FLAMELESS ATOMIC ABSORPTION ANALYSIS: *AN UPDATE*

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Foreword

The symposium on Flameless Atomic Absorption Analysis: An Update was presented at the Seventy-eighth Annual Meeting of the American Society for Testing and Materials held in Montreal, Canada, 22-27 June 1975. Committee E-3 on Metallography sponsored the symposium. O. P. Bhargava, Steel Company of Canada, Ltd., presided as symposium chairman.

Related
ASTM Publications

Manual on Recommended Practices in Spectrophotometry (E-13), (1969)
(03-513069-39)

A Note of Appreciation to Reviewers

This publication is made possible by the authors and, also, the unheralded efforts of the reviewers. This body of technical experts whose dedication, sacrifice of time and effort, and collective wisdom in reviewing the papers must be acknowledged. The quality level of ASTM publications is a direct function of their respected opinions. On behalf of ASTM we acknowledge with appreciation their contribution.

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Introduction

Introduction

The early work of L'vov in the 1950's with a graphite oven to provide the atom reservoir utilized in atomic absorption spectroscopy went largely unnoticed in the West until about 1965. Many variants of this original concept were then explored, with the Massmann-type and the West-type flameless device being perhaps the most noteworthy versions.

With the commercialization of these developments, the techniques now available to the analytical chemist greatly enhance the attractiveness of flameless atomic absorption spectroscopy. A symposium was consequently organized to update the interested members of the American Society for Testing and Materials, particularly those of Committees E-2 on Emission Spectroscopy, E-3 on Chemical Analysis of Metals, and E-16 on Sampling and Analysis of Metal Bearing Ores and Related Materials, in the broadened possibilities.

The papers selected for publication in this volume highlight the potential of the flameless atomic absorption approach but include some recent advances in the field of inductively coupled plasma-emission spectroscopy as well to provide a balanced outlook. They represent the distilled expertise of internationally recognized academic scientists and industrial chemists required to analyze complex real-life materials both accurately and precisely.

As such, this volume should prove valuable both to those just beginning to venture into the field of flameless atomic absorption spectroscopy and to those already familiar with it and who wish to keep abreast of the most recent developments. Judging from enquiries already received from numerous individuals and international institutions, we hope that its appearance will fill a real need.

Om P. Bhargava

Steel Company of Canada Ltd., Hamilton, Ontario, Canada; symposium chairman.

Ray Woodriff,[1] *J. R. Amend,*[1] *and D. A. Bath*[1]

Nonflame Atomic Absorption with a Constant Temperature Atomizer

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REFERENCE: Woodriff, Ray, Amend, J. R., and Bath, D. A., "Nonflame Atomic Absorption with a Constant Temperature Atomizer," *Flameless Atomic Absorption Analysis: An Update, ASTM STP 618*, 1977, pp. 3-10.

ABSTRACT: A short review of the present state of nonflame atomic absorption spectroscopy is provided. The effect of a number of matrix components on the determination of analyte elements in a constant-temperature furnace is discussed. A new method for multielement analysis is described. Components of the analytical apparatus have been used in two different ways to correct for broadband absorption and scatter. Results are reported using these two different methods of background correction with a nonflame atomizer designed by Woodriff.

KEY WORDS: atomic absorption, atomic spectroscopy, elements, temperature, furnaces, analysis, absorption band, scatter, atomizers

There must be reasons for the spectacular development and acceptance of atomic absorption spectroscopy as a means of obtaining analytical data. Two reasons for this acceptance must surely be relative freedom from matrix effects and simplicity of the spectrum in comparison to emission methods. If atomic absorption is not merely a passing fad, it is interesting to speculate what direction new developments will take. Flames have received the most attention so far, but they have some inherent limitations. Because of the combustion process, there are turbulences and nonuniformities which tend to give a noisy signal. Also, the combustion gases dilute the sample. The combustion process limits the analyte residence time, except for flames in tubes, and these have undesirable memory effects because the confining walls are cooler than the flame.

Nonflame devices are newer than flames, and there is still much research to be done. Strips, filaments, and rods have been given considerable attention [*1-3*].[2] They use rapid heating and depend on the support gas to confine the sample atoms to the optical path. They are simple, inexpensive, and, in many ways, more convenient than flames. However, it is hard to make consistent,

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

dependable measurements when the sample is not at constant temperature, and the problem is made even worse by the rapidity with which the sample diffuses out of the light path.

Massmann type furnaces [*4,5*] and the Varian carbon rod [*6*] are intermediate between strips, filaments, and rods, and the constant temperature furnaces such as the one developed in Russia by L'vov [*7-10*], and the one developed at Montana State University (MSU) [*11-14*].

Woodriff, in a recent article, reviewed the advantages of the four major kinds of tube furnaces in detail [*15*]. Koirtyohann and Wallace provided an interesting critical comparison of three of these systems [*16*].

The increase in sensitivity brought about by these units has rekindled interest in the study of all aspects of atomic absorption spectroscopy. Provision for multielement capability and systems for background correction are subjects of current interest.

Procedures and Instrumentation

Figure 1 shows a Woodriff constant temperature furnace. Samples are introduced in small, graphite crucibles from either the side or bottom. If introduced from the bottom, as in the unit shown in Fig. 1, the pedestal on which they rest makes the seal so that both walls of the crucible are in the chamber. This is especially important for porous crucibles which are used to filter particulates from liquids or gases. For example, 200 ml of air filtered through such a crucible is ordinarily sufficient to give a dependable measure of lead in air at that time and place [*17*]. Liquid samples for dissolved analytes are pipetted into crucibles held in a tray. The tray is placed under a heat lamp or in

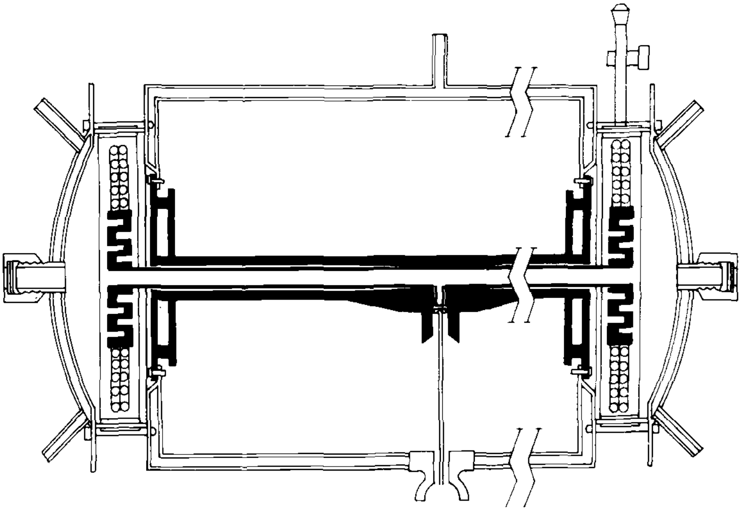

FIG. 1—*Woodriff furnace with pedestal sample injection system.*

an asher. In this way, a hundred or more samples can be processed simultaneously. Conditions can be precisely controlled even to the extent of using a microwave asher. Solid samples are weighed into the crucibles and inserted into the furnace. Instrumentation is as reported in prior publications [*13,14*]. The dual wavelength spectrophotometer was built at Montana State University [*18*]. Samples analyzed were reference materials provided by National Bureau of Standards (NBS) and Hoffmann-LaRoche (H-L).

Results

Cation Effects

Much work in nonflame atomic absorption spectroscopy is done using peak height mode of data acquisition. Several studies have been made to determine the effect of various cations on the peak height mode determinations of other elements, particularly silver. Table 1 shows that, in general, the quantitative results obtained with the Woodriff furnace do not depend upon the matrix cations present. Table 2 shows exceptions to this generalization. For the more refractory elements, tantalum and tungsten, a reduction in peak silver absorbance was noted. This effect could be eliminated by increasing the temperature. A reduction of peak absorbance was also found when cadmium, zinc, lead, and manganese were determined in the presence of tantalum and tungsten. For aluminum, iron, nickel, and cobalt, the peak absorbance signal could not be corrected by increasing temperature. Reducing the amount of tantalum and tungsten by a factor of 10, from 1×10^{-5} to 1×10^{-6} g eliminated this matrix error. Reduction of peak absorbance in the presence of refractory metals is indicative of a change in vaporization rate of the absorbing element. In such a case, peak heights would be decreased. Subsequent work using peak area mode of measurement has led to the elimination of most of these problems.

Multielement Analysis

Multielement capability is most desirable. Obviously, it is better to run ten elements on one sample of baby's blood rather than one element on each of ten samples. Even aside from limited sample size, it is often a great saving in effort to run several elements simultaneously on the same sample.

The use of double-windowed, multielement consecutive hollow cathodes is one way to answer this need (Fig. 2). The use of consecutive hollow cathodes makes use of the advantages of atomic absorption and sharp line sources with only a small loss in light intensity. This system requires a multichannel spectrophotometer. An ideal instrument for this purpose is the spectrophotometer-direct reader combination described in Ref *18*. It consists of one or two channels which scan the spectrum. In addition, provision is made for five or ten fixed channels which can be set and left on specific element lines. The instrument has two arms that rotate about the center of the Rowland circle. The

TABLE 1–*Effect of various cations on the absorbance of silver at 1750°C.*

Cation Added	Amount Added	Blank Absorbance	Absorbance (Blank + 5 x 10^{-10}g Ag)	Net Absorbance for 5 x 10^{-10}g Ag
None	. . .	0.030	0.517	0.487
	. . .	0.030	0.472	0.442
	. . .	0.030	0.488	0.458
	. . .	0.030	0.486	0.456
Al	3 x 10^{-5}	0.021	0.480	0.459
	3 x 10^{-5}	0.027	0.516	0.489
	5 x 10^{-5}	0.022	0.488	0.466
Cr	5 x 10^{-5}	0.026	0.484	0.485
	5 x 10^{-5}	0.036	0.467	0.431
	1 x 10^{-4}	0.029	0.476	0.447
Cu	4 x 10^{-6}	0.041	0.491	0.450
	1 x 10^{-5}	0.044	0.490	0.446
Fe	4 x 10^{-6}	0.033	0.486	0.453
	1 x 10^{-5}	0.035	0.494	0.459
Ni	4 x 10^{-6}	0.031	0.476	0.445
	1 x 10^{-5}	0.033	0.488	0.455
Mn	4 x 10^{-6}	0.029	0.502	0.473
	1 x 10^{-5}	0.027	0.475	0.448
Zn	4 x 10^{-6}	0.028	0.476	0.448
	1 x 10^{-5}	0.029	0.484	0.455
Mg	4 x 10^{-6}	0.029	0.486	0.455
	1 x 10^{-5}	0.029	0.467	0.438

TABLE 2—*Effects of tantalum and tungsten on the absorbance of silver at various temperatures.*

		Absorbance 1×10^{-9}g Silver		
Cation Added	Weight Cation Added, g	1750°C	2050°C	2400°C
None	...	0.965	0.970	0.966
Ta	1×10^{-5}	0.888	0.943	0.962
	1×10^{-4}	0.834	0.921	0.960
	1×10^{-3}	0.765	0.834	0.921
W	1×10^{-5}	0.810	0.935	0.961
	1×10^{-4}	0.795	0.911	0.956
	1×10^{-3}	0.720	0.795	0.911

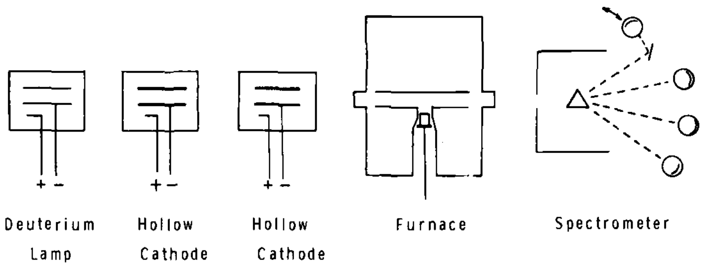

FIG. 2—*Consecutive hollow cathode system.*

arms carry photomultiplier tubes on their outer ends and narrow mirrors which reflect light up and down from the plane of the Rowland circle into the photomultipliers. Mirror combinations are made to face the grating by collapsible tubes attached above and below the grating. This leaves the Rowland circle free for fixed photomultipliers except for the two narrow shadows of the mirrors carried on the rotating arms.

Initial multielement work using this monochromator with commercial hollow cathodes has been reported [*16*]. This instrument is now being fitted with consecutive hollow cathodes in order to continue the study. Work done with other monochromators indicates that this system has much promise.

The system allows the combining of several light sources with only a small loss of light intensity. The advantages are obvious when compared with half-silvered mirrors or rotating mirror choppers.

In addition, the use of several sequential hollow cathodes rather than one multielement hollow cathode allows the user to adjust each source independently and achieve optimum conditions for each element.

Background Correction

In order to provide background correction, the dual wavelength monochromator described has been used with one channel set on an element line and the other set on a nearby nonresonance line. Table 1 shows the results of determinations of lead in various matrices. Of the three matrices, the "sulfur drug" presented the most problems. The samples yielded large amounts of smoke and hydrogen sulfide (H_2S) when inserted into the furnace. Addition of nitric acid (HNO_3) reduced these problems sufficiently for the analysis to be performed. The background absorption varied depending upon the nonresonance line used, indicating that molecular absorption, rather than scattering by particles, was occurring. This problem was overcome by plotting wavelength versus background absorption on both sides of the resonance line and interpolating an average background absorption/mg of sample. This was done both with the nonresonance lines emitted from the hollow cathode and with a hydrogen continuum lamp. Using this technique, the result reported in Table 3 was obtained.

TABLE 3—*Results of determinations for lead using dual wavelength spectrophotometer.*[a]

Sample	Pb Reported, ppm	Pb Found, ppm	RSD,[b] %
Orchard leaves (NBS)	44	43.2	8.4
"Sodium vitamin" (H-L)	1	1.04	8.3
"Sulfur drug" (H-L)	1	0.98	16.5

[a] Channel A set on Pb 283.3 nm line. Channel B set on nearby nonresonance line.

[b] RSD = relative standard deviation.

For several years, an improved background correction technique based on the sequential hollow cathode arrangement just described has been used at MSU. The system consists of a deuterium continuum source followed by one or more of the double-windowed hollow cathode lamps and then by the furnace and monochromator. The deuterium lamp and hollow cathodes are pulsed on alternate cycles. With proper electronics, the background correction can be made automatically. Even with an oscilloscope, useful values for background correction were obtained. This background correction system has advantages over others presently being used. It makes use of all the light, whereas the method developed by Koirtyohann and Pickett [*19,20*] as well as the one published by Skogerboe [*21*] used only half of the light. Also, these two methods make the assumption that the continuous light absorbed by the analyte atoms is negligible. This is approximately true since the spectral line width is small compared to the slit width. With the background correction system developed at MSU, this assumption is unnecessary since the continuum light passes through the analyte hollow cathode on its off cycle, and the atomic line wavelengths are removed from the continuous light before it enters the sample chamber. Thus, the background signal will stay constant regardless of how many analyte atoms are in the chamber and is therefore a faithful measure of background or continuous absorption.

Some of the first work was done using an oscilloscope as a readout system. This is not the most desirable way to obtain numbers on real samples, but it gives an insight into the functioning of the components of an instrument. Also a hydrogen or deuterium hollow cathode that could be pulsed was not available, so an iron hollow cathode was used to correct for background absorption of the silver line. The iron lines are close enough to the silver lines to go through the slit but not close enough to be absorbed by the silver atoms. This arrangement is not as satisfactory as having the background wavelengths on both sides of the analyte line. Known silver samples with and without known background absorption-producing material present were analyzed. Also, the background producing material was analyzed. These samples were run both with the light from the iron hollow cathode blocked and unblocked. From the oscilloscope patterns and readings, it was possible to obtain a background correction and calculate the true absorbance. Subsequent work with the proper amplifiers and other electronics showed that it is possible to make the correction automatically. The system has shown itself capable of eliminating interference from large amounts of molecular species such as silicone dioxide (SiO_2) and from smaller amounts of organic matter and water. Background absorptions up to 1.5 absorbance can be corrected for by this system. This compares quite favorably to values claimed for commercial units. Light source stability was found to be ±2 percent. The same stability was obtained using a commercial hollow cathode tube with the system electronics. Commercial multielement or one-element hollow cathodes, of course, have only one window so continuous hydrogen light cannot be passed through them for background correction.

Table 4 shows results obtained for copper using this system.

TABLE 4–*Results of determinations of copper using sequential hollow cathodes.*[a]

Sample	Cu Reported, ppm	Cu Found, ppm	RSD,[d] %
Glass (NBS)	0.80	0.82	4.9
Water[b]	0.004[c]	0.004	7.0

[a] Double-windowed copper lamp preceded by a H_2 lamp.

[b] 5 ml of water left in cup to produce background.

[c] Amount added.

[d] RSD = relative standard deviation.

Conclusions

Interelement effects have been studied. The correct choice of temperature and mode of data acquisition has been found to correct for these effects.

A system for multielement analysis and background correction which would require the manufacture of a new type of hollow cathodes has been described. These hollow cathodes could be used in present instruments to replace standard hollow cathodes, but, with windows on each end, they would be the only kind suitable for these new techniques. Until such time as these hollow cathodes are commercially available, these techniques probably will not be widely accepted. This system, with spectrophotometer-direct reader combinations such as the one described, will surely be applied in the future to analytical problems because of the increasing need for multielement capability with simultaneous background correction capability in atomic absorption spectroscopy.

Acknowledgment

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J. Y. Marks[1] *and G. G. Welcher*[1]

Determination of Trace Elements of Metallurgical Interest in Complex Alloy Matrices by Nonflame Atomic Absorption Spectroscopy

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REFERENCE: Marks, J. Y. and Welcher, G. G., "Determination of Trace Elements of Metallurgical Interest in Complex Alloy Matrices by Nonflame Atomic Absorption Spectroscopy," *Flameless Atomic Absorption Analysis: An Update, ASTM STP 618*, American Society for Testing and Materials, 1977, pp. 11–21.

ABSTRACT: Atomic absorption with the high-temperature graphite tube furnace as an atomization source has proven to be particularly versatile in the determination of trace elements in complex alloys such as those used in gas turbine engines. Elements which are harmful to mechanical properties at levels of from 0.1 to 10 ppm include lead, bismuth, thallium, selenium, and tellurium. Indium, antimony, tin, and gallium are harmful at concentrations between 10 and 50 ppm. Accurate and reliable nonflame methods have been established in our laboratory for the determination of all these elements in complex alloys. Proper optimization of several variables is important in obtaining good results. The choice of dissolution medium is important to prevent volatilization losses of trace elements during sample preparation and during the thermal cycle before sample atomization. Selection of proper heating parameters before atomization can be instrumental in reducing background absorption and in realization of best sensitivity. Good alignment of analyte hollow cathode beam with background correction beam is critical for realization of maximum sensitivities. A comparison of the direct nonflame atomic absorption technique with other methods for trace element analysis such as emission spectroscopy, mass spectrometry, and flame atomic absorption after preconcentration shows advantages of speed, accuracy, and versatility. Recent work in our laboratory has suggested that some trace element determinations may be possible using direct atomization of the element from alloy chips. Significant advantages in sensitivity, reduction of background absorption, and speed may result from atomization from metal chips.

KEY WORDS: atomic absorption, atomizing, alloys, trace elements, analysis

Atomic absorption spectrometry utilizing a variety of electrically heated furnaces as atomization devices has proven to be the most successful method of analysis for a variety of important trace elements in high-temperature alloys.

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Methods have been published or reported on for the determination of lead, bismuth, selenium, tellurium, thallium, gallium, antimony, tin, and indium.[2,3] Optimum conditions for the determination of arsenic will be discussed in this presentation. Both chemical and instrumental variables important in obtaining reliable trace element analyses are reviewed, and a critical comparison of the merits of the technique with other analysis methods such as emission spectroscopy, mass spectroscopy, and flame atomic absorption will be made. Finally, current developments in direct atomization of trace elements from metal chips will be discussed.

The trace elements of most metallurgical interest are shown in Table 1. Present Pratt & Whitney Aircraft specifications allow no more than 0.3-ppm bismuth, 3-ppm selenium, or 10-ppm lead in materials for use in high temperature-high stress applications. While there are, at present, no Pratt & Whitney Aircraft specifications on tellurium and thallium, the harmful effect of these elements on physical properties at levels of 0.3 and 5 ppm, respectively, is recognized, and the concentrations of these two elements must also be reported. Recently, the Aerospace Material Specification Division of the Society of Automotive Engineers, Inc. has drafted a new specification, AMS 2280, for trace element control in nickel alloy castings. This specification is intended for use in highly stressed rotating parts such as turbine blades and calls out maximum allowable levels of antimony, arsenic, cadmium, gallium, germanium, indium, tin, gold, mercury, potassium, silver, sodium, thorium, uranium, and zinc at 50 ppm in addition to lead, bismuth, selenium, tellurium, and thallium in certain classes of materials. While the bulk concentrations of many of these elements are quite low, there is experimental evidence that some elements may concentrate in alloy grain boundaries, and thus the effects are magnified.

Analysis Procedure

The procedure developed for the analysis of high-temperature alloys for trace elements by furnace atomization atomic absorption is outlined in Table 2. The preferred method of standardization depends on the trace element analysis workload in the laboratory. When only occasional trace element analysis is required, the use of synthetic standards is recommended. These may be prepared by doping solutions prepared from stock solutions of the alloying elements combined to simulate alloy composition with varying concentrations of the trace elements. Control is maintained over acid concentrations to match unknowns. If alloy material similar to that to be analyzed is available which is relatively free of the trace elements to be determined, then portions of this material can be dissolved and subsequently doped with trace elements at varying concentrations.

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TABLE 1—*Important trace elements in high-temperature alloys.*

Element	Concentration, ppm in alloy
Bi	0.3
Te	0.3
Pb	10
Se	3
Tl	5
Sb,As,Cd,Ga,Ge,In,Sn,Au, Hg,K,Ag,Na,Th,U,Zn	50

TABLE 2—*Sample analysis procedure.*

1. Weigh 1-g metal chips and transfer to a Teflon beaker.
2. Add 30 ml of a 1:1:1 volume mixture of water, nitric acid, and hydrofluoric acids. Warm gently.
3. After dissolution is complete, reduce the volume to approximately 5 ml by evaporation.
4. Add approximately 25 ml water and warm to dissolve all salts. Cool, transfer to a 50-ml polypropylene volumetric flask, and dilute to volume.
5. Atomize samples and standards using suggested conditions.

If, however, the laboratory is involved in a continuing program of trace element analyses in materials of similar composition, the fabrication of cast alloy standards is worthwhile. An ingot of alloy material which is relatively free of the trace elements of interest is obtained. The ingot is then cut into several sections. The weight of these sections should be approximately one half the weight of the final standard ingot desired. For each standard, a hole is drilled into one of the ingot sections. The trace elements are weighed carefully to result in the desired final concentrations in the ingot and transferred to approximately 10 g of aluminum powder. After mixing, the powder is pressed into a pellet which is placed inside the hole drilled in the ingot section. The drilled ingot section containing the pellet is then spot welded to an undrilled ingot portion. This material is then transferred to a crucible inside a vacuum induction furnace, and the furnace is evacuated. Argon is bled into the furnace to bring the pressure to slightly less than 1 atm. The crucible is heated to melt the material. When melting is complete, the crucible is held at temperature for approximately 2 min to ensure proper mixing, and then the charge is poured into a mold and cooled to produce the doped ingot. The mold is removed and the ingot cleaned and cut into a number of sections from top to bottom. Metal chips are removed for each section and analyzed to check for homogeneity and to establish trace element concentrations in the material. The materials are then ready for use as standards.

Experimental Variables

Dissolution Medium

The proper choice of acid or acid mixture for sample dissolution will have a major effect in the determination of trace elements in high alloy samples. An important consideration is the volatility of the trace element salts formed with the acids. Trace elements may be lost due to volatility during both the dissolution step and during preatomization heating cycles. The choice of dissolution acids may also have a large effect on nonanalyte light attenuation during the atomization step.

When matrix salts which are relatively more volatile than analyte salts are formed, volatilization of much of the matrix may be effected during the char cycle before atomization. The acid mixture that we have found to be most successful in the analysis of complex alloys is a combination of nitric and hydrofluoric acids. Metal samples of up to 1 g may be dissolved quite rapidly in 30 ml of a 1:1:1 volume mixture of water, nitric acid, and hydrofluoric acid. After dissolution, the volume is reduced to approximately 5 ml by evaporation, transferred to a 50-ml volumetric flask, and diluted to volume with water. In this single solution, lead, bismuth, selenium, tellurium, thallium, gallium, antimony, tin, and indium may be determined. The solutions are stable for at least two months for all elements except tin. Sample and standard solutions should be prepared daily for tin.

Background Correction

The use of background correction when determining trace elements in high salt matrices is usually imperative to obtain a meaningful analyte signal in the presence of high nonspecific light attenuation. Some instrument manufacturers offer the choice of a ramp heating cycle during atomization to improve the analyte signal to nonanalyte light attenuation ratio by a separation of the signals with time. In most practical analyses of complex alloys, the differences in volatility are not great enough to achieve the needed separation of signals. The origin of the nonanalyte light attenuation in furnace atomization-atomic absorption is not certain; however, light losses may be due to molecular and atomic absorption or scattering. Corrections of absorbance signals for these nonanalyte sources of light loss have been made using both continuum and "nonabsorbing line" light sources. Both systems offer advantages in specific cases. When utilizing furnace atomization, it is important that background correction be made simultaneously with the analyte signal measurement for maximum accuracy. Proper alignment of the optics such that the beam geometry of the correction beam is carefully matched to the analyte beam is also important to obtain optimum absorbance correction.

Choice of Analyte Light Source

The advantage of the increased emission intensity from the electrodeless discharge lamp can be important in the determination of some elements where hollow cathode lamp output is marginal. Of the eleven trace elements which we have measured in complex alloys, selenium and arsenic have been the only elements where the electrodeless discharge tube was required to give the desired precision over the entire concentration range of interest. A disadvantage of electrodeless discharge lamps is that they are slower to stabilize than hollow cathode lamps. This is particularly important in instruments which operate without the double beam mode when background correction is required. Once the electrodeless discharge lamp has stabilized, we have found it convenient to use neutral density filters to make minor intensity adjustments rather than readjusting the power to the lamp which results in another wait for stabilization to occur.

Heating Program

Most instrument manufacturers offer at least three separate stages of heating in electrically heated furnaces: a drying step to remove solvent and excess acids; a char or ash step to remove organic matter, if present, or to decompose thermally unstable species in the case of alloy analyses; and an atomization step where the analyte species is vaporized and dissociated. The time and temperature of the dry cycle is normally not important in determining sensitivity. Drying temperature should be high enough to dry the sample in the minimum time without splattering.

The char or ash cycle may be used advantageously to remove excess matrix material when the matrix salts are relatively volatile compared with the analyte. The proper choice of acids for sample dissolution is important in taking full advantage of this method of reducing background. Proper selection of atomization temperature is important to achieve maximum analyte signal with acceptable nonanalyte light attenuation. Higher atomization temperatures result in higher background levels and should be avoided if possible.

Operating Parameters and Detection Limits

A summary of optimum heating parameters, wavelengths, and detection limits for ten trace elements in complex alloy matrices is tabulated in Table 3. These parameters were determined with a spectrophotometer (Perkin Elmer Model 403) and a furnace atomizer (Model HGA 2000) using the sample analysis procedure outlined in Table 2. The temperatures tabulated for char and atomization are those indicated on the HGA 2000 temperature scale. A comparison of measurements of furnace temperature by optical pyrometry with the indicated temperature showed the HGA 2000 scale to be accurate within

±50°C throughout the entire range where comparison was possible. A wide variation in optimum temperature for the char cycle is noted in the table (400 to 1600°C). The char temperature should be as high as possible without resulting in losses of analyte due to volatility. This results in minimum background absorbance on atomization. Optimum char temperatures in Table 3 can be correlated with the boiling points of many of the analyte salts or oxides.

TABLE 3—*Operating parameters and detection limits.*

Element	Wavelength, nm	Char, °C	Atomize, °C	Detection Limit, ppm in alloy
Se	196.0	1000	2400	0.1
Te	214.3	600	2200	0.2
Sb	217.6	400	2200	1
Bi[a]	223.1	800	2200	0.1
Ge[b]	265.2	1600	2700	0.5
Tl	276.9	500	2000	0.1
Pb	283.3	400	2000	0.1
Sn	286.3	1000	2300	0.5
Ga	294.3	1500	2600	1
In	303.9	800	2000	0.5

NOTE—Char—45 s.
Dry—100°C • 45 s.
Sample concentration—1 g metal/50 ml.
Injection volume—50 μl.
Bandwidth—0.7 nm.

[a] 0.2 nm bandwidth.

[b] Lost on dissolution of sample.

Optimum atomization temperatures for maximum sensitivity also cover a wide range (2000 to 2400°C). The temperature for maximum sensitivity is determined by analyte volatility and background absorption considerations. The atomization temperature should be as low as possible to atomize the analyte. This helps in keeping background absorption to an acceptable level.

New Type of Interference

When trace elements are determined in complex alloys without separations, there exists the possibility of an interference not normally encountered in flame atomic absorption or with furnace atomization in simple matrices. The interference is due to atomic absorption by the alloy matrix atoms of the continuum source used for background correction. This phenomenon can result in overcorrection of the absorption signal, and thus bias readings low or give erractic results. Figure 1 shows a series of percent absorption readings using the deuterium lamp in the PE 403 as the only light source. Samples of B 1900 alloy solution were injected into the furnace and charred at 800°C using standard conditions. The signal was recorded on atomization at 2200°C with the monochromator set for various wavelengths of interest. The signals recorded

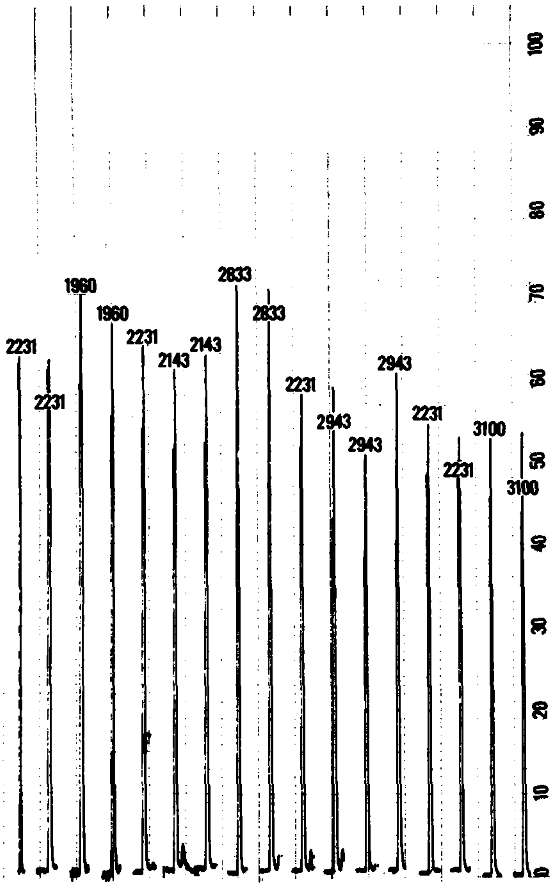

FIG. 1–*2200°C atomize temperature continuum source.*

show the background signal to be relatively constant from 1960 to 3100 Å. Figure 2 shows the results of a similar study using an atomization temperature of 2500°C. As expected, the signals are all higher than at a temperature of 2200°C. However, some wavelengths show particularly large enhancements. These areas are regions rich in matrix spectral lines. At the higher atomization temperature, these matrix elements are atomized and produce significant errors in the measurement of background signal.

Determination of Arsenic in Alloys

Arsenic cannot be determined after initial sample dissolution in acid mixtures containing fluoride. The sample must first be digested in a mixture of nitric acid and hydrochloric acid until no further reaction occurs. The insoluble residue remaining after this treatment may be dissolved by adding 1 ml of hydrofluoric acid at room temperature and swirling until the solution clears. The samples are

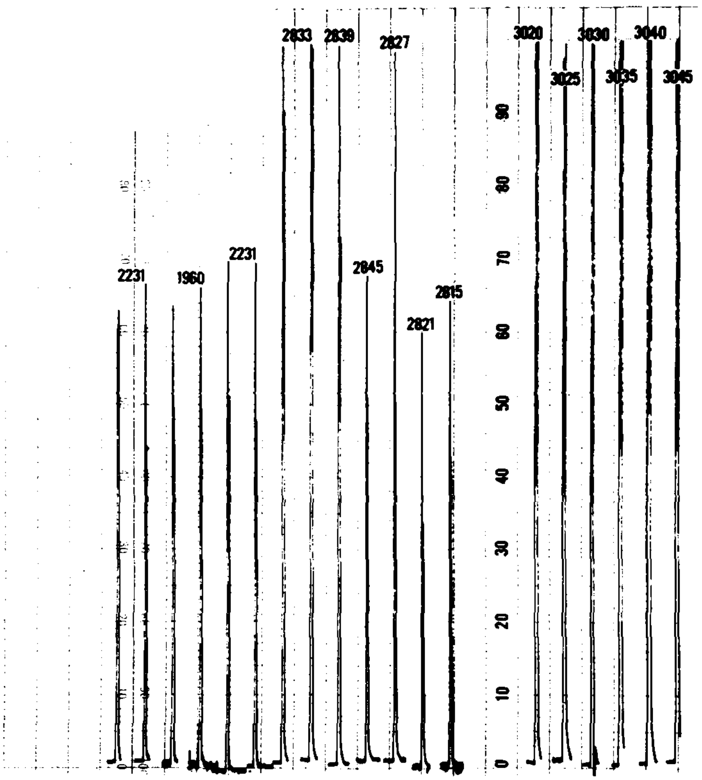

FIG. 2–*2500°C atomize temperature continuum source.*

then transferred to 50-ml volumetric flasks and diluted to volume with water. Standards are prepared by spiking alloys of known arsenic content after dissolution in a manner similar to the samples. Both samples and standards are atomized according to the conditions tabulated in Table 4. The electrodeless discharge lamp is necessary to obtain the detection limit needed for arsenic in high-temperature alloys. The chemistry leading to the successful determination of arsenic after dissolution in the nitric-hydrochloric acid mixture is unclear. Both +3 and +5 halides or complex halides may form. The fluorides are reported to be much more volatile than the chlorides. The char temperature resulting in maximum sensitivity is far above the reported boiling points of the oxides or halides of arsenic or the metal.

Comparison With Other Techniques

Atomic absorption utilizing furnace atomization techniques has proven to be the most successful method available for the accurate determination of metallurgically significant trace elements in complex alloys. The excellent sensitivity of the method allows direct atomization of trace elements without

TABLE 4—*Suggested instrument parameters for determination of arsenic.*

Wavelength, nm	193.7
Bandpass, nm	0.7
Dry, °C • s	95°C • 40 s
Char, °C • s	1400°C • 30 s
Atomize, °C • s	2100°C • 5 s
Sample concentration	1 g/50 ml
Injection volume	50 μl
Detection limit, ppm in alloy	2

prior separation, thus avoiding problems of mechanical or chemical losses and contamination possibilities. The determination is quite rapid compared with other trace element techniques, particularly in the analysis of samples for a single element.

Emission spectroscopy techniques have the advantage of recording spectral information for the determination of many elements simultaneously; however, sensitivity is poor for some trace elements of greatest interest, and spectral interferences are a serious problem in complex alloys. Spark source mass spectrometry has excellent sensitivity for a large number of elements, but, to date, quantitative analysis by this technique has been applied only infrequently. The method is quite effective for a qualitative examination of alloy samples prior to quantitative analysis by atomic absorption. Special techniques have been described for determining selected trace elements in complex alloys by polarography, X-ray fluorescence, or wet spectrophotometry. These methods are capable of quite good accuracy; however, the lengthy separations are a disadvantage.

Current Developments

Procedures have now been established for the determination of lead, bismuth, selenium, and tellurium in complex alloys by direct atomization from metal chips. A sample of 1 ± 0.5 mg is weighed and placed in the furnace using a solid sampling device. The sample is then atomized directly. Absorbance signals are recorded and then normalized for sample weight variations before calculations are performed. Examples of calibration relationships for lead, bismuth, and selenium are shown in Figs. 3, 4, and 5. The "ng of analyte" plotted on the x-axis may be roughly translated into "ppm analyte" since all sample weights are approximately 1 mg. Several advantages are realized with the new technique. The first is the advantage of increased speed of analysis. The sample dissolution time is saved; however, the major time saving results from the freedom of the need for preatomization heating cycles. This can amount to as much as 1.5 min/sample.

Lower detection limits are achieved by atomization from the solid by factors of from two to ten. Background absorbance is greatly reduced; however,

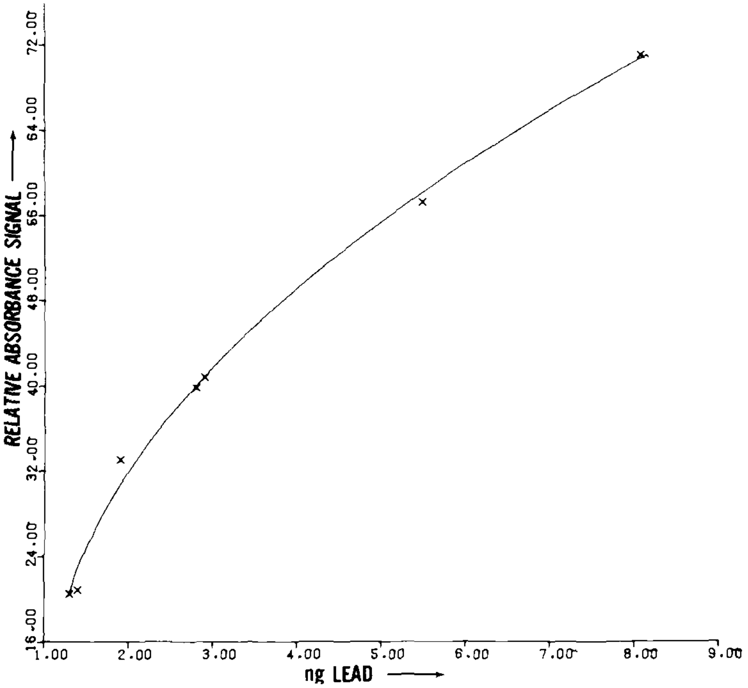

FIG. 3—*Calibration relationship for lead.*

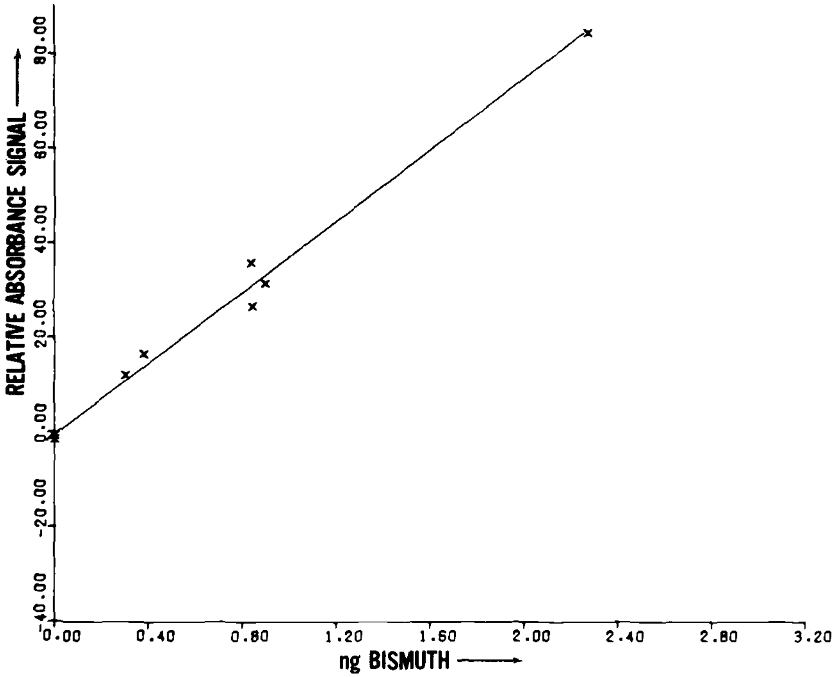

FIG. 4—*Calibration relationship for bismuth.*

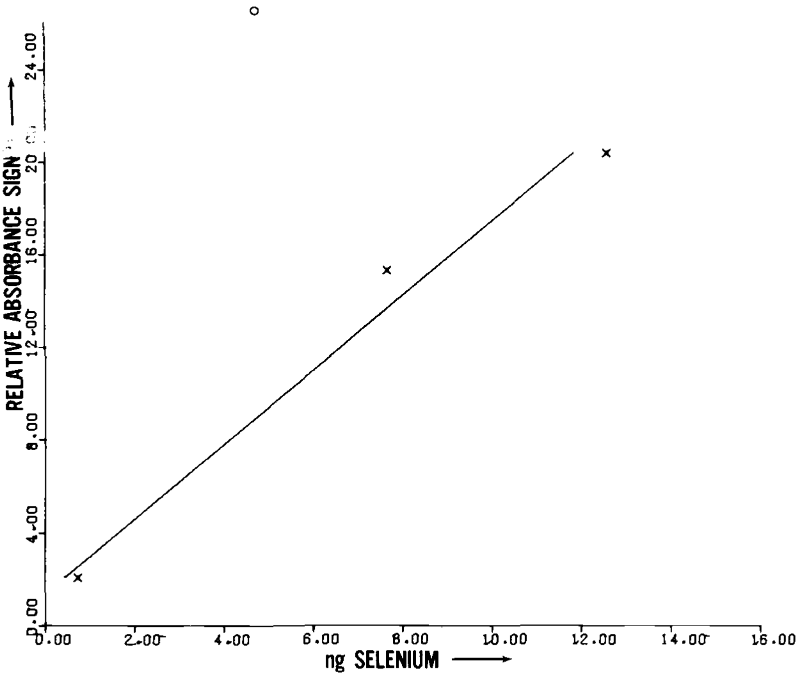

FIG. 5–*Calibration relationship for selenium.*

background correction must still be used for accurate results. The very small sample weight requirement can be a big advantage when sample is limited. A possible disadvantage of the solid technique is segregation of the trace elements on a macroscale; however, we have not observed this phenomenon in actual samples studied to date.

V. A. Fassel[1]

Inductively Coupled Plasma-Atomic Emission Spectroscopy: An Alternative Approach to "Flameless" Atomic Absorption Spectroscopy

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ABSTRACT: Atomic emission spectroscopy (AES) combined with an inductively coupled plasma (ICP) excitation source is discussed as an attractive alternative approach to "flameless" atomic absorption spectroscopy for the determination of trace elements in liquid samples of limited volume. The AES-ICP approach offers the potential advantage of: (*a*) being able to perform these determinations on a simultaneous multielement basis, and (*b*) possessing an unusual degree of freedom from interelement effects if solution nebulization techniques are utilized. For 1-ml sample volumes, the relative powers of detection (ng/ml) of the AES-ICP approach are comparable to the values reported for flameless atomic absorption procedures.

KEY WORDS: atomic absorption, emission spectroscopy, atomic spectroscopy, trace elements, liquids, plasmas

Because the focus of this symposium is on "flameless" and cold vapor atomic absorption spectroscopy (AAS), the reader should be forewarned that the discussion in this paper will not be concerned with either of these techniques. The analytical systems and experimental approaches that will be discussed are indeed flameless, but, beyond that word, there is little or no similarity except in the final analytical results. The purpose of this paper is to suggest alternative approaches for the performance of those analytical tasks that flameless atomic absorption techniques do best, that is, the determination of trace or ultratrace elements in samples of limited size. The unique features possessed by the alternative approach are its unusual freedom from interelement or matrix effects and its capability for simultaneous multielement determinations in a practical manner.

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It is unfortunate that the term flameless is now so commonly used by analysts. Key words describing any scientific process should communicate positive descriptors rather than stating what the process does not involve. Would it not have been far more desirable to use such key words as thermal or electrothermal sample vaporization and atomization (TSVA or ESVA)? In the remainder of this paper, I shall follow this suggestion and refer to electrical heating of the vaporization substrate (the furnace, rod, or filament) as electrothermal, and I shall use the acronym ESVA to designate the overall vaporization-atomization technique.

Historically, a number of motivating factors led to the development of ESVA atomic absorption or fluorescence techniques. Undoubtedly, the most important of these was the need to determine trace elements in microlitre-sized samples at higher sensitivities. The dilution of samples of this size to larger volumes amenable for analysis by the conventional solution nebulization-flame atomization techniques was, in many cases, self-defeating because sensitivities or powers of detection for many purposes were inadequate even without further sample dilution. Second, there was the justified indictment that solution nebulization-flame atomization systems were grossly wasteful of samples. Typically, only a small fraction (~10 percent) of the nebulized sample was eventually atomized. Third, the realization that much higher free-atom number densities could be realized if the dilution effect of the high-flow rates of primary fuel and oxidant and the expansion of the flame combustion products could be circumvented also contributed to the search for "nonflame" atomization systems. Fourth, there was general recognition that flames were basically not ideal atomization cells. The complex chemical reactions that sustain flames were known to generate highly reactive environments hostile to the very existence of free atoms of the elements. Moreover, for atomic fluorescence observations, the relatively high quenching cross sections of the combustion products of conventional flames was a further limitation. Finally, exposed combustion flames presented a safety hazard in some situations, and, as a consequence, their use was occasionally prohibited.

The popularity that ESVA-AAS techniques have attained attests to the success that they have achieved in overcoming some of the limitations of solution nebulization-flame atomization techniques. ESVA techniques do provide, at least momentarily, a higher analyte free-atom number density from limited amounts of samples than is possible when flames are used as atomization cells. ESVA techniques also allow greater freedom of choice in the selection of environments more favorable to the existence of free atoms.

There have been many publications on ESVA-AAS or atomic fluorescence spectroscopy (AFS) techniques since the pioneering papers by Lvov [*1*],[2] Massman [*2*], and Woodriff [*3*] appeared. An obvious reason for the rapidly expanding literature in this field is that the technique is useful. But ESVA-AAS or AFS techniques also present inherent problems, and many of the papers have

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

called attention to one or more serious limitations of the technique. Among the foremost of these limitations is the inability to perform simultaneous multielement determinations if conventional AAS or AFS techniques are utilized. Efforts are being made to adapt AAS or AFS to simultaneous multielement determinations, but problems related to the development of attractive methods of general application are certain to remain for quite some time [*4*]. Even if the primary source and other problems are solved eventually in a viable manner, additional experimental constraints are encountered in efforts to adapt AAS or AFS to ESVA techniques. These constraints are imposed by the desirability or necessity of optimizing critical vaporization-atomization parameters for each element, whereas, for simultaneous multielement capability, a single set of operating parameters should suffice.

Another important limitation of ESVA-AAS techniques is their sensitivity to serious interelement interference effects. These effects have been described, often in a fragmentary way, in a large number of papers too numerous to mention. Several recent reviews or general articles on this subject cite many of the more serious interactions [*5–14*]. These interactions are assuming more and more importance as ESVA-AAS techniques are applied to samples in which there are changes in the total composition, even at the minor constituent level. The analytical measures, whether observed in absorption or fluorescence, may be affected by: (*a*) recombination or nucleation of the free atoms after atomization or both; (*b*) the premature volatilization of relatively volatile compounds (for example, lead chloride) that are not atomized at the low temperatures prevailing at the early stages of the vaporization cycle; and (*c*) variable or incomplete analyte vaporization of the sample from the substrate. Other limitations or problems presented by ESVA-AAS techniques are: (*a*) spectral background interferences may arise from nonspecific absorption or scattering of the primary beam; (*b*) analytical curves may be nonlinear and limited in concentration range; (*c*) volatile constituents may be lost in the drying, charring, or ashing cycles; and (*d*) reproducibility may be affected by variations in the physical state of the substrate from which the sample is vaporized.

The rather long list of limitations and disadvantages just recited invites speculation on whether refinements or modifications of ESVA techniques will eventually provide viable solutions to the problems. Robbins has recently documented [*13*] a number of procedures aimed at avoiding or reducing the magnitude of these inherent problems. For example, some interelement interferences in the vaporization-atomization process may be reduced or eliminated by prior matrix-analyte chemical separations. Alternatively, a variety of standard addition, matrix compensation, matrix matching, or sample composition modification procedures, such as the molybdenum addition technique described by Henn in this publication [*16*], may be applied to reduce the magnitude of the interelement effects. Although these approaches have been applied ingeniously in overcoming one of the inherent limitations of ESVA methods, it should be noted that the additional sample manipulations and dilutions that are required detract from the attractiveness of the overall techniques. Thus, the additional manipulations may involve sample contamination, and any sample dilutions that are involved are counterproductive. Moreover, most of these procedures only temper the magnitude of the interference for a specific analysis; the basic problems remain unsolved.

Are there alternative atomization approaches not constrained by these factors? Because of recent improvements in the vaporization, atomization, and excitation sources used for atomic emission spectroscopy (AES), this technique now appears to offer a viable solution to most of the problems defined previously, while retaining the capability of measuring nanogram amounts of the elements quantitatively on a simultaneous multielement basis in microlitre- or microgram-sized samples.

Atomic Emission Spectroscopy

The observation of free atoms or ions in atomic emission has been the classical approach to simultaneous multielement determinations at the trace level. In contrast to conventional AAS or AFS, there is no requirement for an auxiliary primary source for each element to be determined. It is only necessary to devise an acceptable scheme for generating free atoms and ions of the analyte and for exciting their emission spectra. The appropriate analyte emission lines may then be isolated, in the classical way, by employing multichannel polychromators of the type shown in highly schematic form in Fig. 1.

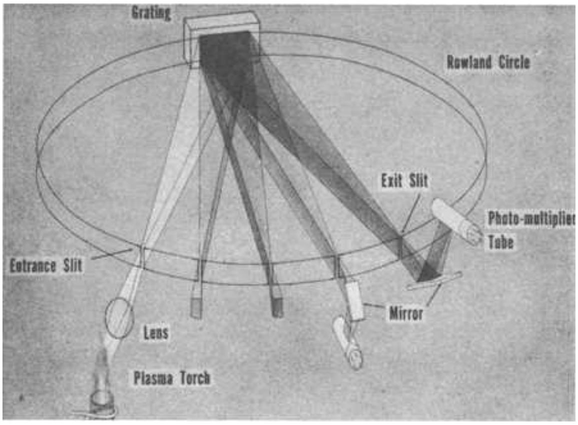

FIG. 1 – *Schematic diagram of a typical atomic emission [15] (courtesy of* Analytical Chemistry*).*

In the minds of many analysts, the importance of AES as an analytical tool for the determination of trace elements has declined during the past decade for several reasons. The foremost of these has been the remarkable success flame AAS has achieved in the years since Walsh published his first paper on the application of atomic absorption spectra to chemical analyses [*17*]. In recent years, however, the potential importance of AES for the determination of trace elements in solution has made a sharp upward turn, primarily because of major developments in the heart of any AES analytical system, that is, the vaporization-atomization-excitation source. These advances have resulted primarily from the recognition that state-of-the-art sources possessed properties that were far less than ideal. The combustion flame was such a source. As mentioned earlier, the highly reactive environment in which atomization occurs and the subsequent dilution of the analyte atoms constitute fundamental limitations to the usefulness of combustion flames. This realization led a number of investigators into devising various electrically generated "flames" or plasmas which had higher gas temperatures and less active chemical environments, and which caused less dilution of the free atoms or ions while retaining precise control of sample introduction. This search in our laboratories [*18–20*] and those of Greenfield et al [*21–23*] led to the development of a superior vaporization-atomization-excitation source for AES. This source is an inductively coupled plasma (ICP), a special type of plasma that derives its sustaining power by induction from high-frequency magnetic fields [*24,25*]. The AES analytical applications of these plasmas have been reviewed recently by Fassel and Kniseley [*15,26*], Greenfield et al [*27*], and Boumans and DeBoer [*28*].

Inductively Coupled Plasmas

To understand the nature of these plasma, it is essential to remember three simple facts: (*a*) by definition, plasmas are gases in which a significant fraction of their atoms or molecules is ionized; (*b*) that being so, magnetic fields may readily interact with plasmas; and (*c*) one of these interactions is an inductive coupling of time-varying magnetic fields with the plasma, analogous to the inductive heating of a metal cylinder. As shown in Fig. 2, the plasma is formed and sustained at the open end of an assembly of quartz tubes. The open end of the tubes is surrounded by the induction coil, which is connected to a high-frequency current generator. In our systems, the latter provides forward powers of up to ~2 kW at a frequency of 27.12 MHz. To form a stable plasma, a pattern of two, or sometimes three, argon flows, as shown in Fig. 2, is used. When these flows are adjusted properly, the plasma is readily initiated by "tickling" the quartz tube inside the coil with a Tesla discharge. The plasma is then formed virtually spontaneously. The overall plasma configuration shown is based on the pioneering work of Reed [*24,25*].

Let us now examine the course of events leading to the formation of the plasma. The high-frequency currents flowing in the induction coil generate oscillating magnetic fields whose lines of force are axially oriented inside the quartz tube and follow elliptical closed paths outside the coil as shown schematically in Fig. 3. The induced axial magnetic fields, in turn, induce the seed of electrons and ions produced by the Tesla coil to flow in closed annular paths inside the quartz tube space. This electron flow—the eddy current—is analogous to the current flow in a short-circuited secondary of a transformer. If

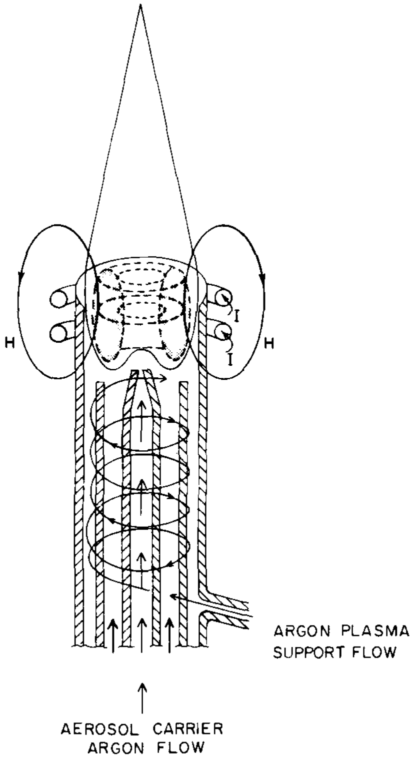

FIG. 2—*Typical inductively coupled plasma configuration.*

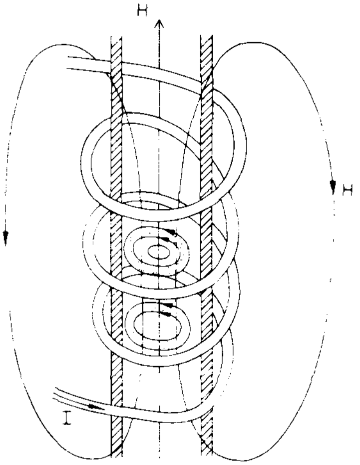

FIG. 3—*Magnetic fields and eddy currents generated by the induction coil [15] (courtesy of* Analytical Chemistry*).*

we recall that the induced magnetic fields are time varying in their direction and strength, then we can appreciate the fact that the electrons are accelerated on each half cycle. The accelerated electrons (and ions) meet resistance to their flow; Joule or ohmic heating is a natural consequence, and additional ionization occurs. The steps just discussed lead to the almost instantaneous formation of a plasma of extended dimensions whose unique properties and characteristics make it a very promising excitation source.

Thermal Isolation of Plasma

The plasma formed in this way attains gas temperatures in the 9000 to 10 000 K range [*24,25*] in the region of maximum eddy-current flow schematically indicated by the cross hatching in Fig. 2. At these temperatures, it is desirable to provide some thermal isolation of the plasma to prevent overheating of the quartz containment cylinder. This isolation is achieved by Reed's vortex stabilization technique [*24,25*] which utilizes a flow of argon that is introduced tangentially in the manner shown in Fig. 2. The tangential flow of argon, which is typically in the 10 litres/min range for the apparatus shown, streams upward, cooling the inside walls of the outermost quartz tube and centering the plasma radially in the tube. The tangential flow of argon also serves as the primary sustaining flow. The plasma itself is anchored near the exit end of the concentric tube arrangement.

In addition to the vortex stabilization flow, there is another argon flow of approximately 1 to 1.5 litres/min that transports the sample to the plasma either as an aerosol, a powder, or a thermally generated vapor. The total argon flow required is therefore ~11 litres/min. Thus, the operating cost of these plasmas, exclusive of electrical power, is approximately 50 percent lower than for a nitrous oxide-acetylene flame.

Sample Injection into Plasmas

If plasmas are to be effective atomization and excitation sources, the sample should be injected efficiently into the plasma and remain in the interior high-temperature environment as long as possible. These physical conditions have been difficult or impossible to attain in non-ICP plasma systems suggested for analytical purposes [*26*]. The ICP poses the same problem. In the ICP, the gases are heated internally, causing them to be accelerated in a direction perpendicular to the exterior surface of the plasma. There is, in addition, a magnetic pumping effect [*29,30*]. The consequence of both of these actions is that sample material tends to bypass the plasma [*20,26*]. The sample injection process must therefore overcome these thrusts, without causing collapse of the plasma.

The skin depth effect of induction heating has been used to good advantage in solving this problem. When the high-frequency current flow in the coil is increased from say 4 to 30 MHz, the region of the highest eddy-current density moves toward the outer surface of the plasma. At frequencies of ~25 to 30 MHz, an incipient annular or "doughnut" plasma shape is developed. Because the hole possesses a somewhat lower temperature than the doughnut, it offers less resistance to the injection of sample material. The annular shape can be further developed by optimizing the flow velocity of the carrier gas that injects the sample into the plasma. Thus, the degree to which the annular or toroidal shape is developed can be controlled by the frequency of the primary current generator and the flow velocity of the carrier gas stream. At ~30 MHz, a carrier gas flow of ~1 litre/min assures effective injection of the sample into the plasma, if properly designed injection orifices are used [*15,20,26*]. When the plasma is viewed from the bottom or the top under these conditions, it has the appearance of a doughnut.

Properties of the Plasma

The plasma just discussed possesses unique physical properties that make it a remarkably successful vaporization-atomization-excitation source. These properties can be interpreted by referring to the scale drawing of the plasma in Fig. 4.

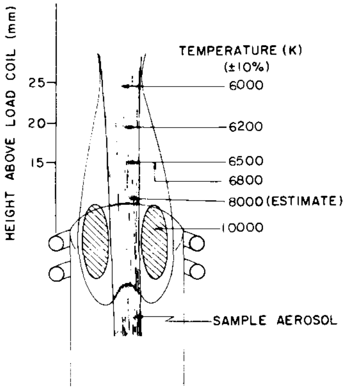

FIG. 4—*Temperatures in the plasma as measured by the spectroscopic slope method.*

According to our temperature measurements above the coil, and by extrapolative estimation down into the induction region [*31*], the sample particles experience a gas temperature of ~7000 K as they pass through the eddy-current tunnel. By the time the sample decomposition products reach the observation height of 15 to 20 mm above the coil, they have had a residence time of ~2 ms at temperatures ranging from about 8000 down to ~5500 K. Both the residence times and the temperatures experienced by the sample are approximately twice as great as those found in nitrous oxide-acetylene (N_2O-C_2H_2) flames, the hottest flame commonly used in analytical spectroscopy. The combination of high temperatures and relatively long sample-plasma interaction times should lead to complete sample vaporization and a high, essentially total, degree of atomization of the analyte species [*32*]. Once the free atoms or ions are formed, they occur in a chemically inert environment, as opposed to the violently reactive surroundings in combustion flames. Thus, their lifetime, on the average, should be longer than in flames.

With reference to interelement or matrix interferences in the vaporization-atomization-excitation process, it is important to emphasize that the sample or its decomposition products are heated indirectly via convection, conduction, and radiation as they pass through the eddy current "tunnel." There appears to be only a negligible interaction of the sample with the sustaining eddy current flow. For reasons not yet understood, the addition of easily ionizable elements to the plasma causes remarkably low ionization type interferences on analytes of low ionization energies, in contrast to the large effects commonly observed in flames.

The plasma possesses other unique advantages. First, after the free atoms are formed, they flow downstream in a narrow cylindrical radiating channel. The optical aperture or viewing field of conventional spectrometers can be readily filled by this narrow radiating channel. In this way, the radiation emitted by the free atoms or ions is used most effectively. Second, at the normal height of observation, the central axial channel containing the relatively high number density of analyte free atoms or ions has a rather uniform temperature profile. The number density of free atoms in the hot argon sheath surrounding the axial channel is far lower. Under these conditions, the analyte free atoms or ions tend to behave as an optically thin emitting source. If a large range of emission intensities can be accomodated linearly by the measurement system, linear analytical calibration curves covering five orders of magnitude change in concentration can be readily achieved. Thus, the variable dilutions often needed in flame AAS techniques are essentially eliminated.

Several unique advantages also accrue from the simple fact that the optimum region of analyte emission is separated spatially from the high spectral background region in which free atom formation occurs. Thus, sample vaporization and atomization occur in the high-temperature environment of the core of the plasma, which otherwise has little analytical utility because of the intense continuum emission. The analyte free atoms or ions released in the core may then be observed downstream in temperature environments ranging downward from 6500 K to typical combustion flame temperatures. In general, the highest signal/noise ratios for analyte species are observed in the second zone. The tail flame or third zone of the plasma is barely visible when distilled water is nebulized but assumes typical flame emission when analytes are added to the plasma. The axial passage of the sample aerosol and its decomposition products through the plasma is clearly visible.

Other advantages of these plasmas are worthy of note. No electrodes are used. Therefore, contamination from the electrodes normally used in other plasmas is eliminated. Because the plasma operates on nonexplosive gases, the system can be used in locations where combustibles are not allowed.

Typical Experimental Facilities

A typical system for the sequential determination of all of the metals and metalloids has been described [*33*]. For simultaneous multielement determinations, we have used classical multichannel spectrometers of the type shown schematically in Fig. 1. Several instrument makers have committed themselves to the design and manufacture of compact spectrometers that provide adequate spectral resolution, and at least four different instruments are now commercially available.

Application of ICP-AES to the Determination of Trace Elements in Limited Volume Samples

Combination of Electrothermal Vaporization with ICP-AES

The combination of furnace or filament vaporization of samples followed by plasma atomization and excitation of the vapor offers promise of overcoming some of the limitations of standard ESVA-AAS or AFS techniques. First, because free atom and ion formation and excitation occur in the plasma, a single set of vaporization parameters should suffice for many types of samples. Second, interelement interferences arising from recombination or nucleation of the vapor above the heated filament should be minimized because the plasma subsequently atomizes the vapor cloud. Third, background interference from the filament or furnace tube and smoke from incompletely atomized samples should be minimized. Fourth, analytical curves obtained from the plasma are commonly observed to be linear over a concentration range of four to five orders of magnitude. The problems associated with variable or incomplete sample vaporization and effects due to changes in matrix composition and substrate condition on the vaporization process would be expected to remain.

Two adaptations of electrothermal sample vaporization into the ICP have been described. A filament type system, employing tantalum substrates has been described by Nixon et al [7]. Although tantalum filaments were initially employed, more recent studies [*34*] have shown that pyrolytic graphite substrates are preferred. At the high vaporization temperatures required for some samples, there is sufficient tantalum volatilization to cause spectral interference with some of the most useful analytical lines. Evidence has also been uncovered that some matrices, such as samples containing alkaline earths as major constituents, form highly refractory compounds with the tantalum substrates. The experimental facilities and mode of operation for the pyrolytic graphite filaments are basically similar to those described for the tantalum substrates [7].

Another adaptation of electrothermal vaporization followed by ICP atomization and excitation uses graphite yarn as the substrate [*35*]. A schematic drawing of this adaptation is shown in Fig. 5. The graphite yarn is incremented for each sample into a chamber through which argon gas continuously flows to the ICP. The yarn incrementing mechanism also provides electrical contact to

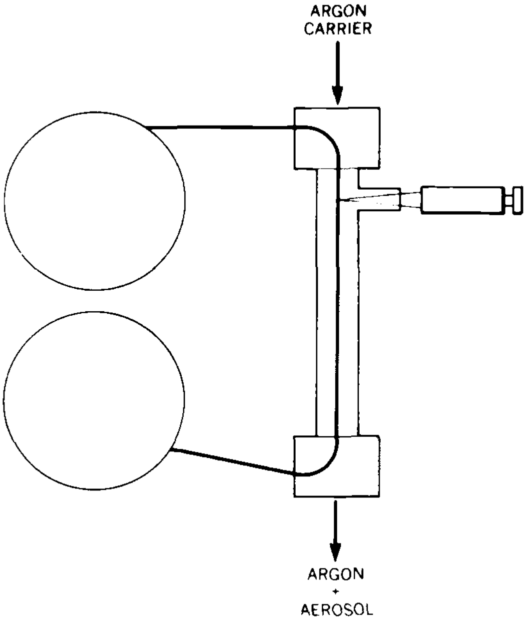

FIG. 5—*Schematic diagram of graphite yarn thermal vaporizer [35] (courtesy of Applied Research Laboratories).*

the opposite ends of the yarn in the chamber. *In situ* purification of each fresh length of yarn is achieved by passing an a-c current of ~8 A through the yarn for several seconds. The impurities evaporated from the yarn are carried to the plasma by the argon carrier gas flow. Because the thermal inertia of the yarn is low, the liquid samples, which typically range from 5 to 50 μl, can be pipetted onto the yarn immediately after the purification sequence. The liquid sample is distributed over the length of the yarn by capillary action, facilitating evaporation of the solvent at low currents. The sample is subsequently flash vaporized by passing a higher current through the yarn. A typical analytical cycle requires from 2 to 3 min. Typical relative and absolute powers of detection measured under simultaneous multielement determination conditions for 25-μl samples are shown in Table 1. A comparison of these detection limits with those reported in the literature for ESVA-AAS techniques reveals that the latter provide values that are generally superior by one to two orders of magnitude. It should be recognized, however, that the values reported in Table 1 were measured simultaneously in a polychromator without adjusting operating parameters from element to element. For ESVA-AAS technique, operating parameters are usually optimized for each element. The analytical calibration curves shown in Fig. 6 were also obtained under simultaneous multielement determination conditions. The high linear concentration ranges characteristic of ICP-AES methods are clearly evident.

The preliminary results reported for various combinations of thermal vaporization with ICP atomization and excitation suggest that the primary merit

TABLE 1—*Detection limits observed for graphite yarn thermal vaporizer.*

Element	Absolute, ng	Relative, ng/ml
Ag	0.3	11
Al	0.6	20
As	0.5	20
Cd	0.2	6
Cr	0.1	5
Cu	0.05	2
Fe	0.3	11
Hg	1	40
Mg	0.08	0.1
Mn	0.006	0.3
Ni	4	14
Pb	0.02	3
Zn	0.2	7

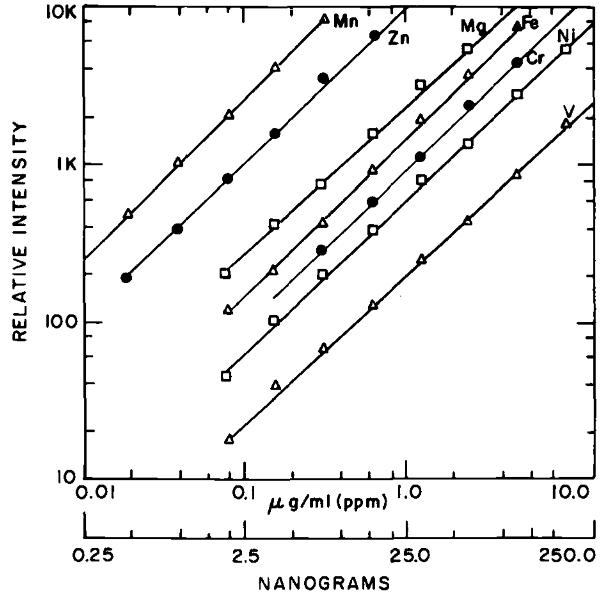

FIG. 6—*Typical analytical calibrations for graphite yarn sample vaporization combined with ICP-AES for 25-μl samples containing 1000 ppm potassium chloride matrix [35] (courtesy of Applied Research Laboratories).*

of the technique lies in the simultaneous determination of many elements in samples of limited volume. In principle, the thermal vaporization, ICP-AES approach also offers the promise of overcoming some of the problems associated with ESVA-AAS techniques discussed in the opening paragraph of this part of the paper. The problems associated with matrix or interelement interaction in the vaporization process, especially for samples of varying total composition, would be expected to remain. These vaporization interferences either do not exist or occur at an unusually low level when aerosols of solutions are injected into the plasma. It is therefore important to inquire whether adequate powers of detection can be achieved when the limited amount of aerosols generated from microlitre volumes are injected into the plasma.

Direct Analysis of Microlitre Solution Samples

During the years that techniques were being perfected for generating aerosols from solutions by pneumatic or ultrasonic nebulization, sample size generally was not an important factor. Historical patterns of investigation rather than technological limitations therefore delayed the adaptation of standard pneumatic or ultrasonic nebulization techniques to sample volumes in the fractional millilitre range. Although a number of schemes were described as long as four years ago, many analysts still do not realize that microlitre solution volumes can be nebulized reproducibly in relatively simple and convenient ways. Let us first consider several methods for performing the aerosol generation by pneumatic means. A very simple scheme has been used by Greenfield and Smith [*36*], who conveyed microlitre volumes of solutions to the nebulizer by touching the open end of the solution uptake tube with filled disposable micropipets or microsyringes, as shown in Fig. 7. The resulting aerosol then passed through a heated chamber before injection into the inductively coupled plasma. Greenfield and Smith employed this scheme for the atomization of 25-μl volumes of a variety of samples including xylene solutions of chromium acelyacelonate, dicyclopentadienyliron, lubricating oils, and methanol solutions of organic phosphorus compounds. These investigators also examined the determination of trace metals in 25-μl volumes of whole blood without any prior treatment other than storage of the sample in lithium heparin bottles.

For the nebulization-atomization of microlitre volumes of blood, serum, or plasma, we have modified our standard solution nebulization apparatus shown in Fig. 8, in the following manner [*37*]. The sample uptake tube is shortened, and a short length of gum rubber or Tygon tubing is attached to the exposed end, as shown in Fig. 9. A simple pressure or pinch clamp is placed around the length of larger tubing to control the sample flow. With the pinch clamp in the open position and the nebulizing gas flow rate adjusted to the proper value, deionized water or reference blank solution is drawn by nebulizer action to fill the uptake tube and its extension. The nebulizer drawing action is then momentarily interrupted by closing the clamp. A small air bubble is then introduced by removing the tubing from the reference blank solution and momentarily opening the clamp. The microlitre pipet (glass disposable micropipettes, Coming No. 7099-S, 25 μl) containing the sample is then inserted into the open end of the rubber tubing with the "extra volume" end (above the calibration mark) open to the atmosphere; in this way, an air bubble is left in the extra volume end. The open end of the pipet is then placed in a beaker containing deionized water or reference blank solution, and the clamp is opened to allow nebulization to proceed. The air bubbles separate the sample solution from the deionized water

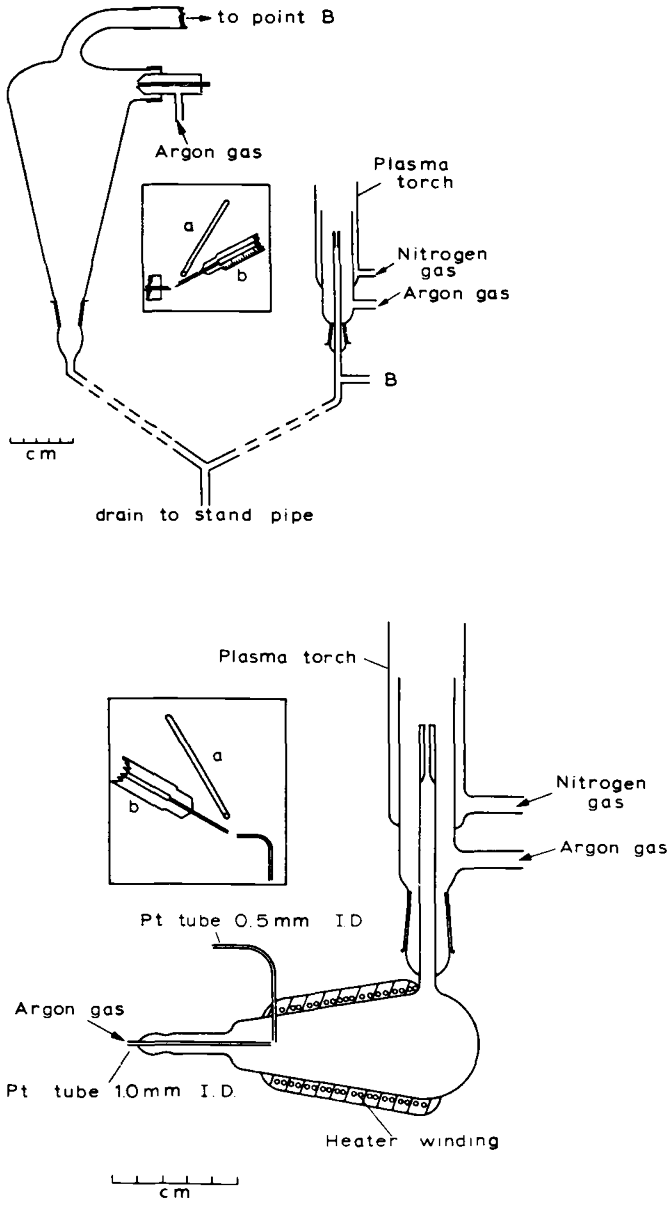

FIG. 7—*Pneumatic nebulization of microlitre samples: (*a*) micropipette, and (*b*) microsyringe [36] (courtesy of* Analytica Chimica Acta*).*

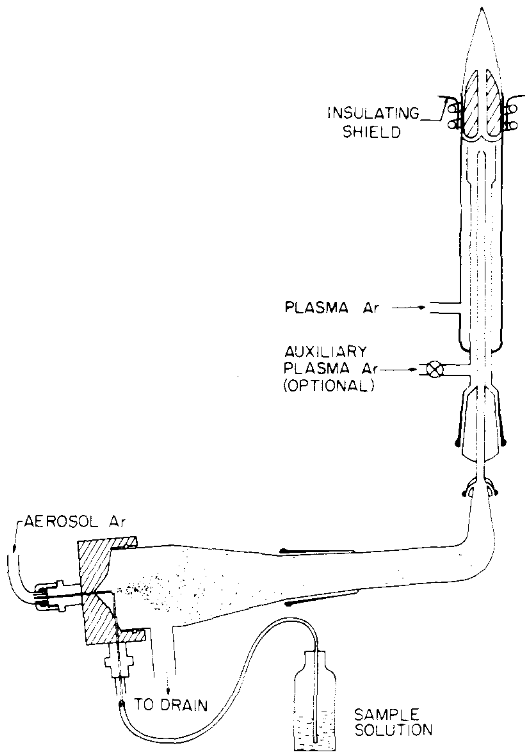

FIG. 8—*Standard pneumatic nebulization apparatus.*

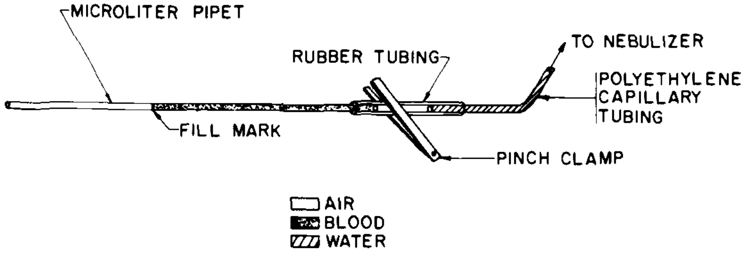

FIG. 9—*Microlitre sample introduction technique [37] (courtesy of* Clinical Chemistry*).*

or reference blank solution. Thus the sample aerosol travels through the plasma as a separate cloud. With minor modifications, this very simple system is readily amenable to automated operation, providing, in sequence, "plugs" of aerosol from deionized water (or reference blank solution) and from the sample solution.

As an aside, it should be noted that microvolume solution nebulization techniques have also been used successfully with flame atomization sources.

Sarbeck et al [*38*] first described a scheme for transporting discrete 10-μl sample volumes of the sample via a flowing stream of liquid carrier to the nebulizer. The carrier stream, which is usually water, was fed directly to a direct nebulizer burner. The 10-μl samples were injected into the carrier stream through an injection port system from a syringe. This scheme was used by Chuang et al [*39*] and Busch et al [*40*] for the determination of electrolytes in blood serum. Sebastiani, Ohls, and Riemer [*41*]; Berndt and Jackwerth [*42*], and Manning [*43*] have demonstrated that volumes as small as 100 μl can be nebulized into combustion flames with only a small loss in the peak atomic absorption signal.

Ultrasonic nebulizers provide a particularly attractive means of nebulizing limited solution volumes. Korte et al [*44*] have described a nebulizer-burner system specifically designed for use with a flame AAS instrument. As shown in Fig. 10, an integral Teflon sample cup and a glass-coated piezoelectric transducer assembly serves as the container for the samples, which typically range from 25 to 200 μl. The Teflon cup has no floor; consequently, the sample contacts the transducer. This assembly is inserted into the bottom of the burner after injection of the sample into the cup. The piezoelectric transducer is driven by a 200-W source operating at a frequency of 3 MHz. Typical sensitivities and absolute powers of detection observed by Korte et al are summarized in Table 2.

TABLE 2—*Atomic absorption sensitivities observed for ultrasonic nebulization of microlitre samples [44].*

Element	Line, nm	Sensitivities,[a] μg/ml	Absolute Detection Limit, ng[b]
Ag	328.07	0.003	0.6
Cd	228.8	0.0018	0.3
Hg	253.65	0.16	30
Ni	232.0	0.0076	1.5
Mn	279.48	0.005	1

[a] Defined as analyte required to give 1 percent absorption.

[b] In 200 μl.

For all of the schemes just discussed, the pulse or transient analyte emission, absorption, or fluorescence signals exist for periods ranging from ~1 to 10 s, depending on the sample nebulization rate. These signals may be recorded as current or voltage versus time plots or integrated in conventional ways. When a multichannel spectrometer is used, the signals may be integrated on a simultaneous multielement basis.

Comparison of ESVA-AAS and ICP-AES Powers of Detection on Limited Volume Samples

Because ESVA-AAS techniques have historically found their most satisfying applications for the determination of nanogram amounts of the elements in

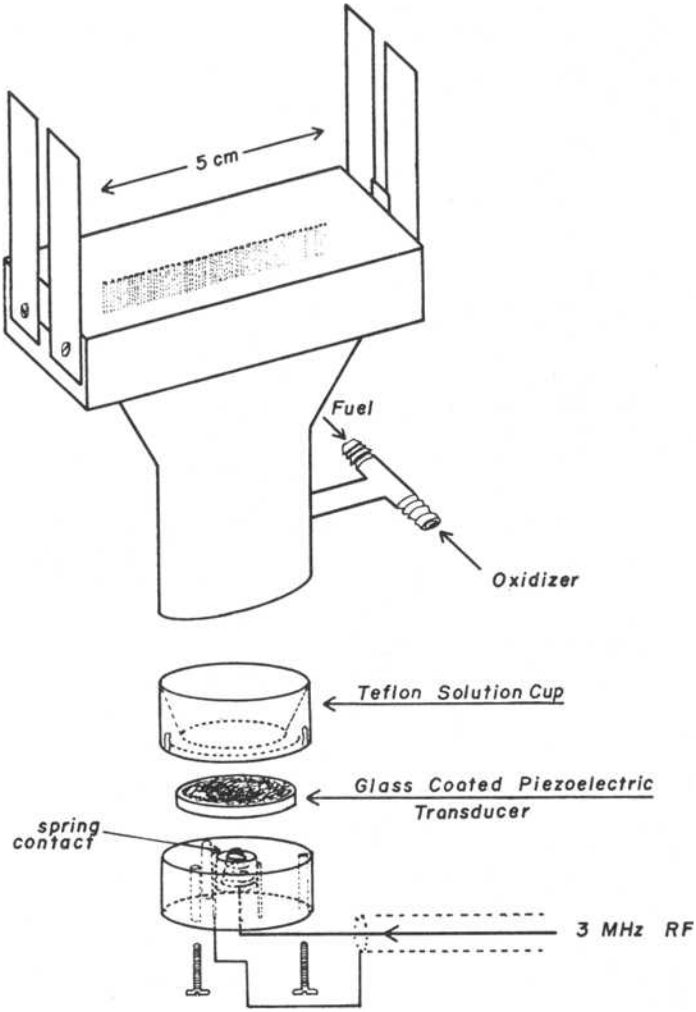

FIG. 10—*Detailed view of a pulsed ultrasonic nebulizer for flame atomic absorption spectroscopy [44] (courtesy of* Analytical Chemistry*).*

microsamples, it is of interest to draw comparisons on the detection limits observed by direct nebulization techniques versus ESVA-AAS methods. Extensive compilations of detection limit data are available for the various ESVA approaches that have been recommended. Although comparable data for the direct nebulization of limited amounts of solutions are rather meager, it is possible to estimate these values from detection limit data observed when solution volumes are not restricted. For these comparisons, it is appropriate to utilize ICP powers of detection observed under the most sensitive operating conditions. The best ICP powers of detection have been observed when ultrasonic nebulization is combined with desolvation of the aerosol [*45,46*]. A representative list of detection limits observed for this combination is shown in column four of the data in Table 3. Although these values were obtained under "unlimited" solution volume conditions, we have found no significant deterioration of the values for pneumatic nebulization when the volumes were reduced to 200 μl. Therefore, the reasonable assumption can be made that the values observed for unlimited samples can be safely transferred to 1-ml volumes for ultrasonic nebulization because both the Boumans-de Boer [*45*] and the Olson et al [*46*] schemes are adaptable to these volumes, utilizing the approach previously described by Kirsten and Bertilsson [*47*].

Table 3 also shows detection limits expressed on both an absolute and a relative basis for two commercial (Varian and Perkin-Elmer) ESVA-AAS systems [*8,48*]. On an absolute basis, the ESVA-AAS values generally show a one to two order of magnitude superiority. When the comparisons are made on a relative basis, on the assumption that at least 1 ml of solution is available, the ICP-AES values are comparable or superior to the ESVA-AAS detection limits. In this context, it is important to emphasize again that the ESVA-AAS detection limits are generally observed under experimental conditions optimized for each element. Although the Boumans-de Boer and Olson et al values were measured under experimental conditions that differed somewhat for the two laboratories, they were not changed for the individual elements examined by each group. When it is also realized that simultaneous multielement determinations are readily made when the free atoms are observed in emission and that the ICP is remarkably free of interelement effects, the potential advantages of utilizing the ICP-AES approach in sample-limited situations are clearly evident.

Stray Light Problem

When atomic emission spectroscopy is employed for the determination of trace elements at concentrations near the detection limit, the spectral background will normally be a large fraction of the total measured signal. Thus, accurate analyses require precise background corrections. In samples of varying composition, changes in the concentration of concomitants may produce subtle changes in the background level. These background shifts may be caused by true spectral interferences, by indirect effects on the spectral background underlying the analysis line or by stray light contributions. These shifts will lead to an analytical bias unless appropriate corrections are applied. If a bias results from stray light contributions, it may masquerade as an interelement interference or matrix effect when, in reality, limitations in the spectrometer components or defects in engineering design or construction are the primary cause. The various forms of stray light, and their origin and relative magnitude have been described [*49*]. It is possible, in principle, to apply normal interference correction procedures for stray light contributions to the background once the concomitants causing the stray light have been identified. Multichannel polychromators simplify this task by allowing simultaneous measurement of the concomitant intensities from which appropriate correction factors may be calculated. Stray

TABLE 3—*Comparison of detection limits.*

Element	Absolute, ng			Relative, ng/ml	
	Carbon Rod, AAS[a], in 5 μl	Graphite Furnace, AAS[b], in 100 μl	Nebulization, ICP-AES, in 1 ml	Carbon Rod,[a] AAS	Graphite Furnace,[b] AAS
Al	0.03	0.005	0.2[d]	6	0.05
As	0.1	0.02	2[c]	20	0.2
Be	0.0009	0.003	0.003[c]	0.2	0.03
Cd	0.0001	0.0003	0.07[c]	0.02	0.003
Co	0.006	0.04	0.1[c]	1	0.4
Cr	0.005	0.01	0.08[c]	1	0.1
Cu	0.007	0.005	0.04[c]	1	0.05
Fe	0.003	0.005	0.09[d]	0.6	0.05
Ga	0.02	0.03	0.6[d]	4	0.3
Mn	0.0005	0.001	0.01[c]	0.1	0.01
Mo	0.04	0.05	0.3[c]	8	0.5
Ni	0.01	0.1	0.2[d]	2	1
Pb	0.3	0.005	1[c]	1	0.03
Sn	0.1	0.1	3[d]	20	1
V	0.1	0.5	0.091[c]	20	5
Zn	0.00008	0.0001	0.1[c]	0.02	0.001

[a] From Ref *8*.

[b] From Ref *48*.

[c] From Ref *46*.

[d] From Ref *45*.

light arising from the cumulative effect of many elements or lines may necessarily complicate the correction procedure. Stray light levels may be decreased significantly through the use of state-of-the-art gratings and optical components as well as through quality engineering in the design of spectrometers. An effective means of rejecting stray light contributions, especially from far scatter, is to insert narrow band-pass interference filters immediately ahead of the photomultiplier tubes. The application of these and other techniques [*49*] for the reduction, elimination, or correction for stray light effects should eliminate this potential source of bias in the final analytical results.

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Use of a Unique Flameless Atomic Absorption Atomizer for the Analysis of Certain Difficult Samples

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ABSTRACT: This article describes the determination of vanadium in crude oils, iron in pitch, and titanium in polypropylene. The sample is placed into a pyrolytically coated graphite microboat and pyrolyzed in an air-acetylene flame. The microboat is then inserted into the cuvette of a flameless atomizer, and the sample is atomized at a temperature up to 3400°C.

KEY WORDS: atomic absorption, vanadium, iron, titanium, crude oil, pitch, polypropylene

Flameless graphite atomization, which began with the work of Lvov [*1*][2] and has since been carried on by Massmann [*2*], Woodriff [*3*], and others [*4–7*], is by now well established. Compared to the use of the flame, the graphite atomizer has well-recognized advantages and disadvantages. Its chief advantage is a great improvement in detection limits; the relative detection limit (μg/ml) is improved typically by 100 times, and the absolute or weight detection limit (μg) by even more, typically 1000 times. A second advantage is that the graphite atomizer can be used, under some circumstances, for solid or undissolved samples.

The flame, however, retains some important points of superiority. Analysis with the flame is faster (15 s/sample compared to 2 to 3 min with the graphite atomizer), more precise (better than 1 percent relative standard deviation (RSD), versus 2 to 10 percent with the graphite atomizer), easier to perform, and substantially less expensive. The graphite atomizer, therefore, is used only for those samples where it is absolutely required.

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

Commonly used flameless atomizers employ a hollow graphite cylinder, shown in a simplified sketch in Fig. 1. The sample is pipetted through a hole in the top and then dried, charred, and atomized at increasing temperatures, produced by passing different electrical currents through the cylinder. The graphite and the sample are protected from oxidation by causing an inert gas, usually nitrogen or argon, to flow through and around the cylinder. All work takes place at near-atmospheric pressures.

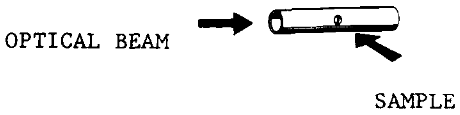

FIG. 1—*Conventional graphite cylinder. Sample is pipetted through the hole in the center. Optical beams travel through length of cylinder.*

Such systems have been used extensively for many analytical applications. However, they do have some disadvantages that can be overcome by different designs. The direct introduction of viscous samples is difficult or impossible. Chemical treatment of samples is limited to what can be done inside the cylinder, and any sample treatment takes the time of the machine while it is taking place.

Also, the precision of the analysis can be no better than that of the pipette, which is usually specified by the manufacturer to be 1 percent.

In this paper, a new system will be described. The intention of this system is to overcome or minimize some of the problems. Applications of the system to some "difficult" samples will be given. Highly refractory elements, which tend to form carbides, are determined in samples which are either viscous (crude oils) or solid and difficult to dissolve (polypropylene). The need for background correction is explored. Finally, pipetting errors are overcome by weighing samples, rather than depending upon pipette repeatability.

Experimental

The atomic absorption spectrophotometer used in this work is the Instrumentation Laboratory IL 251. In order to obtain the high-light throughput which is desirable for flameless operation, the single-beam mode was employed [*7–8*]. Deuterium (broadband) background correction was used where required. IL single-element hollow cathode lamps were used throughout.

The flameless atomizer is an IL 455, a cross-section of which appears in Fig. 2. Above the sample cuvette, a loop of tungsten wire, which touches the cuvette at one point, forms part of a Wheatstone Bridge circuit. The tungsten wire acts as a temperature sensor whose resistance rises with cuvette temperature. The output current of the bridge is therefore proportional to cuvette temperature (and to nothing else), and appears, calibrated in degrees centigrade, on a meter incorporated in the power supply/control unit.

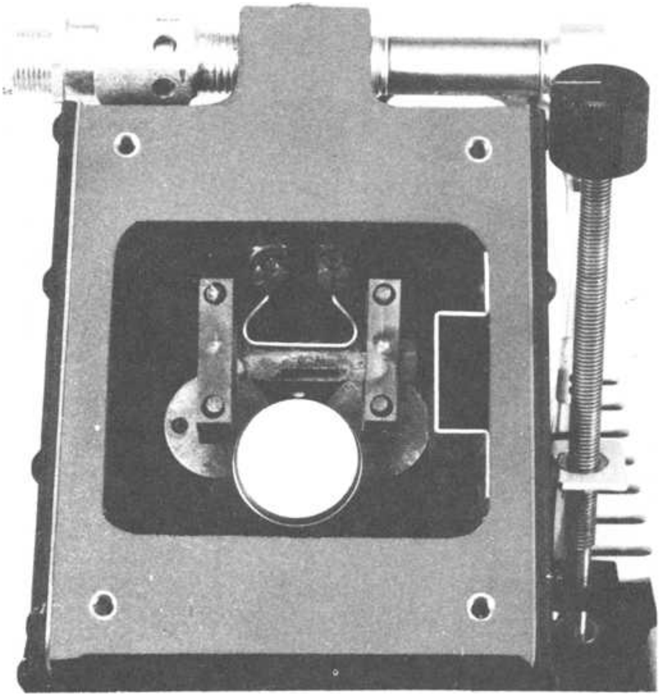

FIG. 2–*IL 455 flameless atomizer with access door removed. Wire loop above cuvette is temperature sensor.*

In operation, the workhead of the atomizer is enclosed completely. The optical beam passes through a pair of fused silica windows. Cooling water passes through the rear of the housing, and a flow of inert gas, controllable by a flowmeter, passes through and around the cuvette. The operator can choose to run the system in a "pressurized" mode, in which atomization occurs at a gas pressure that can be as much as 4 atm. The use of an elevated pressure has been shown to provide improvements in sensitivity, linearity, and precision [7].

Two different types of cuvette can be used. One is cylindrical, as shown in Fig. 1. The second and more interesting cuvette is the hollow rectangular one shown in Fig. 3. The samples are actually placed in microboats, about 10 mm long, 8 mm wide, and 1 mm deep, which can hold about 80 μl. An unlimited number of samples, each in its own microboat, can be dried simultaneously on a hotplate and subjected to other desirable types of pretreatment. Because any desired number of samples can be dried and otherwise treated outside the flameless atomizer, considerable machine time can be saved. Specifically, the drying step, commonly required in most flameless atomizer protocols, can be omitted. Finally, each boat is picked up in a special-purpose pincer and inserted through a slot in the side of the rectangular cuvette that is mounted in the workhead.

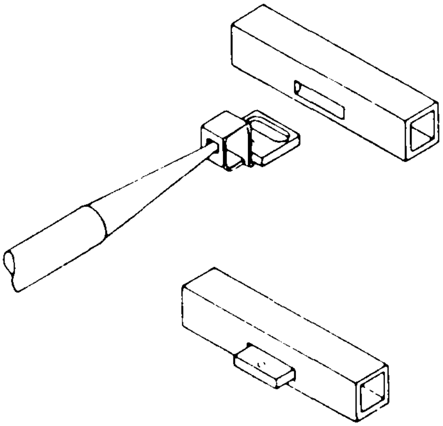

FIG. 3—*Operation of microboats. Sample is loaded into boats which can be dried on hotplate before insertion into hollow rectangular cuvette.*

Both types of cuvette, as well as the microboats, are made of pyrolytically coated graphite. Elements such as barium, titanium, and vanadium are known for their propensity to form carbides; therefore, it is difficult to atomize them in a normal graphite system, and they tend to produce low, broad peaks with substantial memory. The pyrolytic coating is intended to discourage the formation of carbides by such elements.

One method of pretreatment, developed for samples that include an intractable organic matrix, is to char or burn them in their boats in the flame from a premixed air-acetylene miniburner (Fig. 4). The miniburner is mounted in the sample space of the atomic absorption spectrophotometer, although (obviously) outside the optical path. A somewhat similar technique has been used elsewhere [9].

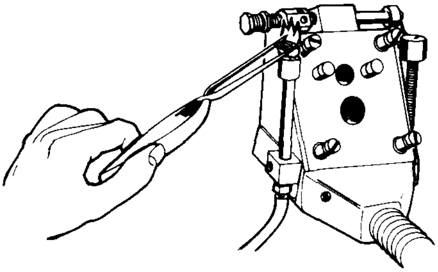

FIG. 4—*Sample in microboat being charred in flame from air-acetylene miniburner.*

Held in a pair of tweezers, the boat is inserted for a few seconds in the flame until the sample begins to burn or smoke. The boat is then withdrawn until burning or smoking ceases and then reinserted to see if the activity continues. The process is repeated until nothing further happens. Tests that were made with thermocouples attached to the boats indicated that the boat temperature does not rise higher than 600°C during these operations; therefore, most metals in most samples will not be lost.

Either nitrogen or argon can be used as the inert protective gas for the flameless atomizer. Argon is more expensive but is typically more pure and sometimes gives better sensitivity. For all the analyses described next, argon was employed.

Results and Discussion

The microboat/miniburner technique was used to analyze three types of samples that ordinarily have presented grave difficulties in atomic absorption analysis.

Vanadium in Crude Oils

The determination of vanadium in crude oils (petroleum crudes, feedstocks) is in many ways a particular challenge to the atomic absorption analyst. Vanadium, being a catalyst poison, must be measured at very low levels, preferably below 0.1 ppm. It is also a refractory element and a carbide former, so that it requires high furnace temperature as well as a protected (pyrolytic) carbon surface. Crude oils are semisolid, so that it is difficult to handle them either as a solid or a liquid.

In the conventional atomic absorption method, the samples are diluted five or ten times in a solvent such as xylene and then inserted into the flame or carbon tube. In the tube, then, a long and careful pyrolyzing step is required to remove the organic material without moving, losing, or blowing away the residue containing the vanadium. The dilution in xylene, of course, degrades the already marginal detectability of the vanadium by an amount equal to the dilution factor.

In the present work, a microboat was tared on the pan of a Cahn Electrobalance, after which a "glob" of crude oil was added and weighed. The sample was then burned and charred in the flame from the miniburner, as described in the previous section. A number of pyrolysis/atomization programs for the Flameless Atomizer were investigated before the program shown in Table 1 was finally chosen. Because of the efficiency of the miniburner step, the final

TABLE 1–*Pyrolysis and atomization programs for the samples considered, Model 455.*

	Oils	Pitch	Polypropylene
	V	Fe	Ti
Pyrolysis time, s	20	30	30
Pyrolysis temperature, °C	900	700	1100
Atomization time, s	10	10	15
Atomization temperature, °C	3400	3000	3400

program could be made relatively brief. Instrumental conditions for the spectrophotometer were taken from Ref *10*. Background correction was not required.

The initial investigation was made with a sample which contained an elevated amount of vanadium, making it possible to compare the results of the new method to the conventional methods (dilution with xylene) by flame and flameless atomization. A summary of the results of 20 determinations by each of the three methods appears in Table 2 and indicates that, at high levels, comparable results are obtained. For the flameless determinations, simple aqueous standards proved adequate.

TABLE 2–*Comparison of three methods for determination of vanadium in crude oils.*

Method	Number of Measurements	Results, ppm
Flame AA	20	6.0 ± 0.2
Conventional flameless AA[a]	20	6.2 ± 0.4
Present flameless AA	20	6.9 ± 0.9

[a] Samples were diluted ×100 with xylene and then analyzed by flameless AA.

Another sample was then analyzed. This was stated by the supplier to have a vanadium concentration of approximately 0.03 μg/g vanadium. A working curve, involving aqueous standards of 0.5, 1, 2, and 5 ng was prepared and proved to be linear. Recorder tracings for a 1 ng aqueous standard, as well as three aliquots of the sample, appear in Fig. 5. The resultant data, shown in Table 3, represent acceptable precision and accuracy. Peak height was used for the calculations. The sharpness of the peaks indicates that carbide formation was not a problem. If it had been, the peaks would have been much lower and shown substantial tailing.

Iron in Pitch

A relatively high concentration of iron was determined in pitch; in fact, the iron level was so high that it could readily have been measured by flame absorption. The flameless analysis was undertaken because it represented an opportunity to test whether the prepyrolysis technique would remove the effects of background absorption completely.

In order to keep the peaks on scale, it proved necessary to use a secondary line at 382.4 nm whose sensitivity is 100 times poorer than that of the primary line at 248.3 nm. Except for this change, analytical conditions for the spectrophotometer were as given in Ref *10*. The pitch was loaded directly into the microboat and burned immediately in the miniflame. The temperature program for the flameless atomizer is given in Table 2.

A plot of absorbance versus different sample weights appears in Fig. 6 and

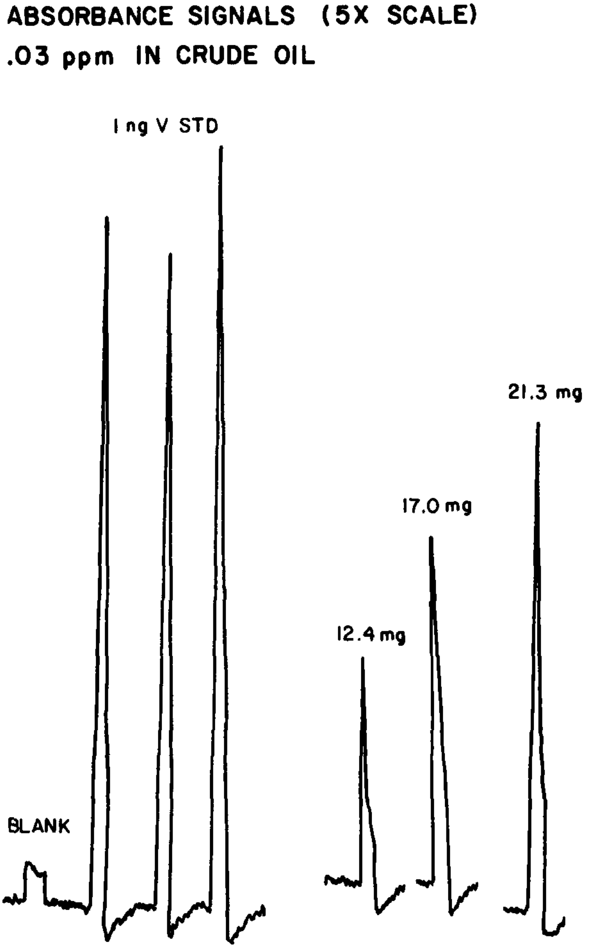

FIG. 5—*Recorder traces for vanadium. First three traces represent 1 x 10^{-9} g vanadium in aqueous standard. Second three traces represent vanadium in different weights of the same crude oil sample. Pen travel is left to right.*

TABLE 3—*Determination of low concentration of vanadium in gas oil with IL 455.*

Sample Weight, mg	Absorbance	Weight of V, ng	Concentration of V, ppm
12.4	0.047	0.36	0.029
17.0	0.066	0.50	0.029
21.3	0.094	0.71	0.033

NOTE—One ng vanadium standard gives 0.132 absorbance. 1% absorption = 0.0044 absorbance.

indicates unsatisfactory results. The points are badly scattered, and the calculator-generated line of best fit does not go through the origin. Therefore,

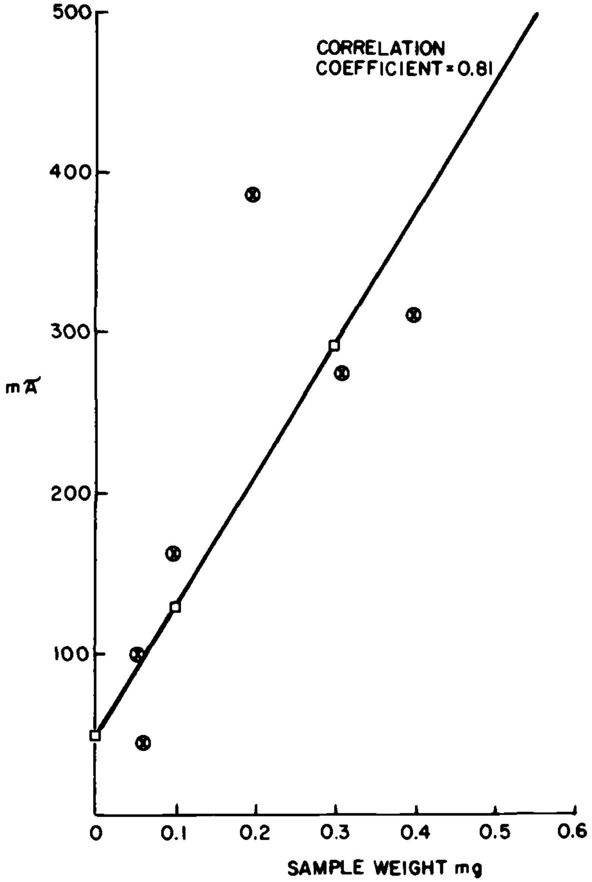

FIG. 6–*Iron in pitch. Results for different sample weights, at 382.4 nm iron line, without background correction.*

background correction is needed. Because the ability of a deuterium lamp to operate at a wavelength as high as 382 nm is, at best, marginal, another line, further down the ultraviolet (UV) range, was selected.

Therefore, the analysis was repeated at the 293.7 nm iron wavelength. Because the latter line is more sensitive, it was necessary to use smaller sample weights. With the use of background correction, the plot of Fig. 7 was generated. This is a representation of repeatable analytical results. Compared to an aqueous standard, the iron concentration was found to be 0.02 ± 0.003 percent.

Titanium in Polypropylene

It is well known that polypropylene is extremely difficult to dissolve, generally requiring a fusion. Titanium tends to form carbides and also, at

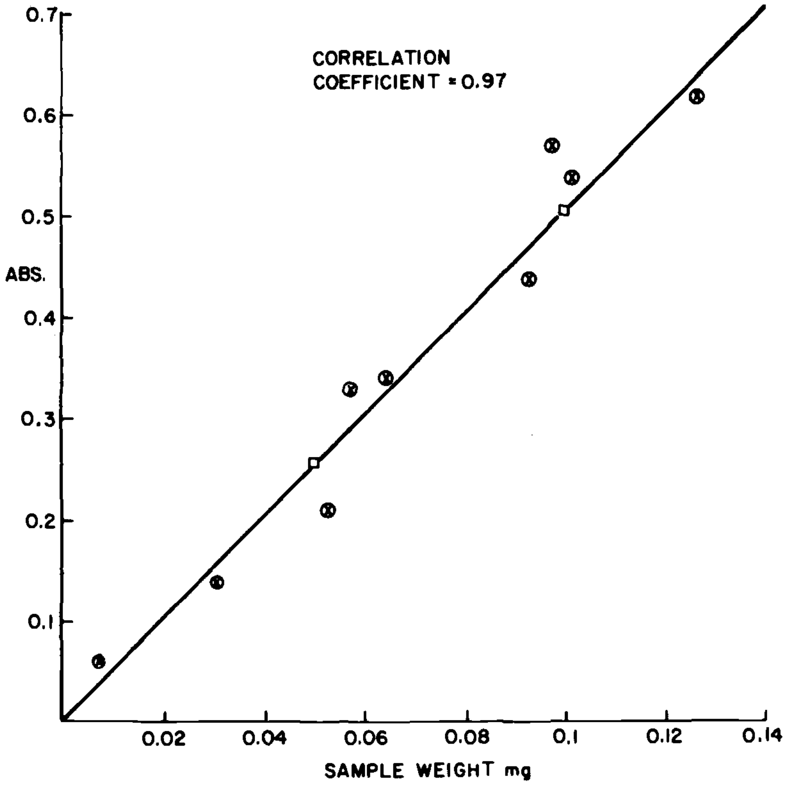

FIG. 7—*Iron in pitch. Results for different sample weights, at 293.7 nm iron line, with background correction.*

insufficient atomization temperature, produces a very substantial memory effect. Therefore, a decision was made to analyze the solid material, pretreat it in the miniburner flame, and investigate the memory effect. The spectrophotometer was used according to Ref *10*. Background correction was not required.

The flameless atomizer program that was used is shown in Table 2, and the peak heights and calculations for one set of analyses appear in Table 4. It can be seen that the memory effect for titanium is real but controllable because repeated atomizations do remove it. Insufficient work has been done to enable a decision about the best way to handle the data. The manufacturer of the plastic had expected concentrations of 100 and 10 ppm, respectively, for the two samples. If, as in Table 4, the peak heights are added up, the analytical results are 125 and 10.3 ppm. If the memory effect is simply ignored, the results are 127 and 10.5 ppm. It could also be argued that it is the peak areas that should be added; however, this was not done. In the example investigated here, the error occurs only in the third significant figure and is probably substantially smaller than the precision that can be expected from the analysis.

TABLE 4–*Direct determination of titanium in polypropylene with IL 455.*

Sample and Weight	Absorbance	Total Absorbance	Weight of Ti	Concentration of Ti
Blank	0			
Standard	0.170			
Blank	0.015			
Blank	0.005	0.190	25.0 ng	
Blank	0			
#1 0.29 mg	0.250			
Blank	0.020			
Blank	0.005	0.275	36.2 ng	125 ppm[a]
Blank	0			
#2 0.70 mg	0.050			
Blank	0.005	0.055	7.2 ng	10.3 ppm[a]
Blank				
Blank				

[a] Expected values were 100 and 10 ppm, respectively.

Manganese in Water

The determination of manganese in water, while not at all difficult, was undertaken in order to check the precision achievable with microboats. It was theorized that any pipetting error could be eliminated almost completely by placing the microboat on the pan of an electrobalance, taring it, and weighing the amount of sample delivered. Since the sample is in solution, inhomogeneity cannot be a problem. Hollow cathode lamps for manganese are bright and stable, permitting the atomic absorption spectrophotometer to operate at its best.

It was felt that the best possible precision would be obtained with ramp atomization and operation at a slightly elevated pressure. The conditions for the spectrophotometer were taken from Ref *10*; those for the atomizer appear in Table 5, which also gives the results. A 25-μl pipette was used to deposit 0.001-μg/ml manganese, giving a nominal sample weight of 25×10^{-12} g of manganese.

As it happened, the pipetting precision for the series was particularly good, comparable with that of the peak heights. The theory that normalization of pipetting volume against sample weight can improve precision was therefore neither proved nor disproved and must await further work with samples which are more difficult to pipette.

Conclusion

A new flameless graphite atomizer has been described whose distinguishing features include the use of pyrolytic graphite, the ability to use atomization temperatures up to 3500°C, and the use of individual graphite microboats. We found it was possible to employ this combination of characteristics to undertake

TABLE 5—*Conditions and results for determination of manganese in water.*

Drying	hot plate at 90°C until dry
Pyrolysis	15 s at 450°C
Atomization	5-s ramp to 2700°C, hold for 5 s
Carrier Gas	argon
Pressure	15 psig

	Sample Weight (10^{-12} g Mn)	Peak Height (absorbance)
Mean	24.84	0.556
SD	0.14	0.003
RSD	0.56%	0.54%

the analysis of samples which are difficult or impossible to analyze by other atomic absorption techniques. The ability to pretreat organics in the flame of an air-acetylene miniburner appears to have some degree of value.

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E. L. Henn[1]

Use of Molybdenum in Eliminating Matrix Interferences in Flameless Atomic Absorption

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REFERENCE: Henn, E. L., "Use of Molybdenum in Eliminating Matrix Interferences in Flameless Atomic Absorption," *Flameless Atomic Absorption Analysis: An Update, ASTM STP 618*, American Society for Testing and Materials, 1977, pp. 54–64.

ABSTRACT: The addition of molybdenum to samples and standards has been found to be an effective method of minimizing matrix interferences in the flameless atomic absorption analysis of lead, cadmium, and selenium. Use of this technique permits the analysis of selenium and lead in natural waters in concentrations as low as 1.0 μg/litre. Cadmium can be analyzed down to 0.1 μg/litre. It appears likely that the use of molybdenum for interference suppression could be extended to other metals. If so, this would greatly expand the usefulness of flameless atomic absorption for trace metals analysis.

KEY WORDS: atomic absorption, trace elements, molybdenum, matrices, cadmium, lead, selenium

Flameless atomic absorption is a highly sensitive method of measuring the concentration of trace metals in solution. For most metals, a mass of less than 100 pg is necessary to provide 1 percent absorption.

Unfortunately, analysts have generally been unable to take advantage of this extremely sensitive technique, due to the many interferences encountered in the method. Unlike its flame counterpart, flameless atomic absorption is subject to severe matrix interferences. The presence of commonly found cations and anions in a sample can cause either depressant or enhancement effects, depending on the metal being analyzed and the concentration and type of concomitant present.

Previously published data by this author show that, in the analysis of 50 μg/litre selenium, 26 out of 31 metals cause greater than 10 percent error at the 10 mg/litre level.[2] The interference effects ranged from 61 percent depression of absorption to 278 percent enhancement.

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[2] Henn, E. L., *Analytical Chemistry*, Vol. 47, March 1975, p. 428.

Caldwell et al[3] have reported severe interference from low concentrations of sulfate in analyzing for lead by flameless methods. Chloride and nitrate also interfered.

Barnard and Fishman[4] have encountered poor agreement between flame and flameless atomic absorption results when analyzing for traces of copper, lead, cadmium, manganese, and chromium in natural waters. However, fairly good agreement was obtained when the method of standard additions was used to quantify results by the flameless method. This indicates that the disagreement between values was due to interferences from substances in the natural waters tested.

Extensive investigations have been conducted in our laboratories into ways and means of obviating the matrix interferences in flameless atomic absorption, with emphasis on the analysis of cadmium, lead, and selenium. We have found that the addition of high concentrations of molybdenum to samples and standards minimizes matrix interference effects. This paper presents the findings of these investigations.

Procedure

Equipment

All analyses were performed with an atomic absorption spectrophotometer (Perkin-Elmer Model 305B) equipped with an HGA-2000 heated graphite atomizer. Eppendorf microlitre pipets were used for injection of samples into the furnace. Background correction was used in measurements of cadmium and selenium but was not used for lead measurements.

Instrumental parameters used in the testing are listed in Table 1. Temperatures quoted are based on instrument settings and not actual measurements. Nitrogen was used as a purge gas in the flameless device. The "gas interrupt" phase, whereby the flow of purge gas is momentarily interrupted during the atomization stage, was used for selenium and lead measurements but not for cadmium measurements.

Reagents

The 1000 mg/litre stock solutions used for preparing metal standards and the 1000 mg/litre molybdenum solution used in fortifying samples and standards with molybdenum were obtained from Fisher Scientific Company, Pittsburgh, Pa. All acids used in the test were reagent grade and used as received (J. T. Baker Chemical Company). The cation exchange resin used in selenium analysis (Rohm

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[3] Caldwell, J. S., Yee, L. M., and McFarren, E. F., Paper XI, *Proceedings*, American Water Works Association Technology Conference, Dallas, Tex., Dec. 1974.

[4] Barnard, W. M. and Fishman, J. J., *Atomic Absorption Newsletter*, Vol. 12, No. 5, Sept.-Oct. 1973, p. 118.

TABLE 1—*Instrumental parameters for metals analysis by flameless atomic absorption.*

			Drying		Charring		Atomization		
Element	Wavelength, nm	Spectral Bandpass, nm	Time, s	Temperature, °C	Time, s	Temperature, °C	Time, s	Temperature, °C	Sample Size, μl
Cadmium	228.8	0.7	30	125	30	700	15	1800	50
Lead	283.3	0.7	30	125	30	800	15	2300	50
Selenium	196.0	2.0	60	125	35	1000	15	2500	100

and Haas IR-124) was converted from the sodium form to the hydrogen form by treatment with hydrochloric acid.

Sample Preparation

All standards were prepared in 5 percent (volume/volume) hydrochloric acid (HCl) solution. Only the 5 percent HCl matrix was used in the test. This is the final matrix of the Environmental Protection Agency's total metals digestion procedure, and the work was done for the purpose of developing a total metals procedure. Appropriate aliquots of 1000 mg/litre molybdenum solution were added to provide the desired concentration of molybdenum.

Sample Analysis

Samples were analyzed by direct injection of appropriate microlitre aliquots of solution into the graphite furnace and running through the programmed drying, charring, and atomization cycles. The graphite tube had to be conditioned with molybdenum by injecting 100 μl aliquots of the 1000 mg/litre molybdenum stock solution into the furnace and running through the programmed drying, charring, and atomization cycles a few times before reproducible results could be obtained.

Experimental Work

In applying flameless atomic absorption to the analysis of cadmium, lead, and selenium, the problems encountered were basically twofold. First of all, most salts of these metals are fairly volatile, a fact which prevents the use of high charring temperatures lest the metal of interest be lost during the charring stage. A high charring temperature is usually desirable when flameless methods are employed because it assures complete decomposition of any organic matter present and sometimes permits volatilization of undesirable matrix constituents which may interfere.

Second, the matrix interferences encountered in the analysis of these three metals are exceptionally severe. Also, the interference problem in cadmium analysis is compounded by the fact that the atomization temperature used for cadmium is fairly low, and heavy metals which may be present in some samples are not volatilized at this temperature. This results in a "poisoning" effect caused by the buildup of residual heavy metals in the graphite tube, resulting in the exacerbation of interference effects.

The problem of cadmium loss during the charring stage was unexpectedly severe. It was found that significant amounts of cadmium were lost even at extremely low charring temperatures, preventing the use of any char in the test. The initial approach to solving this problem was to add a large amount of a substance which would form a more refractory salt with cadmium. Inasmuch as cadmium phosphate is one of the most refractory of all cadmium salts, the addition of phosphate was tried. This eliminated cadmium loss during the charring stage but adversely affected the reproducibility of the test. The use of aluminum, in an attempt at forming a spinel, and addition of hydrogen peroxide to form cadmium oxide were also tried, and both were somewhat successful in permitting higher charring temperatures. However, subsequent tests showed that these additives were not effective in eliminating matrix interferences in the test.

A combination of additives found to be effective in eliminating most of the problems in the test for cadmium was 1.5 percent hydrogen peroxide (H_2O_2) and 100 mg/litre molybdenum. In Fig. 1, the absorption value obtained from 50 µl of a 10 µg/litre cadmium standard in 5 percent HCl which had been fortified with 1.5 percent H_2O_2 and 100 mg/litre molybdenum is plotted versus charring temperature. For comparison purposes, the absorption values obtained for the same concentration of cadmium in deionized water and in 5 percent HCl are also plotted versus charring temperature. Note that no significant loss of cadmium occurs up to 900°C when the H_2O_2 and molybdenum are added. Without these additives, however, cadmium loss occurs as low as 250°C. The addition of H_2O_2 alone also permits use of a high charring temperature, presumably due to the formation of cadmium oxide. However, H_2O_2 alone has very little effect on matrix interferences.

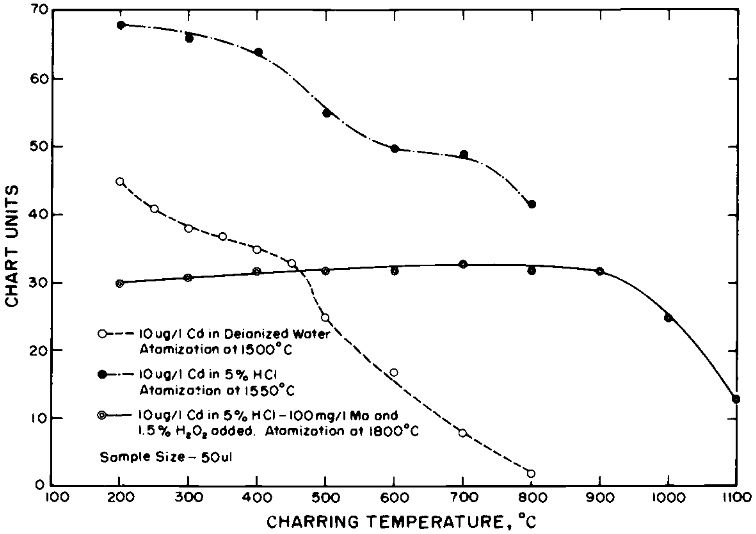

FIG. 1–*Loss of cadmium with increasing charring temperature.*

Most of the interferences in the cadmium test are eliminated or greatly minimized by the addition of both 1.5 percent H_2O_2 and 100 mg/litre molybdenum. In addition, use of these additives permitted the use of a higher atomization temperature without any loss of precision. This increased the sensitivity of the test somewhat. The detection limit for cadmium under these conditions was about 0.1 µg/litre cadmium. In Table 2, the effects of various ions on cadmium sensitivity both with and without added molybdenum and

TABLE 2–*Effect of various substances on cadmium sensitivity in a 5 percent hydrochloric acid matrix with and without added molybdenum and hydrogen peroxide.*

		Cadmium Concentration, 10 µg/litre Cd	
		Enhancing or Depressing Effect on Cadmium Absorption, %	
Concomitant Added	Concentration of Concomitant, mg/litre	No Mo or H_2O_2 Added[a]	100 mg/litre Mo and 1.5% H_2O_2 Added[b]
Al	10	...	0
Ca	10	...	− 2
Ca	50	...	− 9
Ca	100	− 31	− 9
Cu	1	...	+ 7
Cu	10	− 60	+18
F	10	...	+ 2
Fe	10	− 60	+ 2
K	50	+40	+ 2
Mg	10	...	− 3
Mg	50	...	− 7
Mg	100	− 96	− 7
Mn	10	− 89	0
Na	10	...	− 7
Na	100	...	+ 6
Ni	1	...	+ 5
Ni	10	...	+17
Si	10	...	+ 2
Zn	10	− 41	+ 9
Cl	100	...	− 2
NO_3	100	...	0
PO_4	10	...	0
SO_4	100	...	0

[a] 300°C char, 1550°C atomization.

[b] 700°C char, 1800°C atomization.

H_2O_2 are listed. Note that all of the extremely severe matrix interferences are reduced to a tolerable level. The only metals which still cause significant interference are copper and nickel. The only metal found to cause a carryover of interference effects from one sample to another is nickel.

The precision of the cadmium test using the addition of 1.5 percent H_2O_2 and 100 mg/litre molybdenum was measured. Based on 17 replicate analyses, the relative standard deviation at the 10 µg/litre cadmium level was found to be 4.7 percent.

The problem of volatilization during the charring stage is not nearly as severe with lead as with cadmium. In a 5 percent HCl matrix, a charring temperature of 800°C can be tolerated without significant loss of lead. Matrix interferences are not nearly as severe in the lead test either but are still severe enough to cause significant error. Numerous combinations of additives were tried in an attempt to eliminate matrix interferences in the lead test. The most effective additive in this regard was again found to be molybdenum, in the concentration of 200 mg/litre. As in the case of cadmium, a higher atomization temperature can be tolerated when molybdenum is added without loss of precision. This increases the sensitivity of the lead test and permits the attainment of a detection limit of about 1.0 µg/litre lead. The use of 100 mg/litre molybdenum, the same concentration used in cadmium analysis, was not sufficiently effective in minimizing interference from calcium and magnesium. Doubling the molybdenum concentration for lead analysis increased the effectiveness of this interference suppression sufficiently to obtain satisfactory values. In Table 3, the effect of various ions on lead sensitivity with and without added molybdenum are listed. Note that the addition of molybdenum eliminates all significant interferences except that from high concentrations of sodium and potassium.

TABLE 3—*Effect of various substances on lead sensitivity in a 5 percent hydrochloric acid matrix with and without added molybdenum.*

		Lead Concentration, 10 µg/litre Pb	
		Enhancing or Depressing Effect on Lead Absorption, %	
Concomitant Added	Concentration of Concomitant, mg/litre	No Mo Added[a]	200 mg/litre Mo Added[b]
Al	10	+ 3	0
Ca	10	+ 6	0
Ca	50	...	+ 3
Ca	100	+ 3[c]	0
Cu	10	+ 6	+ 3
Fe	10	+ 13	− 2
K	10	...	− 2
K	50	− 36	− 10
Mg	10	...	− 3
Mg	50	...	− 5
Mg	100	− 21[c]	− 6
Mn	10	− 17	0
Na	10	− 19	− 6
Na	50	...	− 13
Na	100	+ 66	− 14
Ni	10	0	+ 3
Si	10	− 33	0
Zn	10	− 3	0
Cl	100	0	0
NO_3	100	+ 3	0
PO_4	10	0	− 2
SO_4	100	+ 6	0

[a] 500°C char, 2000°C atomization.

[b] 800°C char, 2300°C atomization.

[c] Double peak.

Molybdenum also has some effect in preventing the loss of lead at high charring temperatures. In Fig. 2, the absorption obtained from 50 μl of a 10 μg/litre lead standard in 5 percent HCl both with and without molybdenum addition, is plotted versus charring temperature. Note that without added molybdenum some loss of lead is indicated at 950°C, but, with the addition of 200 mg/litre molybdenum, there is no loss of lead until the charring temperature reaches 1200°C.

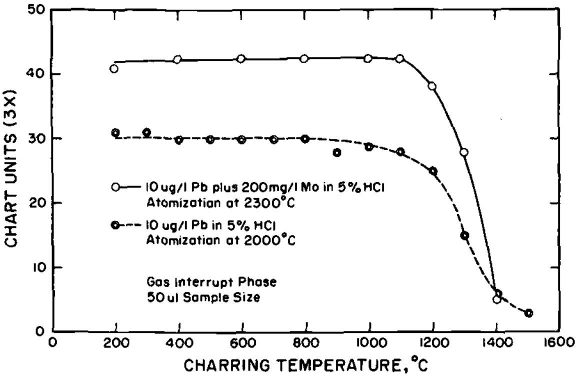

FIG. 2–*Loss of lead with increasing charring temperature.*

Based on twelve replicate analyses, the relative standard deviation of the lead test at the 10 μg/litre lead level (with 200 mg/litre molybdenum added) was 1.54 percent.

In the case of selenium analysis, an additional problem had to be reckoned with. When the concentration of some common salts exceeds about 20 mg/litre, severe background absorption is encountered. In most cases, the background absorption exceeds the compensating capabilities of a deuterium background corrector. Experiments showed that this problem could be solved by passing the solution through a cation exchange resin to replace all metallic cations with hydrogen. Using this technique, the only interference to be concerned with was that from anions.

The presence of various common anions was found to cause severe interference in the test. The use of metal additives was investigated to determine their effectiveness in eliminating interference effects from high concentrations of anions. The only metal which showed promise in this regard was molybdenum. Molybdenum has a very significant enhancing effect on selenium sensitivity in a 5 percent HCl matrix; however, this effect is concentration dependent. This is illustrated in Fig. 3, where the concentration of added molybdenum is plotted versus the peak height obtained with a 25 μg/litre selenium standard at the various molybdenum concentrations. Note that maximum enhancement is achieved at a concentration of 30 mg/litre molybdenum and that, above 50 mg/litre molybdenum, the enhancing effect drops off rather sharply.

As with cadmium and lead, a much higher charring temperature can be tolerated without loss of selenium when molybdenum is present than when it is

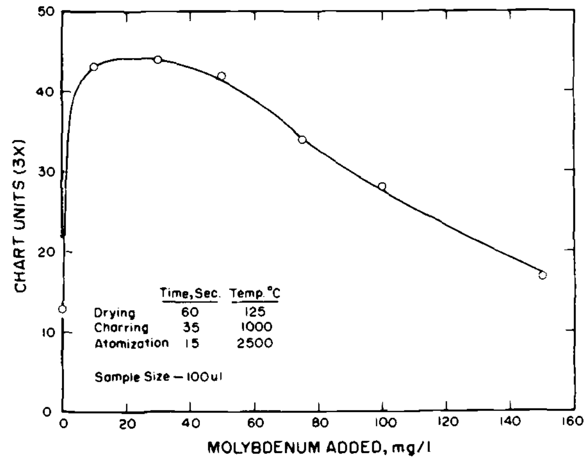

FIG. 3–*Effect of varying concentrations of molybdenum on absorption of 25 µg/litre selenium in 5 percent hydrochloric acid.*

not present. In Fig. 4, the peak height obtained for selenium standards is plotted versus charring temperature for standards containing (*a*) no molybdenum and (*b*)

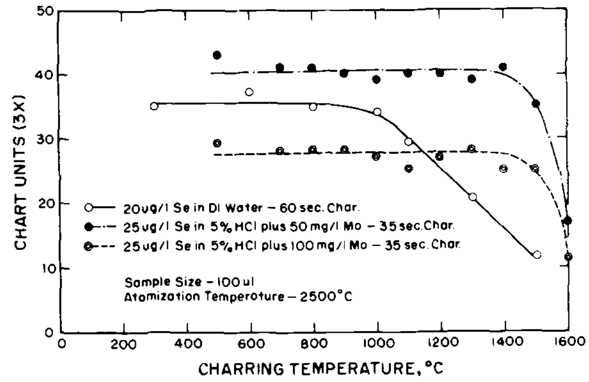

FIG. 4–*Determination of maximum charring temperature for selenium with and without added molybdenum.*

100 mg/litre molybdenum. Note that, when no molybdenum is present, loss of selenium during the charring stage begins occurring at about 900°C, and the apparent sensitivity drops off gradually from that point. When molybdenum is present, however, loss of selenium does not begin to occur until at least 1400°C, and, above this temperature, the apparent sensitivity drops off very sharply.

The effect of added molybdenum on minimizing interferences from sulfate, nitrate, phosphate, and chromate is shown in Table 4. In this table, the percent change observed in selenium sensitivity, both with and without added molybdenum in the presence of different concentrations of anions, is listed. Note that, in most cases, the addition of 100 mg/litre molybdenum is effective

TABLE 4—*Effect of common anions on selenium sensitivity in a 5 percent hydrochloric acid matrix with and without added molybdenum.*

Anion Added, mg/litre (Acid form)	Selenium Concentration, 50 µg/litre Se	
	Enhancing or Depressing Effect on Selenium Absorption, %	
	No Molybdenum	100 mg/litre Mo Added
10 SO_4	-10	0
100 SO_4	-26	-7
1000 SO_4	-49	-19
10 000 SO_4	-62	-26
10 NO_3	-14	0
100 NO_3	-22	-17
1000 NO_3	-22	-20
10 000 NO_3	-49	-49
10 PO_4	-16	+22
100 PO_4	-34	0
1000 PO_4	-47	-60
10 000 PO_4	-62	-87
10 CrO_4	+80	-6
100 CrO_4	-37	-65
1000 CrO_4	-50	-68

in eliminating or minimizing interferences caused by low concentrations of anions. At high concentrations of anions, however, the effect is minimal. Chloride ion does not interfere in the test under any circumstances.

In the presence of 100 mg/litre molybdenum, a detection limit of 1.0 µg/litre selenium can be attained.

Discussion

It would be useful to understand the mechanism whereby matrix effects are minimized by molybdenum addition. Unfortunately, very little is understood about the various chemical and physical phenomena which occur in the graphite tube during the atomization process. In addition, the chemistry of molybdenum is very complex, and many aspects of it are not thoroughly understood.

The fact that a higher charring temperature can be usually tolerated for the metals tested when molybdenum is present than when it is not seems to indicate that the molybdenum somehow binds itself to the other metal salts, rendering them more refractory. In the case of selenium, some sort of selenide may be formed in the presence of molybdenum.

The fact that a higher charring temperature is used when molybdenum is added undoubtedly contributes to the minimization of interference effects by means of volatilization of interfering salts. However, this would not explain why the interference of heavy metals which would definitely not volatilize at the charring temperature is minimized by the addition of molybdenum.

Another explanation for this behavior may be that molybdenum reacts with the metals in the furnace to form a heteropolymolybdate anion in which a central metal atom is surrounded by molybdate ions. In such a chemically bound state, various metals would be isolated from each other, which may have an effect on the atomization process.

Conclusions

It has been shown that molybdenum can be used effectively as an additive in minimizing matrix interferences in the flameless atomic absorption analysis of cadmium, lead, and selenium. It is possible that the use of molybdenum may be effective in minimizing interferences in the analysis of other metals as well.

In order that the technique of flameless atomic absorption may be utilized fully, much more work remains to be done in finding ways and means of eliminating the many interferences that plague the method. This will undoubtedly necessitate further elucidation of the many different physical and chemical phenomena that occur in flameless atomization techniques.

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