are sent to the laboratory for the same preparation and analysis as carried out on preliminary slug tests. The quality of the resulting test is improved, but difficulty has been experienced in filling the book mold since the temperature of the steel is lower during the pouring of the heat as compared with the temperature when the preliminary test is taken. The size of the hole for filling the book mold is much smaller than the hole for filling the mold now being used for the final tests, as can be seen by comparing Figs. 2 and 3. The steel solidifies rapidly in the small hole in the book mold causing difficulty in obtaining a solid sample suitable for spectrographic analysis.

A retraining program on proper testing techniques is being undertaken to determine how much improvement can be realized with the existing test mold sample as shown in Fig. 3. Emphasis is being placed on keeping the mold clean and dry, maintaining proper aluminum concentration in the test, and proper quenching of the poured test.

Dip tests have been taken using a pipe crimped at one end with an entry hole in the side for filling as shown in Fig. 5*b*. Only 50 percent of these samples are satisfactory for spectrographic analysis. The same defects are exhibited as described above on poured final tests. Upon etching of the surface of the tests one often finds several different grain structures which cause variation in the spectrographic analytical results on these tests. Zirconium results, in particular, show poor reproducibility on these tests as shown in Table 1. At present all zirconium bearing heats are being sampled with the ceramic dip test shown in Fig. 5*a*. Over 90 percent of these tests are of acceptable quality for spectrographic analyses. Zirconium results for these tests are also shown in Table 1. Table 2 shows the precision obtained in analyses on the three types of tests just described. Despite the poor sample quality exhibited by the crimped pipe type of dip test, it does offer several advantages. The most important advantage is the agreement between manganese values on the dip test sample and the final end product. This agreement has eliminated the need for obtaining drillings from the final product and analyzing these drillings for manganese by wet

TABLE 2—*Repeatability of final test samples.*[a]

Element	Poured Final Test		Crimped Pipe Dip Test		Ceramic Dip Test	
	Percent Concentration	Standard Deviation	Percent Concentration	Standard Deviation	Percent Concentration	Standard Deviation
C	0.21	0.012	0.11	0.008	0.12	0.005
Mn	0.59	0.016	1.28	0.018	1.29	0.010
P	0.007	0.001	0.010	0.001	0.010	0.001
S	0.020	0.002	0.016	0.001	0.016	0.001
Si	0.057	0.014	0.323	0.006	0.353	0.008
Sn	0.002	0.001	0.002	0.001	0.003	0.000
Cu	0.05	0.005	0.08	0.002	0.08	0.000
Ni	0.02	0.000	0.03	0.000	0.03	0.000
Cr	0.01	0.000	0.03	0.000	0.02	0.002
V	ND[b]	...	0.004	0.000	0.004	0.000
Mo	0.003	0.002	0.003	0.001	0.002	0.000
Al	0.193	0.020	ND	...	ND	...
Co	0.017	0.000	0.015	0.000	0.014	0.000
Ti	ND	...	0.003	0.000	0.003	0.000
Cb	ND	...	0.009	0.001	0.009	0.001
As	0.006	0.002	0.005	0.001	0.005	0.001
B	ND	...	ND	...	ND	...
Zr	ND	...	0.094	0.010	0.090	0.005

[a] Standard deviation of 21 replicate analyses per sample.
[b] Not detected.

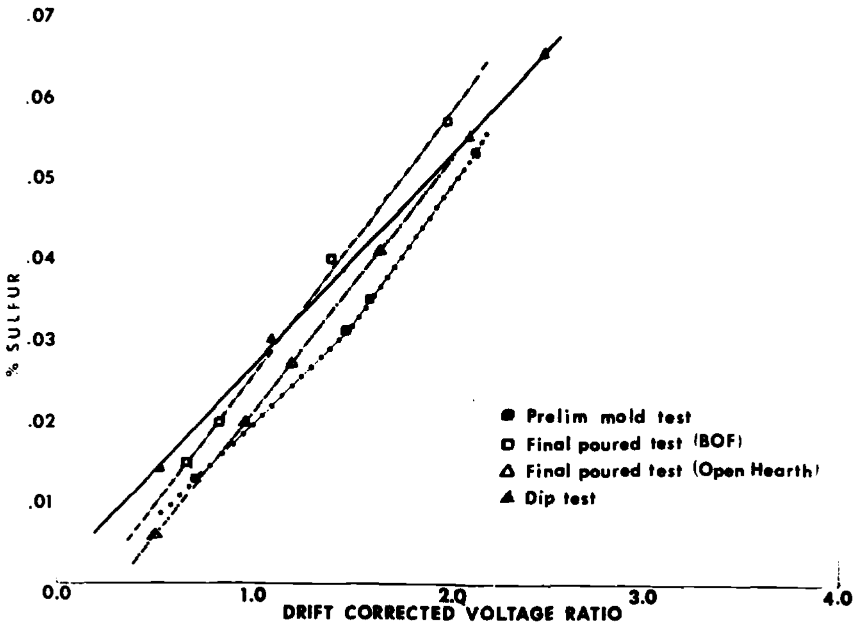


FIG. 6—*Sulfur analysis on various tests.*

chemical methods. The cost of these samplers is about one third the cost of the ceramic dip testers. Repeated spectrographic analyses on these samples will also provide acceptable results after a suitable burn has been obtained. These factors have made it difficult to justify ceramic dip testers for heats other than those containing zirconium additions.

It has been found that sulfur response is quite different for preliminary slug tests, dip tests, and final poured tests. It is also of interest to note the different sulfur curves found for the basic oxygen shop steels and for open hearth steels on the identical type of poured final test. These various curves are shown in Fig. 6.

Spectrographic analyses usually are performed on a 1.5-m vacuum-air spectrometer with a low voltage spark excitation source. The output of the photomultiplier tubes is stored on capacitors and read into an interfaced computer which converts the raw voltage data into weight percent concentration for 19 elements. This analytical procedure requires 35 s to complete. Future changes in the excitation source and the addition of a line printer for data output can reduce the analysis time to 8 s.

Alternative Sampling and Analysis Methods

A wide variety of methods have been used or are being used for the sampling and analysis of the steel prior to tapping.

Wire samples have been obtained with an evacuated glass tube and a glass tube with a suction bulb attached to one end. Carbon values on such wire samples can be obtained by a variety of methods ranging from a carbometer to a combustion furnace interfaced to an infrared cell which measures carbon dioxide absorption and relates this to carbon content of the sample. These methods for carbon analysis on the wire sample have been tested by many people throughout the industry. We feel that the new infrared method for determination of carbon is far superior to any other method on the bases both of speed and accuracy.

Liquidus arrest determination of carbon has been used by a number of people in the industry. This method of carbon determination depends on the inflection in the time-temperature curve due to the heat of fusion liberated as the steel passes from the liquid to the solid state. A sample of steel from the vessel is poured into a cartridge containing a thermocouple. The output of the thermocouple is fed to a strip chart recorder to obtain a time-temperature curve. The liquidus arrest temperature is then related to the percent carbon present in the steel. This method of carbon determination was investigated at Kaiser and found unsatisfactory. The precision of the method was much worse than the combustion method, other materials in the steel also cause changes in the liquidus arrest temperature, and the equipment itself was subject to vibration, temperature changes, and electrical interference resulting in unreliable carbon values.

Carbon and temperature measurements in an upright vessel have been attempted.[2] A lance containing a liquidus carbon thermocouple and a thermocouple for measuring bath temperature is lowered into the vessel. The only difference between this method of sampling and the liquidus arrest method just described is that this method does not require tipping of the vessel to obtain a sample. This method can determine ±4 points of carbon in the 0.11 to 0.20 percent carbon range. Since we need to determine carbon to ±1 point in this range, this method has not been investigated at Kaiser Steel.

The radiation emitted from the flame of the BOF has also been used for carbon determinations.[3] The flame intensity is measured during the blow and it has been shown that a linear relationship exists between flame intensity and percent carbon. The bath carbon can be estimated to ±2 points. We have not investigated this method of determining the carbon content of the bath.

Work has also been done on the effluent gases emitted into the hood above the vessel.[4] Analysis of this gas mixture for carbon dioxide, carbon

[2] Kern, D. W., Stelts, P. D., and Fradeneck, R. J., *Journal of Metals*, AIME, American Institute of Mining and Metallurgical Engineers, Vol. 23, No. 8, Aug. 1971, pp. 9–19.

[3] MacFarlane, D., *Journal of Metals*, AIME, American Institute of Mining and Metallurgical Engineers, Vol. 16, No. 9, Sept. 1964, pp. 715–717.

[4] Yamamoto, N., Hasimoto, H., Matsunaga, S., and Torigoe, T., *Journal of Metals*, AIME, American Institute of Mining and Metallurgical Engineers, Vol. 17, No. 7, July 1965, pp. 718–721.

monoxide, and oxygen can be related to the degree to which the heat has been blown. This type of monitor system could be used to help bring about closed loop control over a BOF furnace.

At the present time we are investigating a ladle stream sample for use in obtaining final tests as the steel is being poured into the ingot molds. This type of sampling device appears to have several advantages over the poured tests being used at present. The quantity of aluminum used in the test can be carefully controlled, the stream of steel from the ladle does not have to be throttled down to take the test, and a wire sample is obtained at the same time for use in combustion carbon and sulfur analysis when necessary. The test mold is filled via a glass tube inserted into the stream of steel from the ladle, resulting in a round test 1¼ in. in diameter and ⅜ in. thick. These samples have been found to be quite satisfactory for spectrographic analysis. Savings in pouring times and ladle stopper life may be realized because the stream does not have to be throttled down to take the test. A disadvantage is the much higher cost of this type of sampler compared with the poured test now being used.

Slag Samples

Tap slag samples are taken from each heat of steel. Existing techniques for sampling, sample preparation, and analysis are too slow for direct use of the slag analyses for control of the steelmaking operation. Instead, the results are used in two different ways.

Samples of slag are crushed and screened to −100 mesh. Planchets are made in a pellet press and analyzed by X-ray fluorescence. The elements magnesium, calcium, silicon, and aluminum are reported as oxides for the base-acid ratio of a slag. Iron content is reported as ferrous oxide. Manganese, phosphorus, and sulfur are determined also and reported as percent element. Correlations between slag analysis and the steelmaking history of the heat are used to develop improved steelmaking practices. Chemical analysis are also correlated with the appearance of slags so that the melter can inspect the slag and have a guide for immediate use.

Summary

Satisfactory methods for the sampling and analyses of steel for the operation of a basic oxygen steel shop have been developed at Kaiser Steel. At the present time, it is considered that analytical methods and reporting are in advance of techniques for sampling and sample preparation. Therefore, development work is emphasized for sampling, sample quality, and sample preparation. Because complete heats of steel are made in as little as 25 min, savings of only a few seconds in any part of the operation add up to substantial time in a 24 h period and this translates into considerable economic improvement. Better, more rapid procedures and techniques are badly needed for slag analysis. Other analyses are considered desirable if techniques of sampling and analysis can be developed. To list some of them, work is being done for direct determination of carbon in the vessel. Many metallurgists believe a rapid method for the determination of the oxygen level in the steel is highly desirable. In this latter case, rapid analytical methods are in existence, but satisfactory sampling and sample handling techniques require further development. Steelmaking is undergoing rapid changes and chemical laboratory investigation and development is striving to keep up with the demands.

T. Y. Kometani,[1] *J. L. Bove,*[2] *and B. Nathanson*[3]

Paper Fiber Filters for Sampling Trace Metals in Airborne Particulate Matter

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ABSTRACT: The standard collection filter medium for particulate air pollutants has been fiberglass. The high metal impurity content of glass and the tedious acid extraction procedure necessary to recover metals from particulates are great disadvantages when trace analysis is to be performed. Samples on paper filters, on the other hand, can be dry ashed to 500°C without serious loss of metals by volatilization. The filter is completely destroyed leaving only inorganic residue to be dissolved for analysis by atomic absorption spectrometry.

Analysis of New York City particulates collected on paper filters indicate that results obtained by dry ashing compare favorably with those of accepted methods such as wet ashing and low temperature ashing. Reported losses of metals during dry ashing of particulates on fiberglass filters are not necessarily due to volatilization as has been commonly supposed. Metals such as lead, zinc, copper, and cadmium are retained to glass to varying extents at high temperature either by formation of insoluble metal silicates or by physical entrapment by softened glass.

KEY WORDS: sampling, filters, air pollution, atomic absorption spectrometry, trace elements

The sampling of airborne particulates has been routinely performed by air pollution laboratories with a high-volume sampler using a fiberglass filter as a standard collection medium [*1, 2*].[4] Fiberglass with its uniform and efficient filtering characteristics is quite suitable for sampling particulates over a 24 h period. Also, its resistance to moisture and organic

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[1] Analytical chemist, Bell Laboratories, Murray Hill, N.J. 07974.

[2] Professor of chemistry, Department of Chemical Engineering, The Cooper Union for the Advancement of Science and Art, New York, N.Y. 10003.

[3] Senior chemist, Department of Air Resources, New York, N.Y. 10003.

[4] The italic numbers in brackets refer to the list of references appended to this paper.

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attack simplifies weight gain measurement and determination of organic constituents. However, there are some significant disadvantages when trace metals analysis in particulate matter is desired.

The determination of trace metals in particulates by atomic absorption spectrometry (AAS) [*3*, *4*] usually involves the initial destruction of organic matter in the sample followed by acid dissolution of residues. Dry ashing at high temperatures, as a method of oxidizing organic matter on glass filters, has been ruled out by some investigators [*3*, *5–7*] because of the observed losses of low melting metals. The most frequent explanation offered for these losses has been the volatilization of metals at high temperatures. Consequently, samples have been oxidized by low temperature ashing with an excited oxygen plasma [*8*] at about 100°C prior to acid extraction of metals. It will be shown that the reported losses of metals during dry ashing of particulates on fiberglass filters are not due to volatilization but due to retention of metal salts to glass surfaces.

Although the collection efficiency of a paper filter is not as good as that of a glass filter, the use of paper offers several important advantages over glass during sample preparation. Samples on paper filters may be dry ashed at 500°C in a muffle furnace without significant loss of metals by volatilization. Lengthy acid extractions and evaporations to recover the trace metals are avoided because the paper filter is completely destroyed during ashing. Residual ash is dissolved in acid and analyzed by AAS. The use of paper instead of glass filters for collecting particulates provides a matrix relatively free of metal impurities.

Experimental

Collection of Samples

Airborne particulates were collected at various locations in New York City for 24 h periods on 8 by 10 in. filter mats using a high volume sampler capable of drawing 0.85 to 1.4 m^3/min of air through the filter. Schleicher and Schuell 589 Green Ribbon paper filter, Gelman Type A glass filter, and Mine Safety Appliance fiberglass filter were used as sampling media. Samples for analysis consisted of 2.54-cm-diameter circles cut out from various portions of the filter mats.

Recovery of Metal Salts

Recovery experiments on salts of low melting metals such as lead, zinc, copper, and cadmium were performed employing various ashing methods and conditions in order to determine the validity of the dry ashing procedure for particulates on paper filters. Methods previously developed for determining the volatility of alkali salts [*9*] were adapted for this study. Known amounts of metal salts in open platinum crucibles were heated at various temperatures in a muffle furnace. The residue was dissolved with nitric acid (HNO_3) and the metals determined by AAS. High purity acids and deionized water were used throughout.

Dry ashing data were compared against data obtained by two methods of oxidizing organic material in which loss of metals by volatilization is negligible, namely, low temperature ashing (LTA) and wet ashing [*10*].

Dry Ashing

Samples and metal salts in open platinum crucibles were heated in air in a carefully regulated muffle furnace. Filter paper samples were first wetted with a few drops of sulfuric acid (H_2SO_4) and placed in a vented furnace at 300°C for ½ h. At this temperature the paper was charred slowly and did not ignite to a flame. The preliminary heating ensures that sample loss will not occur by turbulence and high temperatures associated with flaming. The temperature was raised to and held at 500°C for 1 h. The residue in the crucible was dissolved with 2 ml hydroflouric acid (HF) + HNO_3 (1 + 3) and the solution evaporated to dryness to get rid of silicates. The residue was dissolved in 1 ml HNO_3 and diluted to 10 ml for AAS analysis. Unused filters were similarly treated for determination of metal blank corrections.

Wet Ashing

Filter paper samples were digested with perchloric acid-nitric acid solution (1 + 2) in a conical flask. The flask was then strongly heated to ~180°C until the solution cleared and dense fumes of perchloric acid were evolved. After cooling, the solution was diluted for analysis by AAS. Fiberglass filter samples were digested in the same manner followed by filtering out and washing of the filter pulp. The filtrate was then subjected to metals analysis by AAS.

Low Temperature Ashing (LTA)

Samples were oxidized at ~100°C in platinum crucibles with an excited oxygen plasma provided by a Tracer Lab low temperature asher, Model LTA-600L. Residual material was dissolved with HF + HNO_3 (1 + 3), the solution evaporated to dryness, and the residue dissolved in HNO_3 for analysis by AAS.

Elemental Analysis

Concentration of metals in solutions were determined with a Jarrell Ash Model 82–360 atomic absorption spectrometer incorporating a Techtron laminar flow burner assembly with air-acetylene flame. Absorption measurements were made at the most sensitive resonance line for each element using appropriate calibration solutions.

Discussion

Filter Mats

S&S 589 Green Ribbon paper was used because it had the lowest metal impurity level of the papers tested. Also, the 24 h flow rate change of 589 paper (from 1.1 to 0.99 m^2/min) due to pore clogging was less than the other papers tested. Fiberglass filters, on the other hand, showed essentially constant flow rates throughout the sampling period. Cellulose ester membrane filters, which are the most efficient in trapping very small particulates, were unsuitable for high volume sampling because of the low flow rate and tendency for clogging.

The relative efficiencies of paper and fiber glass filters were determined by backing S&S green paper with Mine Safety glass filters and collecting 24 h particulate samples. An average of 2.9 percent of the total solids collected passed through the paper filter and was retained by the glass filter. Analysis showed the concentrations of metals on the glass filter to be negligible compared to that retained on the paper filter.

Volatilization of Metal Salts

Open platinum crucibles containing known quantities of lead, copper, zinc, and cadmium as chloride, nitrate, and sulfate salts were heated at various temperatures for 1 h. The recoveries of metals from the crucibles after heating at 400, 500, and 600°C are compared in Table 1. Retention of salts by the platinum was negligible when the crucibles were etched with aqua regia and checked for metals. Thus, the material not recovered was assumed to have volatilized. The low recoveries for the chlorides of lead, zinc, and cadmium indicate the tendency of these compounds to volatilize readily at temperature as low as 400°C. The low recoveries for lead chloride were consistent with those reported by Gorsuch [*11*] who heated the salt for 4 h at 650°C. Very good recoveries of the nitrates and sulfates of lead, copper, zinc, and cadmium were obtained at 500°C. Losses of varying magnitude were observed for all metal salts tested at 600°C.

TABLE 1—*Recovery of metal salts from Platinum crucibles after heating at various temperatures (°C) for 1 h.*

		Recovery in Percent								
		Chloride, °C			Nitrate, °C			Sulfate, °C		
Metal	μg	400	500	600	400	500	600	400	500	600
Pb	50	78	54	21	100	102	96	102	102	96
Zn	40	87	87	62	99	97	88	96	97	97
Cd	10	77	56	17	102	100	83	100	100	96
Cu	30	96	96	71	104	98	77	102	100	56

TABLE 2—*Effect of H_2SO_4 on recovery of metal chlorides from Platinum crucible after dry ashing starting at 300°C for ½ h and then at 500°C for 1 h.*

		Recovery in Percent			
		in Pt Crucible		On Paper Filter in Pt Crucible	
Metal	μg	Chloride	H_2SO_4 Added	Chloride	H_2SO_4 Added
Pb	50	74	96	85	98
Zn	40	85	100	95	103
Cd	10	76	98	90	96
Cu	20	91	94	87	102

Table 2 shows the effect of H_2SO_4 as an ashing aid to suppress the volatilization of metals. The recovery of metal chlorides heated at 500°C is compared with that of chlorides converted to less volatile sulfates by the addition of small amounts of H_2SO_4 prior to ashing. Essentially total recovery was accomplished with the addition of H_2SO_4 to metal salts both in the absence and presence of filter paper. The value of wetting samples with H_2SO_4 prior to ashing is evident.

Retention Losses

The loss of metals by retention to glass filters at high temperatures is shown in Table 3. Fiberglass filters were impregnated with metal salt solutions of lead, copper, zinc, and cadmium and heated in open platinum crucibles at 500°C for 1 h. The metals were leached from the filter by

TABLE 3—*Recovery of metals from impregnated glass filtering mats, heated in Platinum crucibles for 1 h at 500°C.*

			Recovery in Percent		
Metal	μg	Anion	Acid Extracted	Retained on Mat	Total
		Cl^-	65	32	97
Pb	50	NO_3^-	56	40	96
		$SO_4^=$	35	65	100
		Cl^-	66	33	99
Zn	40	NO_3^-	53	44	97
		$SO_4^=$	60	38	98
		Cl^-	59	37	96
Cd	10	NO_3^-	32	65	97
		$SO_4^=$	32	65	97
		Cl^-	50	44	94
Cu	20	NO_3^-	44	49	93
		$SO_4^=$	25	71	96

TABLE 4—*Results of New York City particulates collected on fiberglass filter prepared by dry, wet, and low temperature ashing (LTA) for atomic absorption analysis.*

Metal	Ashing Method	$\mu g/cm^2$ Found Acid Extracted	Retained On Glass	Sum
	Dry	5.4	2.5	7.9
Pb	Wet	7.4	0.2	7.6
	LTA	8.4	0.0	8.4
	Dry	0.008	0.022	0.030
Cd	Wet	0.026	0.006	0.032
	LTA	0.014	0.0	0.014
	Dry	0.46	0.37	0.83
Cu	Wet	0.60	0.12	0.72
	LTA	0.56	0.078	0.64

consecutive 2-h extractions with hot dilute HNO_3 (1 + 1). A third extraction showed no further leaching of metals from the filter. The washed filter was dissolved in HNO_3 + HF (1 + 3), the solution evaporated to dryness, and the residue analyzed for metal content. Appropriate corrections were determined for the metal impurities in the glass filter by carrying a clear filter through the same procedure. The low recovery found for each metal by acid extraction was complemented by a substantial retention of metal to the glass mat. The total recovery of metals from extract and filter averaged 97 percent. Thus, volatilization losses from glass mats at 500°C were very small compared to the losses recorded on Table 1 for metal chlorides from paper mats. The apparent "loss" of lead, copper, zinc, and cadmium at 500°C was not due to volatilization but due either to the formation of insoluble compounds as metal salts reacted with the fiberglass or by physical entrapment of metal salts by molten glass surfaces. Gorsuch reported 15 to 28 percent retention losses of lead to silica crucibles when cocoa samples containing 1 ppm Pb were ashed at 650°C [*11*]. It is not surprising that similar reactions can occur at 500°C between metal salts and fiberglass with its large area. For this reason, silica and glass crucibles should not be used for dry ashing because of the possible retention of metal salts to the vessels at high temperatures.

When nickel, iron, and cobalt salts were heated at 500°C for 1 h no loss of metals was observed either by volatilization or retention.

Analysis of New York City Particulate Samples

Thus far, the data demonstrate that metal recoveries can be influenced by the ashing temperature, the nature of the metal compound present, and the filtering medium. The suitability of employing dry ashing on actual

New York City particulate samples collected on glass and paper filters was determined. For comparison, samples were prepared for analysis by various ashing methods.

Table 4 compares results in µg metals/cm^2 found on three adjacent areas of a New York City particulate sample on fiberglass treated by dry, wet, and low temperature ashing prior to acid extraction. In each case, after the ashing and extraction, the glass mat was dissolved in $HNO_3 + HF$ (1 + 1) and analyzed for metals. As in Table 3, the results were divided into acid-extracted and retained portions. The unexposed ½ in. border of the filter mat was used to determine the blank corrections. Dry ashing results for lead, cadmium, and copper show that particulates reacted with fiberglass during dry ashing to form insoluble materials as did the metal salts on Table 3. Volatilization and retention losses were negligible for samples treated by wet ashing (~180°C) and LTA (~100°C) with one exception. The unexpected low LTA results for cadmium can be explained by nonuniformity of the sample at these low cadmium levels. Because cadmium loss by volatilization was not observed during LTA treatment of paper filters, it is not likely that cadmium will volatilize from glass filters under the same ashing conditions. Zinc determination was not possible because of the unusually high zinc content (300 µg/cm^2) of the glass filter used for this particular sample.

Ten metals were determined in duplicate on a New York City sample on paper filter. The results are given in µg/cm^2 of filter rather than the traditional µg/m^3 of air. Ther esults obtained by dry and wet ashing given on Table 5 compare favorably. The agreement between the ashing methods

TABLE 5—*Comparison of AAS results on New York City particulate sample on paper filter prepared by wet and dry ashing.*

	µg Metal/cm^2	
Metal	Wet Ashed[a]	Dry Ashed[b] 500°C
Pb	6.2 , 6.4	6.7 , 6.4
Zn	2.2 , 2.2	2.2 , 2.2
Fe	4.7	5.0 , 4.7
Cu	0.76 , 0.74	0.79 , 0.76
Cd	0.033, 0.039	0.022, 0.033
Ni	0.12 , 0.14	0.12 , 0.12
Mn	0.042, 0.042	0.053, 0.064
Cr	0.025	0.025
Co	ND[c] < 0.1	ND[c] < 0.1
V	0.37	0.43

[a] Perchloric-nitric acids.
[b] 300°C (½ h) and 500°C (1 h).
[c] ND = not detected.

TABLE 6—*Analysis of New York City air particulates on paper filter by wet ashing and dry ashing.*

	µg/cm²							
	Pb		Zn		Cu		Cd	
Sample	WA[a]	DA[b]	WA[a]	DA[b]	WA[a]	DA[b]	WA[a]	DA[b]
1	6.2	6.7	15.0	17.	2.8	3.1	0.17	0.19
2	3.3	3.3	1.1	1.1	0.45	0.43	0.03	0.03
3	9.1	8.8	2.5	2.5	1.6	1.6	0.08	0.08
4	4.7	4.8	2.0	2.3	0.93	1.0	0.03	0.03
5	6.2	6.4	0.31	0.33	0.37	0.31	0.02	0.02
6	5.0	4.8	1.7	1.7	0.37	0.34	0.03	0.03
7	3.9	3.6	1.2	1.2	0.50	0.48	0.03	0.03
8	6.7	7.1	2.2	2.3	0.79	0.84	0.09	0.09
9	3.6	3.4	1.5	1.5	0.31	0.33	0.03	0.02
10	2.3	2.3	0.62	0.65	0.31	0.34	0.03	0.02

[a] Wet ashed, perchloric-nitric acids.
[b] Dry ashed, 300°C (½ h) and 500°C (1 h).

were as close as the agreement between duplicate runs. It is evident that the distribution of particulates on the filter is uniform for the metals tested.

Table 6 compares wet and dry ashing results for samples on paper filters representing a wide range of composition. Another set of samples on paper was analyzed after initial treatment by LTA and dry ashing and the results are listed on Table 7. The close agreement of dry ashing

TABLE 7—*Analysis of New York City air particulates on paper filter by low temperature ashing and dry ashing.*

	µg/cm²							
	Pb		Zn		Cu		Cd	
Sample	LTA[a]	DA[b]	LTA[a]	DA[b]	LTA[a]	DA[b]	LTA[a]	DA[b]
11	4.8	4.7	2.5	2.5	1.2	1.3	0.17	0.17
12	5.1	4.7	0.37	0.42	1.4	1.5	1.0	1.0
13	11.0	11.0	2.5	2.5	2.9	2.9	0.095	0.099
14	4.0	4.2	1.1	1.2	0.60	0.47	0.10	0.11
15	7.9	7.3	1.1	1.1	0.39	0.36		
16	3.7	4.7	1.3	1.3	2.3	2.2		
17	4.7	5.3	2.0	2.2	0.31	0.31		
18	8.4	8.1	0.54	0.67	0.45	0.31		
19	11.0	11.0	0.50	0.56	0.68	0.71		
20	11.0	11.0	5.0	5.1	1.5	1.5		

[a] Low temperature ashed.
[b] Dry ashed, 300°C (½ h) and 500°C (1 h).

data with those of wet ashing and LTA indicate that lead, copper, zinc, and cadmium were not lost at 500°C.

The dry ashing data in Tables 5, 6, and 7 were obtained without benefit of wetting the papers with H_2SO_4 before ashing. The quantitative recoveries indicate that the metals were originally present in the particulates as nonvolatile salts such as nitrates, sulfates, or oxides as opposed to volatile chlorides. Although the addition of H_2SO_4 was unnecessary for the dry ashing of New York City samples, the use of H_2SO_4 prior to dry ashing all samples is strongly recommended to ensure quantitative recovery of metals.

Conclusion

Paper filters are used to advantage over fiberglass filters for sampling and analyzing particulate air pollutants by atomic absorption spectrometry. It has been shown that organic material, including paper, can be destroyed completely by dry ashing at 500°C without significant loss of low melting metals by volatilization. Although the chlorides of lead, cadmium, and zinc are volatile at 500°C, they can be stabilized by treatment with H_2SO_4 prior to ashing. Recovery experiments show that dry ashing lead, copper, cadmium, and zinc salts on fiberglass filters at 500°C results in serious loss of metals by retention to glass surfaces. Analysis of New York City particulates employing dry ashing give results which compare favorably with those obtained by wet ashing and low temperature ashing.

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