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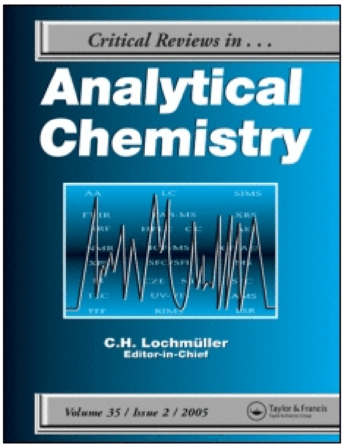

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DEVELOPMENTS IN METHODS OF SAMPLE INJECTION AND ATOMIZATION IN ATOMIC SPECTROMETRY

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I. INTRODUCTION

Many active areas of current research demand methods of analysis of ever increasing sensitivity. Concern over such matters as the pollution of the environment and the roles of trace concentrations of metals in biological systems has prompted and encouraged the development of methods and of instrumentation capable of accurately determining picogram amounts and part per billion concentrations of elements. During the past five years, atomic spectrometry, especially atomic absorption, has seen a large number of improvements in instrumentation, and many applied research papers have appeared in the literature.

Although significant advances in atomic spectrometry have affected radiation sources, as well as the optical and detection systems, this review will concern itself only with improvements in methods of sample introduction into the analysis system and the means of generation of the atomic vapor in atomic absorption, flame emission, and atomic fluorescence spectrometry. Non-flame atomizers, including the graphite-tube furnace, the carbon rod, the tantalum boat, and related devices will be discussed, and the state of the art of these techniques will be outlined. Chemical evolution techniques of sample introduction and advances in different nebulization methods employed in flame spectrometry will also be presented. This review will not include atomic spectrometry work with high frequency discharges, microwave discharges, plasma jets, arc excitation, atomization in hollow cathodes, or work with lasers. It will also not be concerned with varieties of flames used in spectrometry or with modifications in burner design, except where the latter result in a novel method of sample uptake or nebulization. Only papers which appeared during approximately the last five years will be reviewed, except in those cases where numerous recent developments and applications are based directly on a significant discovery reported in an earlier publication, in which case the earlier, fundamental paper will also be reviewed.

II. HEATED GRAPHITE-TUBE ATOMIZERS

A. Development and Sensitivity of Graphite-tube Atomizers

1. Lvov Furnace

The first successful non-flame atomizer in the form of the graphite tube was described by Lvov[1] in the period 1959–1961, but this development attracted little attention for several years. Lvov's atomizer has now been widely described in the literature and is schematically illustrated in Figure 1. Its impressive sensitivity and relative simplicity

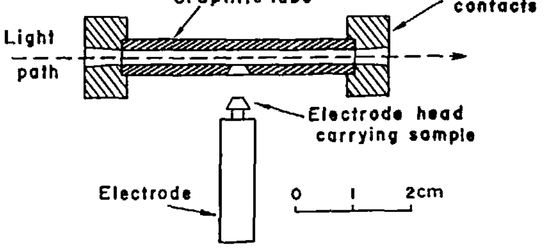

FIGURE 1. Lvov furnace. (From Lvov, B. V., *Spectrochim. Acta*, 24B, 55(1969), Pergamon Press. With permission.)

of design have inspired the recent wide interest and activity in the area of nonflame atomizers. The graphite tube is 30 to 50 mm long with an inner diameter of 2.5 to 5 mm. The optical path of the excitation beam passes through the center of the tube. The tube is heated electrically by an alternating current to temperatures up to 2,500°C. The electrode is fashioned from a carbon rod 6 mm in diameter. The head of the electrode is shaped to fit the orifice in the wall of the tube. In the original design of the atomizer,[1] an auxiliary method of heating the sample was provided by a DC arc struck between the electrode carrying the sample and an auxiliary electrode mounted under the graphite tube. This, however, was later judged to be an inefficient way of heating the electrode and was replaced by heating of the electrode by an additional alternating current, passing the electrode and the tube.[2,3] Since the highest resistance is offered at the contact and the neck of the electrode, it is the head of the electrode which becomes most heated and this of course is desirable for efficient sample vaporization.

The samples are placed on the electrode either in liquid or powder form.[2] For convenient containment of solid samples, grooves are traced into the electrode head. Before depositing liquid samples, electrode heads are treated with a solution of polystyrene in benzene, which prevents the sample solution from soaking into the graphite. After the electrode is prepared, the chamber surrounding the graphite tube is freed of oxygen by flushing with argon or nitrogen for 5 to 10 s, and is filled to the desired pressure. The tube is heated for 20 to 30 s, the electrode is led into the orifice in the tube, auxiliary electrical heating is turned on for 2 to 3 s, and absorption is measured. The electrode is then lowered away from the graphite tube, and the system is ready for the introduction of another electrode carrying a sample.[2] In some of Lvov's atomization systems, the pressure of the inert gas in the chamber surrounding the graphite tube was kept above atmospheric in order to retard diffusion of atomic vapor through the ends of the tube.[4,4a,4b]

Since graphite is porous and atomic vapor can permeate into the walls of the tube, the inside wall of Lvov's atomizer was lined with Ta or W foil or with a thin layer of pyrolytic graphite.[2] In addition to its low gas permeability, a pyrolytic graphite lining possesses the desirable qualities of high heat conductivity, high resistance to oxidation, more uniform heating, and a long life.

The excellent sensitivity of the Lvov furnace is illustrated by the data in Table 1, where sensitivity is defined, consistent with the IUPAC definition, as absorbance corresponding to a given weight of the element. Detection limits attainable with conventional aspiration of sample into the flame fall in the approximate range 0.01 to 1 ppm. Assuming that 1 cm^3 of sample is the minimum volume necessary to make a measurement, the approximate detection limit of the flame methods of 10^{-8} to 10^{-6} g is indicated. Pulse atomization in the Lvov furnace, however, extends to trace amounts of 10^{-13} to 10^{-11} g of elements, and thus offers improvement in detectability by a factor of about 10^5.

In addition to the elements listed in Table 1, Lvov's furnace was used in an atomic absorption determination of P at the 213.5–213.6 nm doublet.[4a] The pressure of the inert gas was held at 3 atm and the tube was heated to 2,700°K, yielding a detection limit of 2×10^{-10} g P. Iodine was determined under similar conditions at the 206.2-nm line with a detection limit of 2×10^{-9} g I.[4c] Lvov and Khartsyzov[4b] also used the Lvov furnace in the vacuum ultraviolet region. The I line at 183.0 nm, the P line at 177.5 nm, and the S line at 180.7 nm had the following sensitivities (absorbance for 1 ng): 0.13 ng^{-1}, 1.4 ng^{-1}, and 0.063 ng^{-1}, respectively. The chamber was kept at an Ar pressure of 1.2 atm.

2. Massmann Furnace

Massmann described a graphite-tube atomizer for atomic absorption and a graphite cuvet for atomic fluorescence.[5,6] Both devices are illustrated in Figure 2. The tube atomizer is 55 mm long, 6.5 mm in internal diameter, and has a wall thickness of 1.5 mm. Unlike the Lvov design, a liquid sample is introduced through a small hole in the center of the tube by means of a micropipet, while solid samples are inserted from one side of the tube. The cuvet has the same diameter and wall thickness, but is only 40 mm high and has a slit cut into its wall through which fluorescence is viewed. A power supply provides currents up to 500 A which can raise the temperature of either atomizer to 2,600°C within a few seconds. The atomizer is enclosed in a chamber and oxygen is kept away from the heated graphite by purging with argon. Sample volumes of 5 to 200 μl are

TABLE 1

Sensitivities Obtained by Atomic Absorption with Heated Graphite-Tube Atomizers

		Sensitivity (absorbance for 1 ng)*			
Element	Wavelength, nm	Lvov furnace[2]	Massmann furnace[6]	Perkin-Elmer HGA-2000[2,8]	Woodriff furnace[8]
Ag	328.1	40	6	0.7	0.6
Al	309.3	4		0.1†	0.02
Au	242.8	4		0.1	
As	189.0		0.02	0.2† (193.7 nm)	
B	249.8	0.02			
Ba	553.5	0.7		0.02	
Be	234.9	100		0.6†	
Bi	306.8	1	0.02	0.1† (223.1 nm)	
Ca	422.7	10		0.1	0.04
Cd	228.8	60	2	4†	0.5
Co	240.7	2		0.2†	0.04§
Cr	357.9	2		0.4†	0.06§
Cs	852.1	10		0.04	
Cu	324.8	7	0.5	0.09	0.05
Dy	421.2			0.007	0.04
Ho	410.4				0.05
Er	400.8			0.003	0.04
Eu	459.4			0.0001	
Fe	248.3	4	0.2	0.1	0.04
Ga	287.4	4		0.002	
Hg	253.7	0.06	0.02	0.0004	
In	303.9	10	0.02	0.006	
Ir	264.0			0.001	
K	404.4	0.1		0.2 (766.5 nm)	
Li	670.8	1		0.07	0.4
Mg	285.2	100	9	1	0.06
Mn	279.5	20	0.6	1†	0.06
Mo	313.3	2		0.05	
Na	589.0		0.7	0.4	
Ni	232.0	0.5	0.06 (352.5 nm)	0.03	0.02
Pb	283.3	2	0.4	0.4†	0.4
Pd	247.6	1		0.03	
Pt	265.9	0.4		0.1†	
Rb	780.0	4		0.09	
Rh	343.5	0.6		0.03	
Sb	231.1	0.9	0.04	0.02 (217.6 nm)	
Se	196.1	0.5	0.003	0.001	
Si	251.6	90		0.04	
Sn	286.3	2		0.04†	
Sr	460.7	4	0.4	0.02	
Te	214.3	4		0.0001†	
Ti	365.3	0.1		0.002	
Tl	276.8	4	0.1	0.03	
V	318.4			0.01	
Zn	213.8	100	6	4	0.5

*The sensitivity is defined, in accordance with an IUPAC recommendation, as the slope of the calibration curve. In order to estimate the amount of material which corresponds to 1% absorption, divide 0.0044 by the listed sensitivity value.

†The flow of purge gas was interrupted during atomization.

§Data from Reference 10.

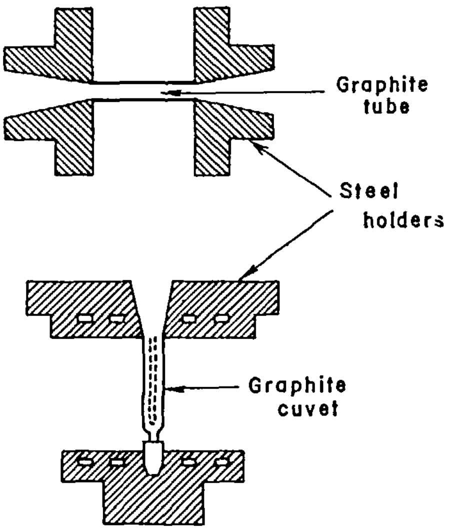

FIGURE 2. Massmann furnace. (From Massmann, H., *Spectrochim. Acta*, 23B, 215(1968), Pergamon Press. With permission.)

used with the tube atomizer, and 5 to 50 μl volumes with the cuvet atomizer.

The sensitivity of the Massmann atomizer for atomic absorption is presented in Table 1. When comparing the sensitivities of Massmann, Lvov, and other tube furnace atomizers, it is helpful to keep in mind that the sensitivities of non-flame atomizers depend very much on the geometry of the graphite cell. For instance, Lvov showed the sensitivity to be inversely proportional to the square of the inner diameter of the graphite tube, as long as only small samples are atomized. The data in Table 1 correspond to a 2.5-mm Lvov and a 6.5-mm Massmann tube.

Massmann also reported^{5} the following detection limits (rounded off to 1 significant figure) for the atomic fluorescence mode: 0.04 pg Zn, 0.2 pg Cd, 2 pg Ag, 0.2 ng Sb, 3 ng Fe, 2 ng Tl, 40 pg Pb, 4 pg Mg, and 0.4 ng Cu.

3. *Other Heated Graphite-tube Atomizers*

Woodriff and co-workers also used a graphite-tube furnace for atomic absorption.$^{7-13}$ A drawing of the Woodriff furnace is illustrated in Figure 3. The graphite tube is 30 cm long and 8 mm in internal diameter. It is electrically heated at temperatures up to 3,000°C and cooled by water. The sample is introduced into the heated tube in the form of pneumatically or ultrasonically nebulized spray carried by an inert gas. Alternatively, the sample is introduced into the tube in a small graphite cup inserted through a side arm. The absorption tube is open at both ends and is continuously flushed with argon, which enters through the side arm. The sensitivity of the Woodriff atomizer is illustrated in Table 1. The sensitivity is somewhat worse than that for the Lvov furnace and only slightly worse than that for the Massmann furnace for some of the elements.

Winefordner^{14} described a heated graphite atomizer system for use in atomic fluorescence studies. Slits are cut in the graphite tube in such a way as to prevent incandescent radiation from the graphite tube itself from reaching the detector along with fluorescence. Sample solutions are injected into the graphite tube through a rubber septum in the front of the atomizer housing by means of a hypodermic syringe. This eliminates

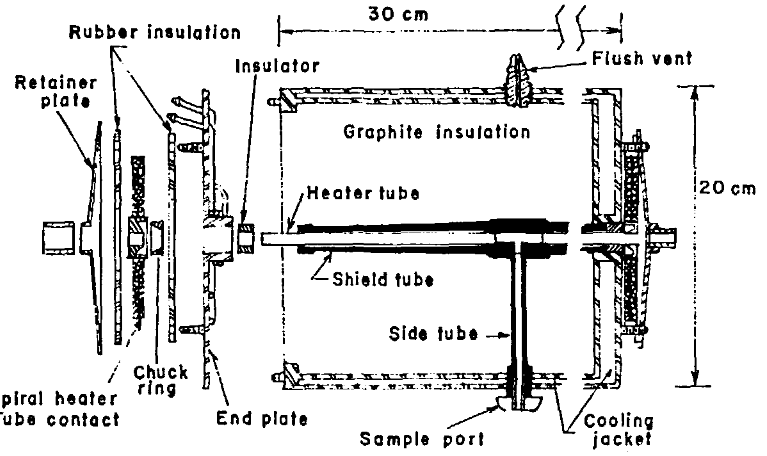

FIGURE 3. Woodriff graphite-tube furnace. (Reprinted with permission from Woodriff, R. and Shrader, D., *Anal. Chem.*, 43, 1919(1971). Copyright by the American Chemical Society.)

the need for opening the door of the cell compartment for every sample injection. The cell is continuously flushed with argon. A xenon arc lamp and line sources are used for excitation, and a photon counting system is used for detection.

Robinson et al.[15-17] described a non-flame heated tube technique for the direct determination of metals in air. In this device, air flows first through a heated tube filled with chunks of carbon. On coming into contact with carbon heated to 1,400°C by a radio-frequency coil wrapped around the tube, oxygen is converted to carbon monoxide, and metallic pollutants in the air are reduced to the elemental state by the action of hot carbon and carbon monoxide. The gas stream then flows through a 41-cm long quartz absorption tube heated to about 900°C, where the atomic vapor of the metallic pollutants is subjected to exciting radiation from the hollow cathode lamp. The system was applied to the determination of lead in air, the results indicating that 3 X 10^{-11} g lead corresponded to 1% absorption and that lead was detectable down to 0.2 μg m^{-3}.[18] The system was also applied to the determination of cadmium in polluted air, and concentrations down to 0.005 μg m^{-3} were measured.[19] The technique was further extended to the determination of cadmium in liquid samples such as water, sea-water, and urine, with an absolute detection limit of about 10^{-13} g.[19] Accuracy, however, was not checked by other methods of analysis and consequently cannot be stated. The mercury line at 184.9 nm in the vacuum ultraviolet was used in the direct continuous determination of mercury in air, with a concentration of 0.1 μg m^{-3} giving a 1% absorption signal.[17] However, because many inorganic and organic vapors exhibit pronounced absorption in the area of 185 nm, careful correction for molecular background absorption was imperative. Overall, the technique has little promise, mainly because of its relatively low atomization temperature. Background absorption is not eliminated, interelement interferences can certainly be expected to be more severe than in the graphite-tube furnace and filament atomizers, accuracy has not been proved, and it is clearly limited to only very volatile elements by the low atomization and absorption cell temperatures.

A simple, inductively heated graphite-tube atomizer, based on the fundamental Lvov furnace, was described by Headridge and Smith.[20] This atomizer, also, is suitable for relatively volatile elements only, as the maximum temperature it attains is 1,900°C. Another high-frequency, induction-heated graphite-tube furnace was described by Langmyhr and Thomassen.[21] Morrison and Talmi[22,23] used an induction-heated graphite cuvet as a thermal means of vaporization and atomization, but it was coupled with excitation by helium plasma formed by the radiofrequency field. Other adaptations of the graphite tube furnace have been described by Aspila et al.,[24] who closed one end of the tube with a quartz window, and by Welz and Wiedeking.[25]

The basic Lvov graphite-tube furnace, simplified by Massmann, was further developed as a commercial product by the Perkin-Elmer Corporation and later by Jarrell-Ash (Fisher Scientific Company). Figure 4 illustrates the cross section of the Heated Graphite Atomizer offered by Perkin-Elmer as models HGA-70 and HGA-2000.[26] The graphite tube is 50 mm long and 10 mm in diameter. The sample is introduced through a 2 mm-hole in the middle of the tube by means of a micropipet. Volumes from 1 to 100 μl can be accommodated. Solids can be introduced into the tube from the side. The tube is continuously purged with nitrogen, at a flow rate of about 1.5 l min^{-1}, which enters the graphite tube through small holes in the walls and exits through the ends, which are open to the atmosphere. The graphite tube is surrounded by a hollow metal jacket through which cold water is circulated. The water helps to dissipate the heat from the tube following the completion of an atomization cycle in time intervals of less than a minute. As many as 40 samples may be run per hour. A recent modification of this atomizer (HGA-2100) offers an

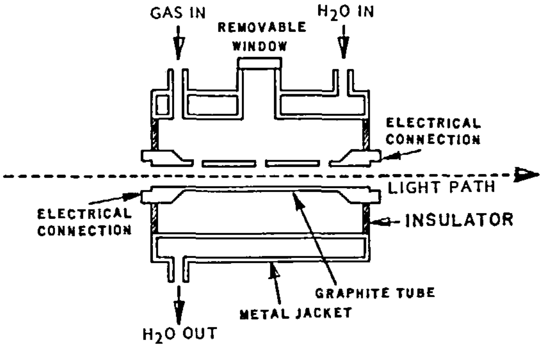

FIGURE 4. Cross section of the Perkin-Elmer HGA. (From Perkin-Elmer Corporation, *Instrument News*, Vol. 21, 4(1970). With permission.)

opposed-flow gas system in which the purge gas enters the tube at the ends and flows towards the center of the tube, where it exits through the sample introduction port. Opposed-flow design is expected to minimize condensation of the atomic vapor in the tube. The manufacturers also claim a better heat distribution in the graphite element in the later model, but no user reports have yet appeared in the literature to confirm or deny these claims.

Electrodes in contact with the ends of the graphite tube are connected to a low-voltage high-current power supply capable of delivering up to 500 A. The sample is first heated at a low current to vaporize the solvent, then at a higher current to char and ash any organic residues, and finally a high current is applied to efficiently atomize the sample. Working temperatures as high as 2,700°C are available. The HGA-2000 power supply is programmed to proceed automatically through the three heating steps at temperatures and heating periods preselected by the operator. Graphite tubes last for 50 to 100 runs. An additional feature of this heated graphite atomizer is the capability for automatic interruption of the purge gas at the start of the atomization step, which can improve the sensitivity of some analyses by factors from 2 to 30 by decreasing the rate of dilution and diffusion of the atomic vapor out of the graphite tube.[27,28]

Some data on sensitivity are presented in Table 1. On the average, the results are 1 to 2 orders of magnitude less sensitive than those reported by Lvov. It must be kept in mind that comparison of reported sensitivities, or of detection limits, is not an entirely adequate way of comparing the performance of different atomizers because different researchers naturally do not work with identical excitation sources and detection systems. In addition to the elements listed in the table, the detection of phosphorus in the heated graphite atomizer has recently been reported, based on molecular absorption by the PO species at 220 nm.[29]

Pickford and Rossi[30] designed an automatic sampling system in which aliquots of a flowing water stream were automatically injected into the HGA-70 tube furnace. Their sampling and injection assembly is sketched in Figure 5. A synchronous motor rotates two eccentric cams, which are rigidly attached to each other. The turning of the larger cam pushes the rod connected to the quartz capillary and causes the tip of the capillary to become lowered into the center of the graphite tube. The motion of the smaller cam acts against the push-rod connected to the sampling valve. The displacement of the central slider by 1 cm causes a 100-μl aliquot of the sample stream to enter the argon stream and be carried to the graphite tube. The quartz capillary is coated with silicone to prevent adsorption. Further movement of the larger cam withdraws the capillary from the tube and actuates the drying cycle of the furnace. After drying, the system proceeds automatically to preselected charring and atomizing cycles, or repeats the sample injection and drying step up to four more times, if increased sensitivity is desired.

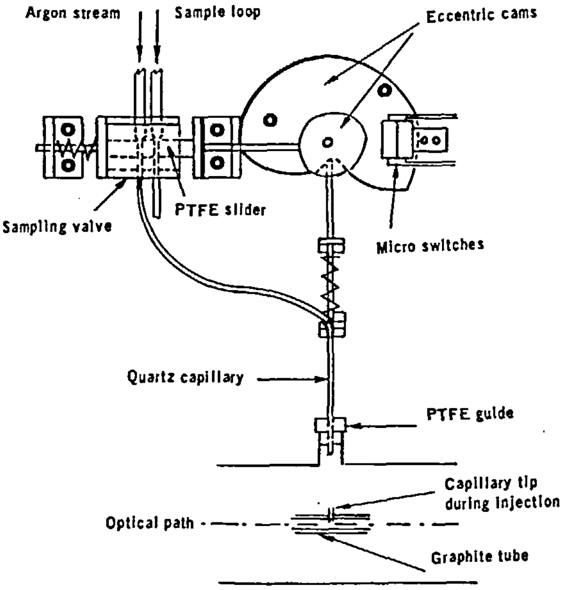

FIGURE 5. Automatic sampling and injection assembly for the heated graphite atomizer. (From Pickford, C. J. and Rossi, G., *Analyst*, 97, 648(1972). With permission.)

The sensitivity of automated analysis remains essentially the same as that reported for pulse injection. The precision of the automated system is, however, superior to that of manual injection, and results show a typical relative standard deviation of only 0.6 to 2.4%.

4. Continuous Sample Introduction Systems

Non-flame atomizers commonly employ discrete samples and pulse atomization, rather than continuous sample introduction. It is the ability of these atomizers to cause efficient atomization of tiny aliquots of sample solutions that constitutes their main superiority over pneumatic aspiration into the flame. Continuous sample introduction has, however, also been coupled with the use of flameless heated tube atomizers.[9,31-34] Such attempts usually suffer from serious losses of sensitivity and are not likely to be a direction of much future attention. Woodriff's original furnace for atomic absorption employed continuous introduction of pneumatically or ultrasonically nebulized sample.[9] Black et al.[31] sprayed the aqueous sample solution through a heated platinum circular strip or a heated platinum tube. The emerging sample vapor thus contained the atomic vapor of the easily atomized elements. The atomizer temperatures were limited by the melting point of platinum, which is 1,775°C. Fluorescence was measured from an optimum point about 2 cm above the top of the atomizer. Scatter by solute particles and unvaporized water droplets was small and readily corrected for by subtraction from the atomic fluorescence signal. The sensitivity of the technique was moderate and compared unfavorably with that attainable with flame nebulization. Clyburn et al.[34] continuously introduced a desolvated aerosol into a heated graphite-tube furnace, and measured atomic fluorescence excited by a single continuum source. Detection limits reported for 13 elements were comparable to those attainable in conventional flame atomic absorption.

Murphy et al.[32] described several non-flame atomizers in their work on the comparison of lock-in amplification and photon counting with flames and graphite atomizers in atomic fluorescence spectrometry. The atomizers (Figure 6) were designed for continuous introduction of the sample aerosol in argon carrier gas. One atomizer is essentially a heated graphite tube, positioned vertically to serve as a cuvet. The sample aerosol enters the graphite cuvet near the bottom and flows up through the heated tube surrounded by a water-cooled jacket. The best detection limits reported for this device are 3×10^{-7} ppm for Zn, 3×10^{-5} ppm for Cu, and 1×10^{-3} ppm for Bi. These results were attained with the use of electrodeless discharge lamps and were essentially the same for both detection systems. Another atomizer described by these workers consists of a horizontal heated graphite rod with a vertical slot in the middle. The sample aerosol spray is directed at this slot in the rod. During passage through the slot, contact with the hot internal surfaces of the slot atomizes the sample. Because of the very short period of time spent by the sample in the hot environment, atomization is incomplete and only considerably higher detection limits are possible.

Graphite atomizers are now usually coated with pyrolytic graphite. Standard graphite is porous, which allows the diffusion of sample vapor into the atomizer walls, and which also causes graphite to be more readily deteriorated by traces of oxygen and even water vapor at high temperatures. A layer of pyrolytic graphite may be deposited on a new atomizer, or an old atomizer may be rejuvenated, by pyrolyzing hydrocarbons in the tube at a temperature of about 2,000°C. Veillon and others[32,35] passed a small flow of methane mixed with argon through the atomizer while heating the graphite atomizer at 2,200°C. These workers[35] further pointed out that in the case of continuous sample introduction into the graphite

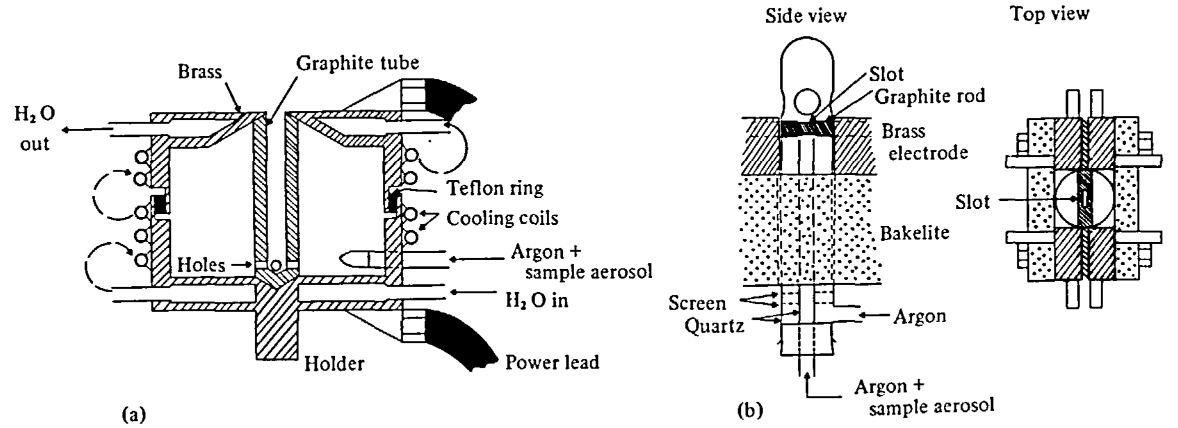

FIGURE 6. Some continuous sample-introduction systems. (a) Cross-section of the vertical graphite tube furnace. (b) Side and top views of the slot-rod atomizer. (Reprinted with permission from Murphy, K. M., Clyburn, S. A., and Veillon, C., *Anal. Chem.*, 45, 1468 (1973). Copyright by the American Chemical Society.)

atomizer, a slow flow of methane can also be introduced continuously and an equilibrium can be established where pyrolytic build up would be taking place at the same rate as the attack of the graphite element by water vapor. If such a steady state can be established, the system can be operated at high temperatures for long periods of time.[33,34]

B. Absorption Signals and Selection of Optimum Temperatures

1. Typical Absorption Signals

A typical sequence of absorption signals recorded when a sample of milk is analyzed directly by pulse vaporization in a graphite-tube atomizer is illustrated in Figure 7.[36] The 25-μl sample of milk is first subjected to gentle heating, which drives off the moisture and results in a spike due to scattering on the left of the recorder trace. After the evolution of water, the temperature is increased to burn off the organic matrix and any volatile inorganic compounds. This often causes visible evolution of smoke from the ends of the tube and broad absorption and scattering peaks in the center of the recorder trace. A final increase of temperature atomizes the copper and gives rise to the sharp peak on the right edge of the diagram. In routine work, only the atomization signals are usually recorded.

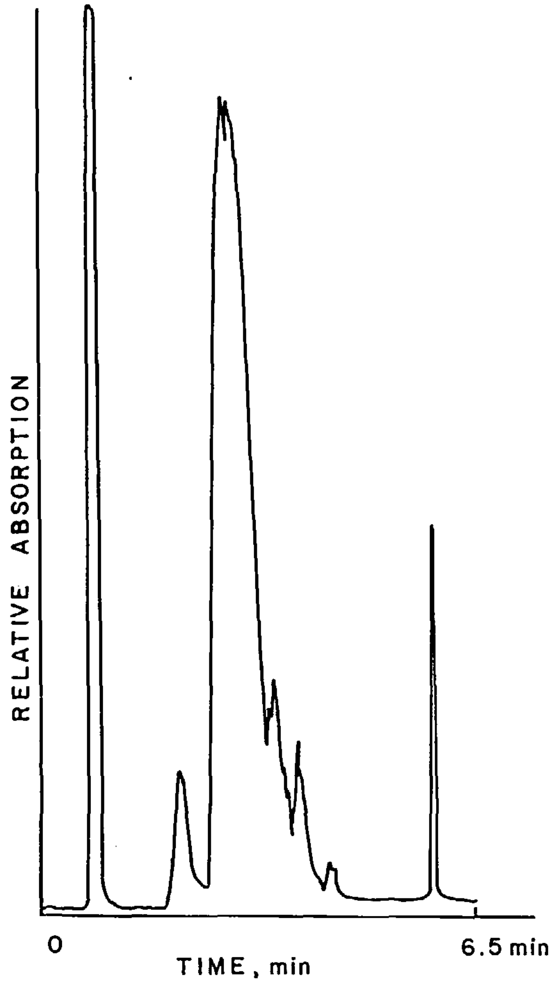

FIGURE 7. Direct determination of copper in milk with the HGA using a 25-μl sample. (From Manning, D. C. and Fernandez, F., *A. A. Newsletter*, 9, 66(1970). With permission.)

Calibration curves are prepared by plotting the atomization peak height or area versus the amount of the element of interest injected into the atomizer. It is best to inject the same volume of all solutions in order to avoid the effect of sample volume on signal intensity which has been noticed by some workers. It was observed that absorption signals decreased as volumes were increased for the same injected weight of metal.[37] This variation may be due to local differences in temperature in the graphite tube.

2. Selection of Optimum Temperatures for Atomic Absorption Work with a Tube Furnace

The selection of proper temperatures and durations for the drying, ashing, and atomization steps is of utmost importance and must be established for each individual element in each different matrix. During the drying step, the atomizer temperature is set slightly above the boiling point of the solvent. The drying time depends on the sample volume; for instance, for a 20-μl sample a 20-s drying period is adequate in the HGA furnace.

To select the optimum atomization temperature and time, an aqueous standard solution is analyzed with the highest atomization temperature setting, and analysis is repeated using successively lower atomization temperatures. The duration of the atomization step must be sufficient to allow the absorption signal to drop to the baseline. Failure to return to the baseline indicates incomplete removal of the sample from the atomizer and must be eliminated before the next sample injection is made. The intensity of the atomization signal is plotted against atomization temperature, and the lowest temperature that gives the maximum signal is selected as optimum.

In selecting the optimum ashing temperature and duration, the operator is looking for those compromise conditions which would allow the volatilization of all interfering and smoke-producing components of the sample matrix, yet cause no loss of the element of interest. This can become a difficult and even impossible task, especially with very volatile elements. First, an aliquot of the sample is charred at a low temperature, and absorption and scatter caused by the incompletely removed matrix are measured during the atomization step at a nearby non-resonance line. Then, the procedure is repeated at successively higher charring temperatures.. A plot of background absorption during atomization against ashing temperature is prepared and the lowest temperature that gives a reasonably low background absorption signal is selected. For example, Figure 8 shows that for the determination of lead in milk at 283.3 nm an ashing temperature of at least 375°C is necessary. Using this minimum ashing temperature, the minimum duration of the ashing step is determined. Higher charring temperatures can be used as long as they do not affect the intensity of the true atomization peak. Thus, in the example of lead in milk, the ashing temperature must not exceed 400°C because of the volatility of Pb.

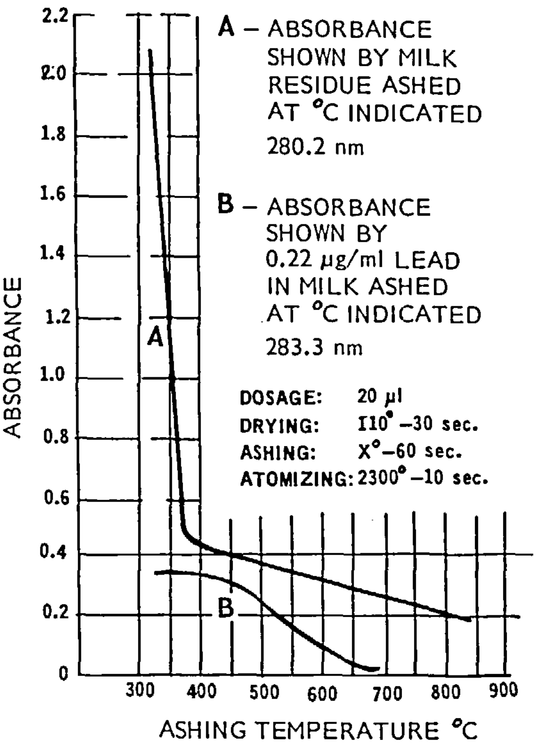

FIGURE 8. Selection of optimum charring temperature for the determination of lead in milk. (From Manning, D. C., *Am. Lab.*, p. 37, August 1973. Copyright owned by International Scientific Communications, Inc. With permission.)

In cases where non-atomic absorption cannot be completely eliminated during the ashing stage, background correction becomes necessary (see discussion below). For the best accuracy, standards and samples should have as nearly identical matrix compositions as possible, and investigators must be aware of the variety of possible interference effects that may affect each kind of sample. Incomplete removal of the matrix may result in interferences not just by nonspecific absorption but by chemical and physical interactions with the atomic vapor during atomization as well.

C. Interferences

1. *Physical and Chemical Matrix Effects*

Like conventional flame sampling, non-flame atomization is subject to some physical and chemical interferences. The element of interest may react with a component of the sample matrix during atomization to form compounds of greater or lesser volatility or thermal stability than the compound present in the standards. Interactions in the gaseous phase are also likely. The resulting effect on the rate and the completeness of atomic vapor formation may distort the recorded atomization peaks and affect accuracy and sensitivity.

Interferences encountered in atomic absorption with tube furnaces were studied by Baudin et al.[39] A typical matrix effect on the atomization of 0.01 µg of silver by variable amounts of copper is illustrated in Figure 9. The duration of atomization increases, while peak height decreases, as increasing amounts of Cu are added. In this case, acceptable analytical results can be obtained only by plotting the integrated area under the absorption peak as a function of the weight of the element of interest. Linear curves can thus be obtained, but do not coincide with those generated in the total absence of any matrix.[39]

Among other interference studies, the effects of various ions on the atomization of the relatively volatile zinc (which volatilizes at a temperature of about 500°C) were studied by Clark et al.[40] Aliquots of 5 µl of solutions containing 0.1 ppm of zinc (as sulfate) and 100-, 1,000- and 10,000-fold excesses of foreign ions were atomized in the HGA-70 at 2,040°C. The results for just the 1,000-fold excesses of foreign ions are reproduced in Table 2. It is interesting to note that all additives interfered, and mostly depressed the zinc

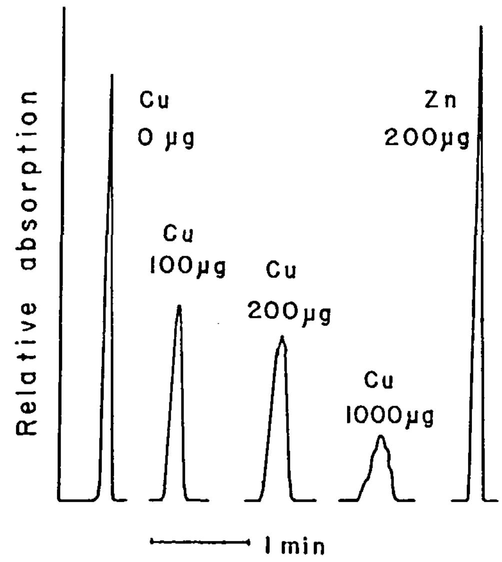

FIGURE 9. Effect of varying amounts of copper on the absorption signal of 0.01 µg of silver. (From Baudin, G., Chaput, M., and Feve, L., *Spectrochim. Acta,* 26B, 428(1971), Pergamon Press. With permission.)

TABLE 2

Effects of 1000-fold Excesses of Various Ions upon the Absorption Signal of Zinc Atomized in a Heated Graphite-Tube Atomizer

Ion	Molecule	% Interference
$SiO_3{}^{2-}$	$Na_2SiO_3 \cdot 5H_2O$	-50
$SO_4{}^{2-}$	H_2SO_4	+30
Cl^-	HCl	-40
$NO_3{}^-$	HNO_3	-18
$PO_4{}^{3-}$	H_3PO_4	-46
CH_3COO^-	CH_3COOH	-37
Na^+	NaCl	-44
K^+	KCl	-35
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	-35
Ni^{2+}	$NiCl_2$	-90
Ba^{2+}	$BaCl_2 \cdot 2H_2O$	-27
Al^{3+}	$AlCl_3 \cdot 6H_2O$	-27
Sn^{2+}	$SnCl_2 \cdot 2H_2O$ in HCl	-37
Co^{2+}	$CoCl_2 \cdot 6H_2O$	-20
Sb^{3+}	Sb_2O_3 in HCl	-34

(From Clark, D., Dagnall, R. M., and West, T. S., *Anal. Chim. Acta,* 63, 11 (1973). With permission.)

signal, possibly because of occlusion of zinc by the less volatile additives.[40] With hydrochloric acid, some loss of zinc as zinc chloride may have occurred. To eliminate these interference effects Zn was complexed and extracted into a variety of organic solvents. The compatibility of organic solvents with the graphite tube atomizer was demonstrated by very similar zinc signals obtained from solvent mixtures consisting of water with acetone, isopropanol, ethanol, methanol, or glycerol.[40]

Rather severe interferences by foreign salts are a common occurrence with many elements analyzed in a tube furnace. Matrix effects are sometimes observed even with such dilute samples as metals in river water. When lead was determined in river water by the method of standard additions[41] the slope of the calibration curve was significantly different from that given by simple aqueous standards. Similar behavior was exhibited to varying degrees by chromium, tin, and arsenic, while aluminum, cadmium, cobalt, copper, iron, manganese, nickel, and zinc showed no matrix effects in river water.

Matrix interference effects are reported by many workers, but much more work and interpretation remain to be done. Data on thermal decomposition processes of compounds and on reactions in mixtures of condensing atomic vapors are needed, before adequate explanations of interference effects can be found. It is reasonable to expect, however, that interactions both in the condensed phase prior to atomization, and in the gaseous phase after atomization, play important roles in the overall effect of a foreign substance on the analyte. While excessive amounts of foreign materials in the condensed phase would affect the rate and temperature of atomization of the analyte, interactions in the gaseous phase, after atomization, may force premature condensation of the atoms of interest in an environment of high concentrations of condensing foreign atoms. Nonuniformity of heating of some tube furnaces, and the fact that atomized vapors carried by the inert gas towards the ends of the tube encounter cooler environments before they leave the analytical light path, may account for the severity of some gas phase interference effects, but may become corrected by improvements in atomizer design.

2. Carbide Formation

The presence of the hot graphite furnace itself gives rise to a chemical interference virtually unknown in flame work: the formation of carbides. Molybdenum, for instance, is one of the elements which readily form carbides at high temperatures. When atomized in the graphite furnace, it rapidly gives rise to a maximum signal, but the latter decays to the baseline at a very slow rate, requiring atomization times as long as 30 s or more. The persistence of the signal is attributed to the slow decomposition of the molybdenum carbide.[28]

Baudin et al.[39] suggest that carbide formation explains some of the experiments with iron illustrated in Figure 10. After drying aqueous iron solutions in the graphite-tube furnace at 100°C, they were subjected to (a) volatilization by rapid heating to 2,000°C, and (b) destruction of nitrate by heating at 1,000°C for 3 min followed by atomization at 2,000°C. The workers suggested that the lowering of curve (b) may be caused by the formation of a carbide. This idea acquires support from the observation that an iron peak reappears when nitric acid is later added to the tube and, furthermore, from the observation that heating at 1,000°C for 3 min in the presence of excess copper has no effect on the calibration curve; it presumably prevents the contact of iron with graphite and thereby the formation of a carbide.

The carbides of molybdenum, vanadium, tungsten, and uranium melt in the temperature range of 2,500 to 3,000°C and thus present considerable difficulty in determinations in heated graphite tubes whose working temperatures do not exceed 2,800°C. Less refractory carbides form with such elements as calcium, strontium, barium, and silicon, and these elements can be readily determined. The carbides of titanium, zirconium, hafnium, niobium, and tantalum are very stable (melting points above 3,000°C), and, with the exception of titanium,[2,28] these elements cannot be determined in heated graphite atomizers.[42] A possible method of elimination of carbide formation is to line the graphite tube with tantalum[42] as described originally by Lvov in his attempts to eliminate diffusion of vapors into the graphite walls.

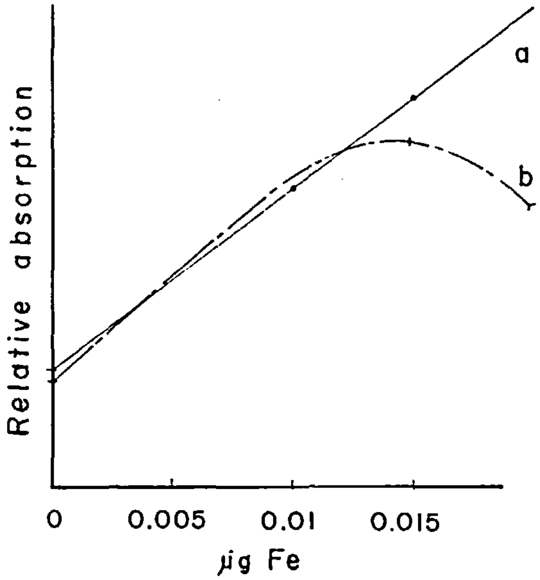

FIGURE 10. Effect of a different sequence of heating on the absorption signal for iron. (a) Volatilization by rapid heating to 2000°C. (b) Heating at 1000°C for 3 min, followed by atomization at 2000°C. (From Baudin, G., Chaput, M., and Feve, L., *Spectrochim. Acta*, 26B, 432(1971), Pergamon Press. With permission.)

3. Background Absorption

a. Occurrence

One kind of spectral interference is caused by scattered light from the incandescent graphite tube, which may reach the detector and distort the atomization signals. Such interference is naturally more pronounced at the visible rather than at the near ultraviolet wavelengths.

When atomization in the graphite tube is carried out at very high temperatures and in the presence of nitrogen as the purge gas, it is possible that molecules of cyanogen may form[28] and exhibit definite absorption in the regions 335 to 359, 374 to 389, and 410 to 422 nm, as they do in some flames. This absorption could, for instance, interfere with the non-flame determination of chromium at its resonance line at 357.9 nm. Workers whose atomizers emit scattered incandescence at these wavelengths are not likely to notice cyanogen interference. However, if present, it would be corrected similarly to other background absorption.

"Broad band" or background absorption interference results when a component of the sample matrix becomes volatilized simultaneously with the element of interest and causes a nonspecific absorption signal which may grossly affect, or be mistaken for, the signal from the element. "Broad band" absorption interference was recognized early in the development of non-flame atomization methods.[2,43] This phenomenon occurs to a very limited extent in the flames and is usually corrected by running a blank, but it becomes much more pronounced with the much more sensitive non-flame methods. It is evident from the literature that authors have on occasion employed the terms "broad band absorption" or "background absorption" loosely to refer not only to actual molecular absorption but to the combined effects of nonspecific absorption and of light scattering.

As shown in Figure 7, a typical absorption sequence may include the drying peak due to absorption or scatter of radiation by water vapor, a charring peak similarly caused by molecular or particulate species resulting from the decomposition of the organic portion of the matrix, and the desired sharp atomization peak due to the atomic vapor of the element of interest. "Broad band" absorption may further complicate this absorption sequence. Figure 11 reproduces the absorption peaks which may be observed for varying amounts of silver atomized in the presence of 1 mg of cupric nitrate (signals were recorded after drying at 110°C). Only the second peak, apparently, is caused by silver, as it is the only one that increases with increasing amounts of silver. The size of the other two peaks increases only in proportion to the total amount of salts injected into the furnace. The first peak disappears when the sample is heated to 450°C before atomization. It has been suggested that the first peak may be due to the OH and the third to the CO species.[39] However, although CO and OH absorb at 328.1 nm, in the absence of more adequate evidence the origin of these peaks must be considered unknown.

Another example of the serious problems caused by "broad band" absorption is offered by the attempted determination of trace metals in sea-water by direct injection into the heated graphite-tube atomizer.[44] When a 20-μl sample of sea-water was heated up to about 1,100°C, a visible "smoke" formed in the graphite tube and almost totally obscured the exciting beam from the hollow cathode (as well as the light beam from the continuum source, which is used for background correction, as shall be outlined below). Beam attenuation was tested at a variety of wavelengths by introducing into the atomizer solutions containing the following major salts at their sea-water concentrations: sodium chloride; sodium sulfate; magnesium, calcium, and strontium chlorides; potassium chloride, sodium bicarbonate, and potassium bromide; and boric acid and sodium fluoride. All solutions caused attenuation of the continuum beam, presumably by scattering and molecular absorption, but only the sodium chloride and sodium sulfate solutions caused attenuations of a magnitude that could not be handled by a background corrector. Since sodium chloride and sodium sulfate are the major component salts, direct atomization of sea-water samples is clearly not possible. Attempts at eliminating the interferents by selective volatilization either before or after the element of interest met with limited success. It has been determined that "smoke" begins to be evolved at about 1,100°C, and almost all the salt becomes eliminated when the temperature reaches about 1,250°C. The relative narrowness of this range, however, does not ensure the success of the selective volatilization technique because the presence of the large excess of the major salts greatly affects the volatilization behavior of many trace elements. Cadmium, which is normally volatilized around 875°C, does not appear at this temperature in the presence of the sea-water salts, and its atomization signal becomes buried in the nonspecific "smoke" signal. Silver, zinc, and lead behave similarly to cadmium.

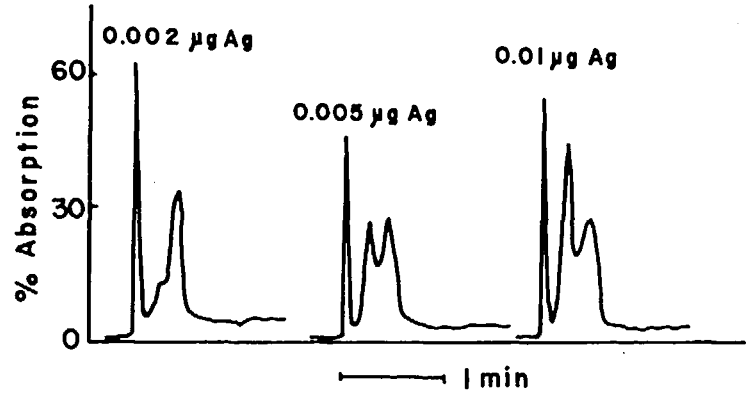

FIGURE 11. Effect of the excess of cupric nitrate on the absorption sequence for silver. (From Baudin, G., Chaput, M., and Feve, L., *Spectrochim. Acta*, 26B, 430(1971), Pergamon Press. With permission.)

Copper, which normally does not become atomized at temperatures below about 1,300°C, becomes partially lost by co-volatilization with the major salts. The percentage of copper that is recovered is dramatically dependent on the total salt content of the solution, as indicated in Figure 12. Varying salinity shortens and broadens the absorption peaks, but measuring peak areas rather than peak heights fails to account for more than a small fraction of the loss in sensitivity. Manganese, cobalt, and nickel behave rather similarly to copper, although the suppression of sensitivity by the total salinity is somewhat less pronounced. Of the elements tested in sea-water, only vanadium and iron do not suffer co-volatilization during selective removal of the sodium salts, and they yield the same sensitivity as standards prepared in distilled water. Since natural levels of vanadium in unpolluted sea-water are fairly close to the detection limit of the tube atomizer, only iron can be determined directly and with accuracy by employing the selective volatilization technique.

It is interesting to note that in some conditions the relative effect of molecular absorption interference is expected to be much lower in atomic fluorescence than in atomic absorption spectrometry. In the absence of fluorescence from the molecular absorber, of collisional quenching, and of scattering by the molecular interferent, West[45] offers the following reasoning in contrasting molecular absorption error in atomic absorption and in atomic fluorescence. Assume that the atomic vapor of interest and a molecular vapor of an interferent are present in a mixture and that each exhibits an absorbance of 0.01 (98% transmittance). In the atomic absorption mode, this interference will result in a concentration error of 100%. In the atomic fluorescence mode, however, assuming that there are no collisional interactions and no molecular fluorescence, the interferent may affect the intensity of atomic fluorescence in only two ways: (a) by decreasing radiation available for absorption by the atomic vapor and (b) by absorbing the fluoresced radiation. If absorbance by the molecular vapor is only 0.01, then 98% of the incident light remains unaffected and thus the error cannot exceed 2%. Similarly, only an average of 1% of the fluoresced radiation will be absorbed by the molecular interferent, since those atoms emitting nearest the detector suffer no molecular absorption, while those furthest from the detector suffer a maximum of 2% absorption. Thus, a total error due to molecular absorption interference of only 3% is expected at this concentration level, so that the error will be only one-thirtieth of that for atomic absorption.

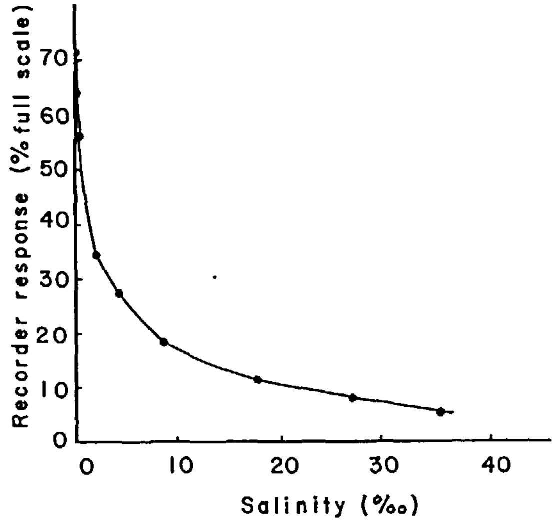

FIGURE 12. Effect of salinity on the copper response in a tube furnace with selective volatilization. (From Segar, D. A. and Gonzalez, J. G., *Anal. Chim. Acta,* 58, 11(1972). With permission.)

b. Detection of Background Absorption

Background absorption can be detected very easily. It is only necessary to use a nearby non-absorbing wavelength emitted by the same or another light source and to atomize the sample. A continuum source at the analytical wavelength can also be used for this purpose. The presence of an absorption signal indicates background absorption interference. After employing one of the means of background correction described below, it is necessary to repeat the atomization at the non-absorbing wavelength to be sure that the extent of correction is adequate.

c. Elimination or Correction of Background Absorption

It must, of course, be realized that it is not feasible to correct for background absorption by the simple application of the method of standard additions. Since the background absorption signal only adds to the desired signal, instead of affecting the atomic signal proper, the extent of its contribution to the overall absorption signal is the same, regardless of the relative amount of the element of interest added. Thus, resolving what fraction of the signal is due to background and what to the atomic vapor is not possible by means of standard additions. Methods of correction for background absorption used with some non-flame atomizers were discussed by Robinson, Hindman, and Slevin[46] and by Kahn and Manning.[47]

One way of eliminating, or greatly decreasing, nonspecific background absorption in favorable cases is by selective volatilization in the tube furnace. By careful programming of the temperature sequence, volatile organic matter and other constituents may be charred away prior to atomization, or the element of interest may be released completely prior to the destruction of the matrix. The selective volatilization technique is limited, unfortunately, by co-volatilization losses, as was illustrated above in the case of sea-water analysis. It is also not entirely safe to assume that loss during the preliminary heating stages will be reproducible and can be corrected by a calibration curve, since the performance of the furnace may not be entirely identical from one sample injection to the next.

The sample may be chemically pretreated prior to its delivery into the furnace. Conventional acid digestion or dry ashing techniques will reduce broad band absorption due to organic matrix, but careful attention must be paid to possibilities of sample contamination and partial loss of volatile elements. Classical separation techniques, such as solvent extraction and ion exchange, have been employed to remove the element or elements of interest from the bulk of the matrix. For instance, furnace determination of trace metals in sea-water was carried out successfully after extraction with the APDC/MIBK system.[48] Bulk sodium was removed from sea-water samples by treatment with hydrated antimony pentoxide.[49] In a recently reported method,[50] it was claimed that bulk sodium chloride was removed from sea-water samples by treatment with excess ammonium nitrate, directly in the graphite tube. This treatment transforms sodium chloride into sodium nitrate and ammonium chloride, both of which are volatile compounds and are easily removed from the furnace by temperatures below 400°C. Published data supporting this claim have not yet appeared.

While with conventional flame atomization, background absorption is corrected by aspirating a suitable blank, such correction is not practical with non-flame atomizers. In principle, the operator can first atomize the sample and measure the absorbance of the atomic line emitted by the hollow cathode lamp, and then atomize a similar sample and measure the absorption of radiation from a neighboring non-resonance atomic line or from a continuum source at the same wavelength. The typical width of an atomic absorption line is in the vicinity of 0.003 nm, while the slit widths employed in most monochromators allow a band of continuous radiation 100 times as wide, or more, to get through to the detector. The first measurement, then, reflects the sum of the absorbances of the background and the element of interest. The second measurement reflects the absorbance of the background alone. Thus, subtraction of the latter absorbance from the former can yield the correct absorbance signal.

There are several drawbacks in this approach to background correction. If a single-channel instrument is used, the measurements have to be taken sequentially, usually with a change of lamp to that of another element or to a continuum lamp. Since measurements are taken at different times, the automatic assumption is made that experimental conditions remained identical, while this is not always entirely true with a flameless atomizer. This drawback is eliminated if a two-channel instrument is used, since this allows the simultaneous determination of background absorption. Another possible pitfall is in the selection of a non-resonance line for the correction measurement. The correction would clearly be inaccurate if the selected line is not extremely close to the analytical wavelength and falls on a slope of the molecular absorption band. The conclusion must be made that optical correction for background absorption can best be carried out during a single run of the sample, and only at the wavelength of the atomic line.

Good background correction techniques were developed based on the early work by Koirtyohann and Pickett[51] and Lvov.[2] Schematically, the modification introduced into a commercial double-beam instrument by the addition of the deuterium background corrector is illustrated in Figure 13. The reference beam of the double-beam instrument is eliminated, and instead, a deuterium arc lamp is positioned behind the rotating sector mirror. The deuterium lamp is more suitable for this purpose than a hydrogen hollow cathode lamp because it is much more intense and it is desirable to have both beams of equal intensity. The rotating sector mirror alter-

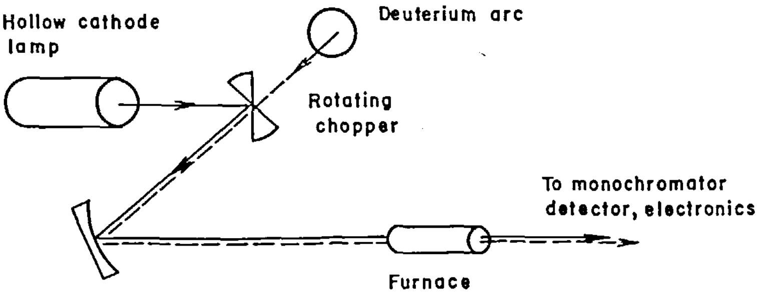

FIGURE 13. Deuterium background corrector. (From Kahn, H. L. and Manning, D. C., *Am. Lab.*, p. 51, August 1972. Copyright owned by International Scientific Communications, Inc. With permission.)

nately allows light from the line source and the continuous source to travel through the sampling device. Undesirable background absorption attenuates both beams equally, while the atomic vapor absorbs the analytical radiation from the line source and does not affect the intensity of the continuum to any appreciable extent. When the ratio of the two beam intensities is taken electronically, background contribution is eliminated.[47]

Essentially the same result is achieved by a background corrector system that employs polarizers in the sample and reference compartments of a double-beam instrument through which the light from a hydrogen lamp and a line source alternates.[10] Another system, described by Woodriff and Shrader,[11] also employs polarizers in a two-source single-beam instrument, which gives a continuous, simultaneous record of absorption of the two beams individually.

Mitchell et al.[52] described a system for correcting for background absorption; it employs a repetitive wavelength scanning technique and sequentially measures the intensities of the line and the line plus continuum radiation. Radiation from a DC operated hollow cathode lamp and the 150 W xenon arc lamp pass through the absorption cell simultaneously. The beams then fall onto a vibrating quartz plate which repetitively scans a narrow wavelength range, including the resonance line. In the resulting photodetector output, the line radiation shows up as a modulated signal and the continuum radiation shows up as a stable DC signal. The signals are measured and the ratio of the two intensities is a function of the atomic concentration of the absorbing species.

The series of atomization peaks reproduced in Figure 14 illustrates the effect of using a background corrector in the graphite tube determination of traces of gold in the presence of a large excess of sodium chloride.[47] A 20-μl aliquot of a solution containing 0 to 0.08 ppm of gold and 510 ppm of sodium chloride was atomized with and without background correction at the 242.8 nm gold resonance line. Clearly, much more

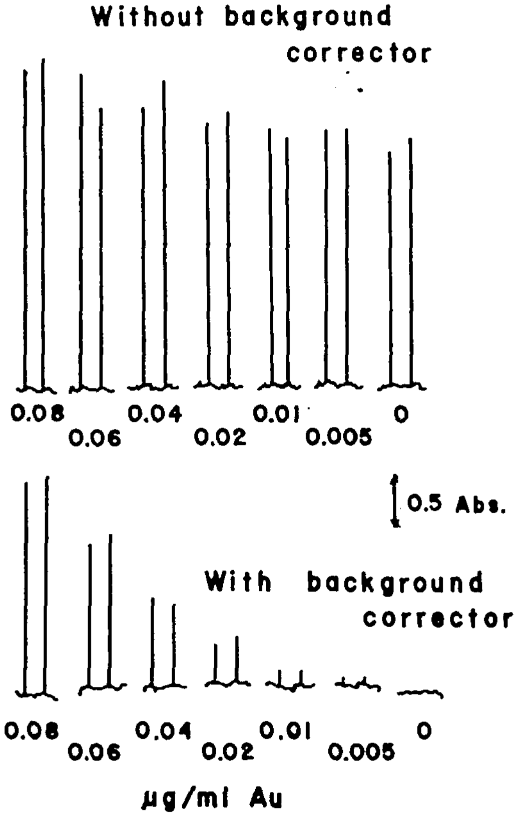

FIGURE 14. Duplicate signals for 20-μl aliquots of solutions containing gold at several concentrations in a sodium chloride matrix, with and without background correction. (From Kahn, H. L. and Manning, D. C., *Am. Lab.*, p. 55, August 1972. Copyright owned by International Scientific Communications, Inc. With permission.)

accurate data are obtained with background correction.

Although a background corrector can compensate for significant amounts of undesirable molecular absorption and scattering, it is important to remember that excessive background signal can overload the system and result in loss of precision and accuracy. For instance, a commercial model of a deuterium background corrector functions optimally when background absorption does not exceed an absorbance of 0.5.[28]

4. *Contamination and Instability of Dilute Solutions*

When working in the 10^{-9} to 10^{-12} g range, characteristic of heated graphite-tube atomizers, contamination can become a major source of error. Contamination may easily enter the sample from reagents, glass and plastic ware, and from the laboratory atmosphere. Extreme care in the preparation and conservation of samples is advisable.

Instability of dilute solutions has been noted by many workers. It is due, at least in part, to interactions with containers. Syringes with stainless steel needles should not be used for measuring out the sample. For instance, the use of a stainless steel syringe was shown to cause error in a determination of silver. The signal appears to decrease as a function of the time the silver solution spends in contact with the needle, and an appreciable error results in as short a time interval as 15 s.[53] A common practice in many laboratories is to inject samples into the atomizer by means of micropipets equipped with disposable plastic tips. Even with plastic tip pipets, delivery of the sample into the tube must be done very carefully. Inadvertently touching the metal rim of the jacket with the tip of the pipet has given some spurious results for zinc, apparently picked up from the metal itself or from condensed deposits of salts previously atomized in the instrument.

D. Applications of Graphite-tube Atomizers

Non-flame atomization in heated graphite-tube furnaces has enjoyed many applications, especially in the analysis of materials of biological origin.

The following elements have been determined in whole blood, serum, or plasma: copper,[25] iron,[54,55] lead,[56-59] nickel,[60,61] chromium,[58,60,62] manganese,[63] strontium,[63] cadmium,[58] and silver.[58] Urine was tested for chromium,[58,64,65] as well as for cadmium, lead, and silver.[58] Copper was determined in fingernails[66] and lead in hair.[67] Aluminum, cadmium, chromium, copper, iron, manganese, lead and vanadium were determined in an International Biological Standard.[68]

Lead was determined in fish[12] and in mussels.[69] Milk was tested for lead[38] and copper,[36,70,71] and for cobalt, iron, manganese, and strontium.[71] Arsenic and selenium were determined in orchard leaves and in bovine liver.[61] Molybdenum was determined in plants.[72]

In materials of geological nature, vanadium,[73] thallium,[74] tellurium,[75] and beryllium[76] were determined in standard rock samples, and iron and copper in high purity silica.[77] Iron, aluminum, copper, and manganese were determined in titanium dioxide.[78] Iron, copper, nickel, cobalt, manganese, and chromium, in proportions ranging down to 1 ppm, were determined in sodium calcium silicate glass, sodium borosilicate glass, sodium carbonate, and calcium carbonate.[79] Nickel and vanadium were determined in fuel oils.[80,81]

Metallurgical samples were tested for aluminum;[82] paper products for copper, iron, manganese, and silicon;[83] pulp and paper for copper, lead, cadmium, and manganese;[84] plastics for aluminum, iron, and copper;[83] and polyester fibers for gold.[85] The feasibility of the determination of iridium by non-flame atomization in a graphite furnace was demonstrated, a detection limit of 5×10^{-9} g of iridium was reported, and iridium was determined, after separation and concentration, in ores and metallurgical materials.[86] An application in the field of forensic science has been the determination of lead, antimony, and barium in gunshot residues.[87]

Several workers determined trace metals in natural waters[41,44,48,88-92] and traces of silver in snow.[13] Molybdenum[93] and copper[94] were determined in sea-water following collection of the metal on *p*-aminobenzylcellulose or chitosan. This chelating agent appears to have a wide applicability to collection of traces of transition metal ions.[94] Lead in atmospheric particulates was determined after passing the air through filters.[95,96]

Aside from the practical analysis applications, pulse atomization in heated graphite furnaces is useful in the study of physical properties such as pressure broadening of spectral lines, the measurement of absolute oscillator strengths of resonance lines, and the determination of the diffusion coefficients of atoms in gases.[2] Lvov and Khartsyzov[97] pointed out that when measuring oscillator strengths, loss of vapor by diffusion through the graphite electrodes must be accounted for. This loss may be as large as 20 to 40%. Nikolaev[98] discussed the theoretical sensitivities for the graphite-tube atomic absorption determination of nonvolatile elements, such as tungsten, tantalum, rhenium, niobium, hafnium, iridium, and zirconium, and discussed the selection of the optimum thermodynamic conditions which would allow the best sensitivity to be attained.

Although many materials required considerable pretreatment prior to sample introduction into the heated graphite furnace, some materials could be analyzed directly. For instance, Schaller et al.[64] determined chromium in urine by direct introduction into the furnace with no sample preparation. Slavin et al.[61] pipetted 50 μl of serum directly into the furnace and determined nickel after treating the sample in the furnace with 20 μl of 1% nitric acid. Direct atomization of trace elements in sea-water was attempted with limited success,[44] due to severe interference of the major salts. However, a recent report,[50] describing the treatment of saline waters in the furnace with ammonium chloride to volatilize sodium chloride as sodium nitrate and ammonium chloride prior to atomization, may make such direct analysis of sea-water possible. Molybdenum in sea-water was first concentrated on *p*-aminobenzylcellulose or chitosan, which enabled the researcher to determine natural molybdenum in as little as 50 ml of sea-water.[93]

In the determination of serum iron, Olsen et al.[54] found it necessary to remove protein and hemoglobin iron by treatment with hot trichloroacetic acid in order to avoid hemolysis interference. Fish samples were digested with perchloric acid and nitric acid before injection of 20-μl aliquots into the furnace,[12] and other biological materials were first wet-ashed with concentrated sulfuric acid and 50% hydrogen peroxide.[68]

For the determination of iron and copper in silica,[77] silica was dissolved in hydrofluoric acid, which resulted in the volatilization of silicon tetrafluoride during the ashing step of the analysis in the furnace. Glasses were treated with hydrofluoric and perchloric acids and extracted as diethyldithiocarbamate complexes into methyl isobutyl ketone prior to analysis.[79] Thallium was extracted from rock into isopropyl ether as a bromide,[74] and gunshot residues were washed from the hand with dilute hydrochloric acid and extracted into methyl isobutyl ketone prior to injection of 20-μl aliquots into the furnace for the detection of lead, antimony, and barium.[87]

The direct injection of solid samples into the heated tube furnace for analysis has been said to be feasible in several reports. Gold was determined directly in polyester fibers,[85] copper in fingernails,[66] trace metals in paper,[83,84] aluminum and iron in polypropylene plastic, and copper and iron in fluorinated hydrocarbon polymer plastic.[83] The difficulties with matrix interference are likely to prevent the extension of direct solid sampling to many materials. Even in the absence of matrix interference, the usefulness of solid sampling is clearly limited by the difficulties involved in measuring and handling extremely small amounts of samples. Kerber et al.[83] found, for instance, that the maximum weight of a solid sample that can be used in the HGA furnace is of the order of 15 mg. Aside from the need for extreme care in measuring out a sample of this size, it is also necessary, of course, to ensure that the portion taken for analysis is quite homogeneous and truly representative of the solid specimen. The dissolution of a larger sample in an accurately known volume of solution and the injection of a tiny aliquot into the analysis system is certain to remain the preferred method of sample introduction into heated graphite-tube furnaces.

E. Advantages and Limitations of the Heated Graphite-tube Furnaces Compared to Flames

1. Equipment

The non-flame atomizer is more difficult to build, costs more to purchase, and is physically somewhat more bulky than a typical nebulizer-burner. However, it does not require the use and storage of flammable gases, as does the flame operation. It is also free of audible noise, which is untrue of flames, especially the turbulent flames.

Flame systems are more convenient and simpler to operate, and burners do not wear out with the speed of the graphite elements. The operation of a burner, however, is potentially not without danger, while voltages involved in the heating of the graphite furnace are usually in the vicinity of 10 V and thus present no danger.

The graphite atomizer requires a large supply of power and fairly elaborate equipment to control it. The flame requires only the supply of compressed gases. Some flames can reach higher temperatures than the graphite atomizers. The non-flame atomizer requires a water line to cool the graphite element. It also requires the use of a good recorder or oscilloscope because signals of short duration have to be measured.

2. Versatility and Speed

Non-flame atomizers require only a few microliters of sample per injection, whereas several milliliters of solution must be available for analysis by flame.

Flame spectrometry in the vacuum ultraviolet is precluded by the intense absorption of oxygen. But, since the graphite atomizer is filled or flushed with an inert gas, work in the vacuum ultraviolet is no longer impossible, provided the rest of the optical path of the instrument is also freed of oxygen.

With the non-flame atomizers, the capability exists for direct solid sampling. Although complications arise with many matrices, some direct analyses of solids have been successful.

The speeds of analysis by flame and non-flame methods are rather similar when, as is often true, the length of the total analysis is determined primarily by the amount of sample pretreatment. However, if it is feasible to inject untreated samples directly into the graphite atomizers, the non-flame technique is much more rapid.

3. Sensitivity

In flame nebulization spectrometry, the sample is introduced into the flame gradually and individual atoms remain in the light path of the hollow cathode beam for only about 10^{-4} s. By contrast, in the graphite-tube atomizer essentially all of the sample can be converted into an atomic vapor at once and its lifetime in the path of the exciting beam is much longer. Lvov[2] estimates that, assuming that 10 s are needed for the establishment of a steady state atomization in the flame and for the measurement of the signal, the total amount of material that must pass through the flame will be $\frac{10}{10^{-4}} = 10^5$ times that present in the light path at any given instant of time. Since with the non-flame atomizer all of the sample becomes atomized at once, it follows that only 10^{-5} times as much sample will be required to make the measurement. Thus, an average absolute sensitivity gain by a factor of about 10^5 is expected. This estimate is borne out by comparing the non-flame detection limits with the typical 0.01 to 1 ppm detection limits observed with flames (0.01 to 1 μg cm^{-3}, corresponding to absolute detection limits of 10^{-8} to 10^{-6} g in a 1-cm^3 sample) and assuming approximately equal noise levels. This estimation assumes that the efficiency of production of gaseous forms of the analyte and the efficiency of free analyte atom formation in the graphite-tube atomizer are equal to those in the flame. Actually, this is a conservative assumption because efficiencies of vaporization and atomization in the non-flame cell are usually superior to those in the flame, especially in the cases of analytes which tend to form refractory oxides in the flame.

Although few real samples are free from matrix background interferences, in the cases where this condition exists, the non-flame atomizers produce an extremely low background for the analytical signal. This contrasts favorably with flames, where background is high and the limit of detection is governed largely by flicker of the background. Winefordner[14] gave a theoretical comparison of the graphite cell and the flame cell for analytical atomic spectrometry and concluded that for trace elemental analysis the combination of atomic fluorescence with a graphite atomizer should offer the best sensitivity. The main factors contributing to the greatly superior atomization efficiency of the non-flame atomizers are the smaller volume of the graphite cell and the absence of dilution with and expansion of the flame gases, as well as the much more complete vaporization.

With a non-flame atomizer, the chemical environment of the atomic vapor can be much better controlled. The formation of refractory oxides, which plagues flame spectrometry, is essentially eliminated by the inert environment from which oxygen is excluded. In atomic fluorescence spectrometry, flushing the system with argon creates an environment for the atomic vapor which is not only reducing, but which also possesses a lesser quenching efficiency than that of the chemical species present in the usual flames.

4. Precision

Flame spectrometry is characterized by very reproducible measurements. Random errors of only 1% or better are common. Heated graphite atomizers are considerably less precise and exhibit a relative variation of about 5 to 8%.[2] Errors involved in measuring a few microliters of a sample solution and delivering it to a reproducible point in the atomizer constitute a large part of this imprecision. In addition, the signal measured in flame atomic absorption or atomic fluorescence represents, as a result of continuous sampling, an effective average of signals over a period of time. With non-flame atomization, the pulse nature of the signal does not have the benefit of this averaging.

Greater automation improves the precision of graphite-tube furnaces[30] as well as that of other non-flame devices. Further developments in automation and computerization of non-flame systems are to be expected in the future.

III. CARBON-ROD AND -FILAMENT ATOMIZERS

A. Design and Sensitivity of Some Carbon-Rod and -Filament Atomizers

1. West Filament Atomizers

West and Williams[99] described a new non-flame atomization device in 1969 and showed that it was applicable to atomic absorption and atomic fluorescence spectrometry. The heart of the atomizer was a graphite filament, 20 mm long and 2 mm in diameter, which was placed between stainless steel electrodes and heated by the passage of electrical current up to approximately 2,500°C in about 5 s. The filament assembly was enclosed in a chamber which was purged with argon and which had quartz windows set into side arms. Sample aliquots of 1 to 5 μl were placed on the filament for analysis.

The original filament system was improved and modified by West and co-workers in several reports. The design of the chamber which enclosed the filament was modified; an efficient way of water-cooling the filament supports shortened the time needed between analyses; argon was led into the chamber through a wide laminated opening and exited at the top of the cell; and a notch was grooved into the center of the rod to hold the sample.[100] In order to assure reproducibility and sensitivity, a very strict timing schedule had to be followed in preheating the cell, introducing the sample, replacing the cover, applying the current for an instant to vaporize the solvent, and then in turning the current on to effect atomization. Exactly 105 s after the filament current was first put on, the atomizer had to receive the next sample, and so on, in order to ensure similar experimental conditions for all runs.[100]

The West-Williams carbon-filament atomizer was further improved by Alder and West.[101] In the new design the filament was not enclosed in a chamber, but was protected from the atmosphere by a sheath of an inert gas, which first flowed through a box below the filament packed with layers of plain and corrugated metal strips to cause laminar flow of the gas. The improved atomizer is illustrated in Figure 15. A light guide, 25 mm long and 4 mm i.d., was placed between the slit of the monochromator and the carbon filament in order to prevent emissions from the glowing filament itself from entering the monochromator.

Later modifications of the fundamental carbon-filament atomizer described by West and others have included decreasing the length of the carbon filament from 25 mm to 10 mm.[102] The advantage of the shorter filament is in its more rapid heating at a given applied voltage. Thus, the new design allows temperatures up to 2,500°C to be reached in 0.18 s. This, in turn, assures more rapid vaporization and atomization and results in higher and sharper recorded absorption peaks. The extent of improvement possible in this area is, of course, limited by the speed of the detector-

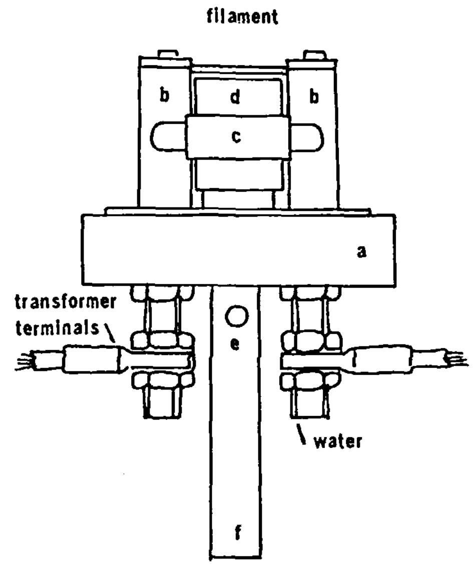

FIGURE 15. Carbon-filament atomizer for use in the open atmosphere; (a) base, (b) watercooled electrodes, (c) water link between electrodes, (d) laminar flow box, (e) inlet for shield gas, and (f) support for reservoir. (From Alder, J. F. and West, T. S., *Anal. Chim. Acta,* 51, 366(1970). With permission.)

recorder system. The researchers also returned to the idea of enclosing the filament assembly in a glass chamber with silica windows in order to extend the life of the filament.[102] When the filament had to be raised to very high temperatures (2,500°C) in the atomization of vanadium, for instance, a shield with a 0.3-mm-diameter aperature was placed 10 mm behind the filament so that only the incident radiation grazing the filament was measured, while the intense continuum emitted by the glowing carbon was eliminated.[102]

The detection limits reported by West and co-workers are indicated in Table 3. In all the experiments, modifications of the West filament atomizer were used.

2. *Belyaev Crucible Atomizer*

Belyaev and co-workers described a graphite atomizer for solid samples which is shaped like a tiny cup, and which is heated by an arc impulse or by resistance heating.[111-113] With the older device, illustrated in Figure 16a, absorption or fluorescence is measured just above the crucible. By this means cadmium[111] and silver[114] were determined in rocks and a series of metals was determined in graphite powder.[112,115,116] A later development[113] in the design of the graphite crucible (Figure 16b) has included an increase of the vertical dimension of the crucible from 5.5 mm to 10.5 mm and the introduction of a transverse hole, 3 mm in diameter, through which the excitation beam for atomic absorption measurement is directed. This atomizer somewhat resembles the cuvet described by Massmann for atomic fluorescence.

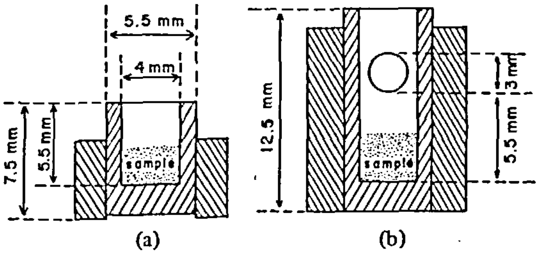

FIGURE 16. Cross section of the graphite-crucible atomizers. (From Belyaev, Yu. I., Koveshnikova, T. A., and Kostin, B. I., *Zh. Anal. Khim.*, 28, 2112(1973).)

TABLE 3

Detection Limits Attained with West Filament Atomizers

	Detection Limit,* g	
Element	Atomic Absorption	Atomic Fluorescence
Ag		1×10^{-12} (100)
Al	1×10^{-9} (103)	
Au	2×10^{-10} (104)	4×10^{-12} (104)
Bi		1×10^{-11} (100)
Cd		2×10^{-13} (101)
Co		2×10^{-11} (105)
Cr	1×10^{-11} (106)	
Cu	5×10^{-11} (103)	1×10^{-12} (105)
Fe	1×10^{-11} (107)	
Ga		5×10^{-11} (100)
Hg		5×10^{-11} (105)
Mg		1×10^{-12} (100)
Mn	3×10^{-12} (108)	6×10^{-13} (108)
Mo	3×10^{-11} (109)	
Pb	4×10^{-11} (103)	1×10^{-11} (100)
Ni	3×10^{-10} (103)	5×10^{-12} (105)
Sb		1×10^{-9} (105)
Tl		5×10^{-11} (100)
V	3×10^{-10} (110)	
Zn	2×10^{-13} (109)	2×10^{-14} (100)

*References are given in parentheses.

Clearly, the advantage of the later design consists in the localization of the atomic vapor in a hot environment, where it is examined before the contact with the cool air or argon above the crucible begins to condense the vapor. Detection limits improve by a factor of about 5 with the new crucible.[113] Belyaev and co-workers tested 15-mg samples of graphite powder and reported detection limits for many metallic impurities in the range of 10^{-7} to 10^{-5}%.[113]

3. *Varian Techtron Carbon-Rod Atomizer*

A commercial atomizer based on the carbon-filament atomization principle and influenced by the tube furnace technique is offered by Varian Techtron as the carbon-rod atomizer (latest model #63). The original form of this atomizer, often referred to as the "mini-Massmann" furnace, consisted of a rod 5 mm in diameter with a transverse hole of 1.5 mm diameter. This tiny furnace accommodated sample volumes only up to 2 μl. Although this design had the advantages of low power consumption and compactness, the necessity to work with such small volumes tended to limit the precision of the analyses. The later model of this atomizer takes the form illustrated in Figure 17. The furnace is supported by two graphite electrodes, which are mounted in water cooled terminal blocks and connected to the power supply. Inert gas and hydrogen are admitted

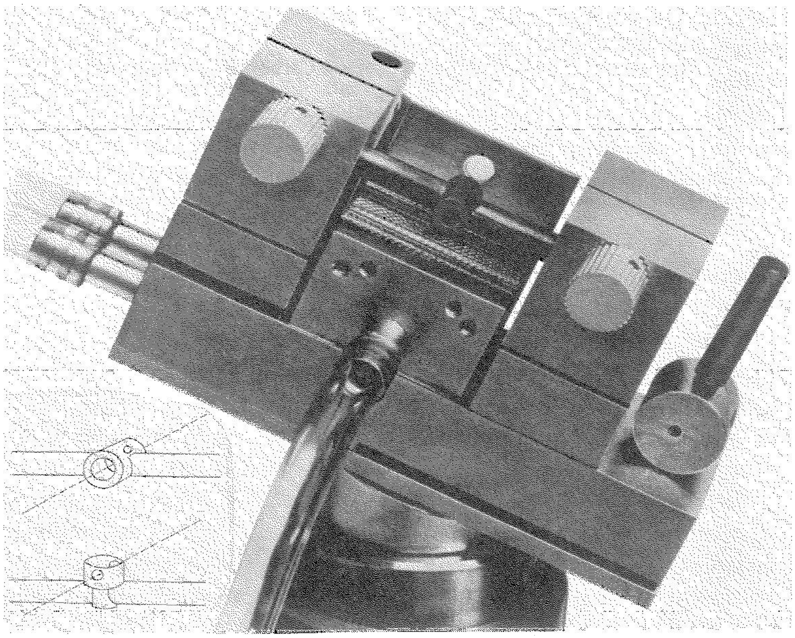

FIGURE 17. Varian Techtron Carbon-Rod Atomizer (Courtesy of Varian Techtron, Springvale, Australia.)

through a diffusing screen in the base of the workhead and sheath the furnace. The tube design is 9 mm long, has a 3 mm internal diameter, and accommodates sample volumes up to 5 μl. The cup design accommodates sample volumes up to 20 μl. Both the tube and the cup atomizers are coated with a thin layer of pyrolytic graphite. The drying-ashing-atomization sequence is accomplished in essentially the same manner as described above for the graphite-tube furnace atomizers.

The interesting feature of the Varian Techtron atomizer, also employed in other designs of rod atomizers, is the provision for hydrogen gas flow around the heated element. If the hydrogen flame is desired, a control unit opens the hydrogen supply valve at the end of the dry cycle and shuts it after the completion of the atomization step. Hydrogen ignites spontaneously when the carbon atomizer reaches a high enough temperature. The resulting diffusion flame is found to decrease many interference effects[117] and to extend the heights above the atomizer at which measurements can be taken.

Detection limits listed for the Varian Techtron carbon-rod atomizer are reproduced in Table 4.

4. Other Carbon-Rod and -Filament Atomizers

Amos et al.[117] described a carbon-rod atomizer with a sample cavity capable of accommodating volumes of 0.5 to 2 μl and essentially similar to the West filament atomizer. It was used both with and without an enclosing chamber and was sheathed by an inert gas. They reported atomic absorption and atomic fluorescence detection limits for several elements in the range of picograms and observed an atomic fluorescence detection limit for lead of 0.005 ppm in blood and urine. Dipierro and Tessari[119] also constructed a filament atomizer similar to the original West filament device.

An atomizer of the electrically heated graphite rod type was also described by Molnar et al.[120] The general design of the system resembled that of Alder and West[101] and that of Amos et al.[117] Underneath the carbon filament was positioned a brass burner head which contained 77 holes and which could maintain a laminar H_2-Ar-entrained air flame around and above the graphite rod. The amount of air entrained into the flame was partly controlled by removable brass plates mounted parallel to the graphite rod. Graphite rods 50 mm long and 6.15 mm in diameter were used, and the sample was placed in a cavity on the top of the rod. Detection limits were similar to those reported by Amos et al.[117] and by West and co-workers.[103]

A graphite rod atomizer was also coupled with the continuous mode of sample introduction.[121]

TABLE 4

Detection Limits for Varian Techtron Carbon Rod Atomizer*

Element	Detection Limit	
	Absolute weight, g	Concentration,† ppb (5-μl sample)
Ag	2×10^{-13}	0.04
Al	3×10^{-11}	6
As	1×10^{-10}	20
Au	1×10^{-11}	2
Be	9×10^{-13}	0.2
Bi	7×10^{-12}	1
Ca	3×10^{-13}	0.06
Cd	1×10^{-13}	0.02
Co	6×10^{-12}	1
Cr	5×10^{-12}	1
Cs	2×10^{-11}	4
Cu	7×10^{-12}	1
Eu	1×10^{-10}	20
Fe	3×10^{-12}	0.6
Ga	2×10^{-11}	0.4
Hg	1×10^{-10}	20
K	9×10^{-13}	0.2
Li	5×10^{-12}	1
Mg	6×10^{-14}	0.01
Mn	5×10^{-13}	0.1
Mo	4×10^{-11}	8
Na	1×10^{-13}	0.02
Ni	1×10^{-11}	2
Pb	5×10^{-12}	1
Pd	2×10^{-10}	40
Pt	2×10^{-10}	40
Rb	6×10^{-12}	1
Sb	3×10^{-11}	6
Se	1×10^{-10}	20
Sn	6×10^{-11}	10
Sr	5×10^{-12}	1
Tl	3×10^{-12}	0.6
V	1×10^{-10}	20
Zn	8×10^{-14}	0.02

*Data for model 63, tube configuration.

†Rounded off to 1 significant figure. (Courtesy of Varian Techtron, Springvale, Australia.)

The sample aerosol was carried by argon through a small vertical slot drilled through the graphite rod (Figure 6b). During passage through the rod, the sample was atomized. The detection limits obtained by this technique were much inferior to those obtained under the same experimental conditions with heated tube and ordinary carbon-rod atomizers instead of the slotted rod. For zinc the detection limit was 1×10^{-3} ppm (as against 3×10^{-7} for the tube and 8×10^{-6} for the rod) and for copper it was 5×10^{-2} ppm (as against 3×10^{-5} for the tube and 5×10^{-3} for the rod).

A new atomizer of the carbon-filament variety has recently been reported by Montaser and Crouch,[122-124] who referred to it as the "graphite braid" atomizer. The device has the form of a thread of 1.5 to 2 mm diameter, and contains fibers of graphite which are flexible and have a high degree of strength. The braid is heated electrically up to a temperature of 2,900°C. Only 350 W of power are required to reach the temperature of 2,500°C with a braid about 3 cm long, and even smaller power requirements are presented by shorter braids. In contrast to the braid, most carbon rods, filaments, and tubes require more than 1 kW of power. In view of such low power requirements, it is possible to operate the atomizer without a cooling system. Aliquots of sample (usually 2 μl) which are placed on the braid soak down between the graphite fibers. The efficiency of the heating processes is enhanced by the contact of the solution with a large surface area of the hot graphite. As with other non-flame devices, the dry-ash-atomize sequences are automated. Good detection limits are reported (Table 5). The relative standard deviation is usually in the range of 4 to 7% at concentrations one order of magnitude above the detection limit.[123]

Montaser and Crouch pointed out[122] that there are five different ways of programming the heating of non-flame atomizers, depending on which electrical or physical parameter is controlled during the heating steps. Programmed heating may be carried out by controlling the current or the voltage applied to the atomizer, the power dissipated in it, the radiation emitted by the atomizer, or the actual temperature of the atomizer. They discussed instrumentation for controlling each of the parameters and the advantages and disadvantages of each. An automated computer-controlled atomic absorption and atomic fluorescence spectrometer using a braid atomizer has been developed.[125]

TABLE 5

Detection Limits for the Graphite Braid Atomizer in Atomic Absorption and Atomic Fluorescence

Element	A.A. or A.F.	Detection Limit,* ppm
Cd	a.f.	0.002
Hg	a.f.	0.01
Pb	a.f.	0.005
Zn	a.f.	0.005
Ag	a.a.	0.007
Au	a.a.	0.02
Cd	a.a.	0.0005
Co	a.a.	0.004
Cu	a.a.	0.01
Fe	a.a.	0.004
Mg	a.a.	0.002
Mn	a.a.	0.006
Ni	a.a.	0.02
Pb	a.a.	0.01
Pt	a.a.	0.9
Sn	a.a.	0.1
Tl	a.a.	0.04
Zn	a.a.	0.0005

*2-μl volumes were used.

(Reprinted with permission from Montaser, A. and Crouch, S. R., submitted to *Anal. Chem.* (1974). Copyright by the American Chemical Society.)

B. Filament or Rod Temperature

The systematic selection of optimum working temperatures is carried out similarly to the procedure described for tube furnaces. The analytical signal varies with the voltage applied to the graphite element. As voltage is increased, recorded peaks typically become more high and narrow. Depending on the volatility of the metal, a different voltage is optimum. The West filament, for instance, reaches the optimum temperature of 2,300°C for the determination of manganese at a voltage of 6.4 V,[126] while with chromium no significant improvement of the atomic absorption signal is seen above 11 V.[106] At this voltage the half-life of the atomic absorption peak for chromium is only 0.17 s. With molybdenum, the maximum temperature of 3,500°C had to be achieved by applying a voltage of 13.8 V in order to detect useful absorption having a duration of about 0.5 s.[109]

Molnar et al.[120] studied temperature-current curves for the graphite rod surrounded by the hydrogen diffusion flame. At the lower currents, the curves for the cavity temperature have slopes that increase with increasing current. The shape is explained by the rate of heat loss by conduction. At higher currents, the slopes begin to decrease with increasing currents due to heat loss by radiation. The slopes change at the point corresponding to the ignition of the hydrogen surrounding the rod.

The population of free atoms, and therefore the magnitude of the analytical signal, depends not so much on the equilibrium temperature of the atomizer as on the rate of atomization which, in turn, depends on the rate of heating of the atomizer. Since many designs of rod and filament atomizers have different heating characteristics, it is to be expected that different signal intensities, calibration curves, and interference effects will be observed.

Torsi and Tessari[127] studied the influence of heating rate on the atomic absorption signal with carbon rods of different geometrical dimensions.

They described a theoretical model for the atomization process and, as predicted by the model, observed a linear relationship between peak absorption and both the input power and the thermal derivative at the evaporating surface.

Cresser and Mullins[128] used a simple theoretical approach to calculate the temperature-time and power-time curves for graphite and tungsten filaments, 25 mm by 1 mm radius, operated at a number of different voltages. Voltage, filament size, and the nature of the filament material all have a large effect on the rate of temperature increase of the filament. Contrasting the behavior of tungsten and graphite, they observed that the tungsten filament subjected to a potential difference of 2 V reaches 2,200°K more rapidly than a graphite filament subjected to 9 V, thus indicating that, for volatile elements in particular, tungsten is the preferable atomizer material.

Both sensitivity and freedom from interferences are improved by employing the fastest heating rate compatible with the response time of the detector system. Future developments in filament design are likely to reduce the power requirements of these atomizers and allow high temperatures to be reached in fractions of a millisecond without overheating the filaments.

C. Simultaneous Determination of Two Elements

Patel and Winefordner[129] reported a simultaneous determination of silver and copper by the carbon-rod atomic fluorescence technique. Both elements were atomized simultaneously from the graphite rod at an intermediate temperature of 1,800°K. The monochromator was set to transmit the silver line at 328.07 nm and the copper line at 327.40 nm. Two resolved atomic fluorescence peaks were observed. A hydrogen-argon-entrained air flame surrounded the carbon rod. The relative standard deviation for 10 to 15 determinations of silver and copper in oil samples ranged between 6 and 12%. Although this is less precise than separate determinations of each element would be, the method offers convenience and speed. Silver and copper had previously been determined sequentially by atomic absorption using a single aliquot of oil samples.[130] Silver was atomized at a temperature in the vicinity of 1,000°C, followed by the copper atomization at 1,800°C. Again, the two close lying lines of the elements were used with a wide slit width.

D. Flame Emission with the Carbon-filament Atomizer

Although rod and filament atomizers are used primarily for atomic absorption and atomic fluorescence work, some workers reported atomic emission of sodium from the nitrogen-hydrogen diffusion flame surrounding a carbon-filament atomizer.[131] Due to the coolness of the flame, the detection limit was only 10^{-9} g Na, while the relative standard deviation with 20 ng of sodium was 8.6%. The workers noted that sulfates suppressed the sodium emission by delaying the atomization of sodium and attributed this to the low volatility of the sulfates.

Useful molecular emission originating from the S_2 and HPO species excited in the hydrogen-nitrogen diffusion flame around a carbon filament has also been reported.[132] Detection limits for sulfur and phosphorus were 5×10^{-10} g and 4×10^{-9} g, respectively. Many metals caused serious interferences.

It is clear that atomic emission from graphite atomizers is of very little practical utility. Conventional flames provide much more favorable excitation environments than do graphite atomizers. With molecular emission from S_2 and HPO species, the presence of the electrically heated graphite element in the flame is less superfluous than with sodium emission because species like S_2 and HPO exist only in very cool flames, in which vaporization of pneumatically sprayed aerosols is very incomplete and therefore sample vaporization can greatly benefit from the initial electrical heating.

E. Solvent Effect

In their work in atomic absorption and fluorescence with the carbon filament, Aggett and West[133] reported no changes in the signals of silver, cadmium, copper, lead, and zinc when these metals were deposited onto the atomizer as organic complexes dissolved in benzene, chloroform, carbon tetrachloride, or methyl isobutyl ketone instead of simple aqueous solutions. Other workers, however, have observed some solvent effects. Yanagisawa et al.[134] extracted antimony as a chloride into methyl isobutyl ketone, as a diethyl dithiocarbamate complex into methyl isobutyl ketone and as a tri-*n*-butyl phosphate complex into toluene. Although extraction efficiency was good in all cases, calibration curves for antimony in the different systems were not identical, being significantly lower in toluene than in methyl isobutyl ketone. Hall et al.[135] also observed appreciable effects of solvents on the atomic absorption signals of several metals. Absorption signals from solutions in carbon tetrachloride were broader and occurred later in the atomization cycle than those from solutions in xylene or methyl isobutyl ketone. This effect was attributed tentatively to different degrees of penetration of the solvent into the carbon rod. Penetration of sample into the rod can be prevented by using pyrolytic graphite. It may also be prevented by impregnating the rod with an immiscible solvent,[136,137] such as xylene for aqueous samples, or by adding the sample to the carbon rod while the drying step is already in progress[136] so that the solvent evaporates before it can soak into the rod. The suggested penetration of the solvent into the graphite does not completely explain the solvent effects. More experimentation is needed to identify the mechanism of solvent interference.

F. Purge and Sheath Gases

Several comparisons of the performance of different sheathing gases have been reported. For atomic fluorescence, argon is preferred over nitrogen because of its lower quenching ability. Different fluorescence lines of an element can, however, be affected by a change in purge gases in a quite different way. Alder and West[101] studied the effect of 5 gases on the atomic fluorescence of cadmium at 228.8 and 326.1 nm. Changing from argon to nitrogen caused a decrease of the former line by a factor of 5 and an increase of the latter line by a factor of 15. An explanation for the observed effects is based on the consideration of the energy levels of the excited cadmium atoms.[101]

For atomic absorption, replacing argon with nitrogen usually does not result in large changes in signal intensity. The rate of gas flow is not critical, especially with relatively volatile elements. On the other hand, the absorbance due to molybdenum[109] decreased as the rate of gas flow fell below about 2.5 l min^{-1}, probably due to less efficient shielding from the atmosphere and consequently, oxidation of molybdenum vapor. In a fully enclosed atomization cell, the atomic absorption signal due to chromium was greatest for nitrogen flow rates from 2.5 to about 6 l min^{-1} and dropped quickly at slower flows.[106]

The use of hydrogen as the sheathing gas improves the atomic absorption sensitivity for some elements and significantly decreases the extent of many interferences.[117,120] The hydrogen-argon-entrained air flame envelops the rod and burns above it. Molnar et al.[120] determined the temperature profiles of the H_2-Ar-entrained air flame with and without the graphite rod. Temperatures of the flame anywhere above the rod never exceed 500°C, which indicates that the flame itself does not aid significantly in the atomization process. However, it creates a reducing and warm environment extending several millimeters above the rod, and thus delays the condensation and chemical reactions of the atomic vapor. For instance, the sensitivity for molybdenum improves by a factor of 2 to 3 when hydrogen is substituted for nitrogen or argon as a sheathing gas.[109] The presence of hydrogen also significantly decreases the absorption of the blank (filament heated without any sample). It is possible that the background signal is due to volatilized carbon and that it decreases in the presence of the flame due to hydrocarbon formation and vaporization.[109] Some results showing the effect of the hydrogen diffusion flame on the atomic absorption signal of lead in the presence of various interferents are presented in Table 6.

TABLE 6
Effect of Hydrogen Diffusion Flame on the Atomic Absorption Signals of Lead Observed with a Carbon-Rod Atomizer in the Presence of Various Interferents*

	Without hydrogen flame		With hydrogen flame	
Interferent	Signal†	Blank§	Signal†	Blank§
–	100	0	100	0
H_3PO_4	32	19	103	0
NaCl	110	51	92	1
KCl	87	37	87	1.5
$MgCl_2$	6	11	20	0
$CaCl_2$	0	46	92	1.5

*All the signals are for 5 X 10^{-9} g of Pb in the presence of a 1,000-fold excess of the interferent, at 217.0 nm.
†Corrected for the appropriate blank.
§No lead present.

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The presence of the H_2-Ar-entrained air flame allows absorbance measurements at greater distances above the carbon rod than those at which signals must be measured in the presence of only inert gases alone. Figure 18 illustrates some typical observations.[138] Clearly, the rate of decrease of the atom population with height above the rod is much faster in the absence of a hydrogen flame. The warm environment of the flame helps maintain a fairly high population of atoms at heights of at least 10 mm above the rod, while with argon alone most elements become practically immeasurable at heights as small as 5 mm above the rod.[138] The free-atom population decreases with height mainly due to chemical reactions, dilution, and diffusion of atoms out of the light path of the exciting beam. The precision of results at the higher points decreases somewhat, probably because of greater turbulence in the gas flow.

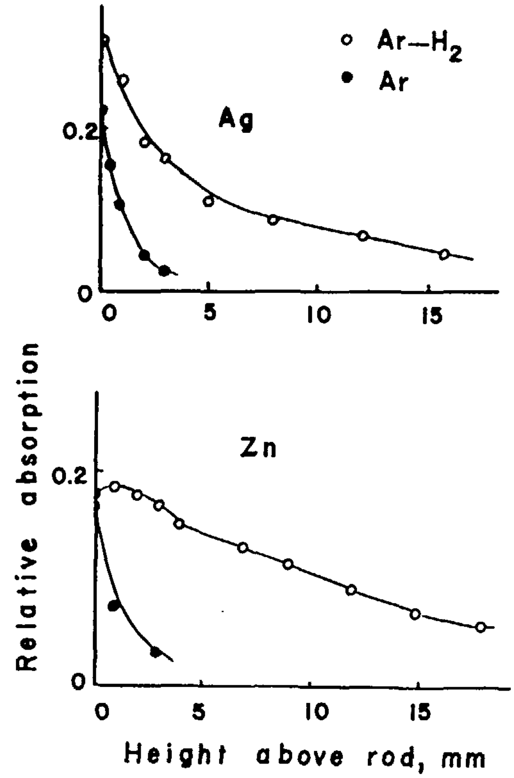


FIGURE 18. Decay of silver and zinc atom populations with height above the graphite rod atomizer. The top curves are for argon-hydrogen sheath gases and the bottom curves are for argon alone. (Reprinted with permission from Reeves, R. D., Patel, B. M., Molnar, C. J., and Winefordner, J. D., *Anal. Chem.*, 45, 246(1973). Copyright by the American Chemical Society.)

G. Interference Studies

Many workers have tested the effect of other elements on the signals of the elements of interest. Among others, Jackson et al.[102] studied the suppression of atomic absorption of vanadium by interfering cations, and Eldon et al. studied the interferences on manganese[126] and iron.[107] While all interferences on iron were negative, aqueous ammonia and ammonium phosphate enhanced iron absorption.[107] Alder and West[101] reported the effects of 20 metals on the atomic fluorescence signal for cadmium. Ebdon et al.[108] studied the effects of foreign ions on atomic absorption and atomic fluorescence of manganese. Twenty cations were tested, in excesses of 10-, 100-, and 1,000-fold over the chromium concentration,[106] and most of the 20 interfered except for magnesium, lithium, sodium, and potassium. Yanagisawa et al.[134] studied the effects of 11 foreign ions in 100-, 1,000-, and 2,000-fold molar excesses on the carbon-rod atomic absorption signals of antimony. Silver, chromium, vanadium, and molybdenum suppressed the signal due to antimony even at the 100-fold level, but aluminum and calcium did not interfere even at high levels. Hydrochloric and nitric acids did not interfere at concentrations less than 0.1 *M*.

Johnson et al.[109] tested interferences on the atomic absorption of zinc and molybdenum with a carbon filament. As usual, all the interferences were negative. With zinc, the ions that caused no interferences were Cu^{+2}, PO_4^{-3}, and SO_4^{-2}. The interference of tungsten in determinations of molybdenum persisted for many runs. Thus, the suppressive effect was felt for about 20 determinations after a single application of a solution containing 100 ppm of tungsten, and an application of a solution containing 1,000 ppm tungsten had effects that persisted for the lifetime of the filament. With a few exceptions, the determination of the very non-volatile molybdenum is relatively free from interference because most interferents can be removed by selective volatilization. With zinc, interference effects are much more severe because the volatility of the element does not allow selective volatilization of most matrices.

Aggett and West[104] studied the effect of interferents on the atomic fluorescence signal of gold from a carbon-filament atomizer, and followed the variations of gold fluorescence and extent of interferences as a function of height above the filament. As expected, interferences increased rapidly with height of observation above the filament. The effect of tungsten, for instance, was very slight at a height of one mm, but the signal was approximately 90% suppressed at about 9 mm above the filament. Alger et al.[105] studied the interference effects of 62 ions, present in 1,000-fold excesses, upon the atomic fluorescence and atomic absorption signals of 10^{-9} to 10^{-11} g amounts of silver, bismuth, cadmium, copper, mercury, magnesium, lead, thallium, and zinc atomized with the carbon filament in an atmosphere of argon. Pronounced suppressions were observed.

Assuming that adequate ashing is possible without loss of analyte and that relatively high atomization temperatures are used, these suppressions must be regarded as being due primarily to interactions in the gas phase rather than in the condensed phase. High temperatures minimize the effects of condensed-phase interactions which affect efficiency and rates of atomization. Several kinds of experiments point to the importance of gas-phase interactions. On examining the effect of height above the atomizer (employing the limited area viewing technique) on the analytical signal in the presence and in the absence of interferents, very little interference is found at heights of about 0.5 to 1 mm.[104,105] Aggett and West[104] also offered the results of the following experiment as further evidence that the effect of interferents is mostly a result of gas-phase interactions. An atomizer arrangement of two filaments was devised, with one filament slightly above the other. A 0.5-ng sample of gold was placed on the upper filament and 500 ng of cobalt, copper, or lead on the lower filament, and the filaments were heated simultaneously. Pronounced interference was still observed in spite of the fact that the two species were not mixed before vaporization. Apparently, the condensation and reaction of the atomic vapor of the element of interest is promoted by the presence of large excesses of condensing foreign elements. Other similar experiments confirm this observation.[105] The further observation that the severity of interference decreases with decreasing sample size[105,126] although the same excess of interferent over analyte is maintained, also indicates that a less dense atomic population in the space just above the atomizer causes less pronounced premature co-crystallization of the element of interest. If the predominant role of gas-phase interference is accepted, it is reasonable to expect that elements of similar volatility might tend to interfere most severely on the analyte,[106] but exceptions to this hypothesis are often observed.

In all cases, interferences are decreased by raising the temperature of atomization and observing the signal from a height as close to the atomizer as possible without allowing excessive light from the graphite element itself to enter the monochromator. The hydrogen diffusion flame surrounding the carbon rod also decreases interferences, as was pointed out above.[117,120]

In spite of the large volume of data that has been published on interferences, the exact nature of interactions is still largely unclear. Direct comparison of numerical data has limited meaning as long as atomizer designs (and, consequently, atomizer temperatures and rates of heating) vary among laboratories. A systematic study of interferences would benefit from examination of detailed information on the thermal dissociation characteristics of all salts to be employed, on the vapor pressures of the species studied at a number of temperatures, and on the temperatures at points above the atomizer where observations are made.

H. Applications of Carbon-Rod and -Filament Atomizers

Many reported analyses have involved samples of biological origin. Lead was determined in blood or plasma.[117,137,140-142] Most procedures involved very little sample preparation. For instance, blood was pipetted onto the atomizer after a 1:2 dilution with xylene[142] or a 1:3 dilution with Triton X-100.[137] Blood, serum, or plasma was also tested for copper,[123,140,143,144] iron,[140,145] zinc,[140,146] magnesium,[140,147] gold,[148] chromium,[149] and lithium.[150] Most of the analyses were done by direct sampling, with or without dilution. An automated system for the determination of lithium in serum by atomic absorption was described,[150] based on the Varian Techtron Carbon-Rod atomizer. The sample was taken in 1-μl aliquots, without any pretreatment.

Copper was determined in animal tissue.[151] Urine was tested for cadmium, lead, and thallium.[152] Cadmium was determined in foods, beverages, hair, and tobacco.[153] Chromium was determined in fresh and sea-water, in sugar, and in glycine.[149] Fairless and Bard[154] separated copper from sea-water by electrodeposition on a mercury drop and successfully subjected the mercury drop to atomic absorption analysis in a carbon-rod atomizer. Mercury became volatilized without causing co-volatilization of copper. They reported a practical detection limit of 0.2 $\mu g\ l^{-1}$ of copper for the technique and a relative standard deviation of 15%.

Brodie and Matousek[136] determined chromium, silver, aluminum, copper, magnesium, nickel, and lead in petroleum products. Bratzel and Chakrabarti[155] determined lead in petroleum samples and later extended this analysis to silver, nickel, copper, and iron in jet-engine lubricating oil and crude oil,[135] and to vanadium in crude oil.[156] Winefordner and co-workers determined wear metals (silver, copper, iron, nickel, lead, tin, and chromium) in used engine oils.[120,129,130,157] West and co-workers determined vanadium in fuel oils,[110] and copper and silver[158] and nickel[159] in lubricating oils. Robbins[160] determined lead in gasoline. In the latter application, the signal variation observed with different tetraalkyl lead compounds was corrected by an iodine-addition procedure. Apparently, all the lead was transformed into lead iodide prior to the atomization step.[160]

Selenium was determined in sewage and waste water samples following acid digestion.[161] For the determination of vanadium in titanium dioxide,[102] the sample was fused with sodium carbonate and the extract was placed on the C filament for analysis. The excess Na_2CO_3 did not interfere because it was volatilized by heating at an intermediate temperature prior to atomization.

The determination of antimony in several metallurgical samples involved acid dissolution and extraction into methyl isobutyl ketone.[120] Gold and silver in rocks and metallurgical samples were determined by a similar procedure.[162] Metal impurities in powdered graphite were determined by direct solid sampling.[112,115,116]

Airborne lead was determined by filtration through Millipore filters and their analysis in the carbon-rod atomizer. The relative standard deviation was 4.2% with 1 $\mu g\ m^{-3}$ of lead, based on 200-cm^3 samples of air.[163] The graphite cup of the Varian Techtron model 63 atomizer was modified by perforating its base with 5 holes of 0.35 mm diameter and covering the base with a disc of a Millipore filter. Air was then pumped through the filter already in position in the cup. Alternatively, a porous graphite cup was used to filter the air and atomize the residue.[163]

Siemer et al.[164] adapted the carbon-rod atomizer to the determination of mercury in air. Air was drawn through the walls of a gold-plated tube of porous graphite. Elemental mercury was retained by amalgamation, while particulate mercury was trapped in the pores. The tube was then placed in the carbon-rod atomizer and mercury was determined by atomic absorption. The efficiency of this method for collecting mercury was shown to be good. The reproducibility of the method corresponded to a relative standard deviation of about 6%.

I. Discussion and Comparison with Graphite-tube Furnaces

The filament-type atomizer is more open to the atmosphere than the tiny tubelike or cuplike rod where the heating element surrounds the atomic vapor. As a result, atomizers of the latter variety keep the atomic vapor at a higher temperature and also preserve a more reducing atmosphere. The sensitivities and detection limits of both types of atomizers are, however, essentially comparable.

Compared to the graphite-tube furnace atomizers, the lifetime of the atomic vapor generated by the carbon rod or filament is considerably shorter and the vapor spends a much shorter time in the light path of the exciting beam. As the atomic vapor rises from the heated surface, it immediately encounters a much cooler atmosphere above the filament and rapid condensation begins to take place. As a result, atomic absorption or fluorescence of the vapor must be measured very close to the heated surface to ensure sensitivity and to decrease the interference effects of the concomitants. Even a few millimeters away from the rod itself, however, the temperature is at least several hundred degrees cooler than at the surface and thus, measurements are never taken at the most optimum points. Enveloping the rod with a hydrogen diffusion flame extends the lifetime of the atomic vapor, increases sensitivity, and decreases many interference effects.

Just as with the other non-flame pulsed atomization techniques, it is important to employ fast response detector-recorder systems in order to follow accurately the rise and fall of the transient signals which typically last for a fraction of a second. Inadequate speed of the response system is one of the causes contributing to the curvature of the calibration curves. Also, just as with other non-flame atomization techniques, means of background correction are often necessary.

Graphite-tube furnaces have larger power requirements than rods and filaments. Tube furnaces are not conveniently applicable to atomic fluorescence, which is very successful with the cuplike rod and filament atomizers. Atomic fluorescence benefits especially well from the low background present with the heated graphite atomizers. For atomic absorption work, the carbon-rod and -filament atomizers appear to be somewhat less versatile than the graphite-tube furnace. They are applicable to fewer elements and seem subject to more interference problems.

Sample handling is similar for rod, filament, and tube furnace techniques. Both can, for instance, handle viscous liquids that are difficult to atomize by flame, and both have the capability of solid sampling, although this is limited to samples of relatively simple compositions because severe matrix effects may be encountered.

The sensitivities and detection limits of the carbon-rod and -filament atomizers are essentially similar to those obtained with the graphite-tube furnaces. As far as comparison to conventional flame sampling is concerned, most of the advantages and limitations of non-flame atomizers considered in connection with graphite-tube furnaces apply equally well to carbon-rod and -filament atomizers.

IV. SAMPLING BOATS, LOOPS, RODS, AND METAL FILAMENTS

The idea of introducing the sample into the flame by means of a metal loop is not new, having been employed over 100 years ago by Bunsen in his original reports on flame emission spectrometry. The method of mechanically injecting the sample into the flame was abandoned in favor of pneumatic nebulization, which offered the advantages of convenience and of yielding a continuous and stable, rather than transient, signal. However, in recent years, the interest in alternative methods of sample injection has grown rapidly as researchers have shown it to be feasible to obtain greatly improved sensitivity by mechanically placing some samples in the flame and especially by using flameless atom cells. Many reports in the recent literature which deal with flameless atomization describe the use of heated graphite rods, graphite filaments, and graphite tubes, and are discussed earlier in this review. In this section, the use of metal boats, graphite microprobes, metal filaments, rods, and loops as means of sample injection in both flame and flameless atomic spectrometry are discussed.

A. Sampling Boat and Other Devices Which Employ Flame Atomization

1. Graphite Microprobe

Prudnikov and others[165-171] introduced solid and liquid samples into the flame on a microprobe and showed a great enhancement of sensitivity of flame emission and atomic absorption analysis.

The microprobe is prepared from a layer of pyrographite and has the form of a small rod about 20 to 25 mm long and 0.1 by 0.5 mm across. The microprobe is fastened onto a metal rod; by turning the rod, the probe is placed into the flame. The probe is positioned just above the blue cone of the flame and in such a manner that the tip carrying the sample is in the optical path of the monochromator.[166] Samples of 1 μl are normally used. For the analysis of dry samples with a mass of 1 mg or larger, the probe is increased in size and a depression is made in its center.[170] The detection limits reported by Prudnikov[166] for pulse vaporization from a microprobe into a nitrous oxide-acetylene flame range mostly in the vicinity of 10^{-10} to 10^{-12} g (Table 7).

For volatile elements, the introduction of the sample into the flame generates a sharp signal with a duration of less than 1 s. For less volatile elements the pulse is neither as sharp nor as rapid. When the microprobe enters the flame, a slight decrease in flame emission background in the ultraviolet and visible portions of the spectrum and a slight rise in intensity in the infrared part of the spectrum are observed. The former effect may be due to a slight lowering of the flame temperature by the probe and the latter may be due to the added emission from the hot microprobe itself.

Prudnikov also studied the possibility of introducing samples into the flame for the measurement of atomic absorption on a platinum wire microprobe.[171] The determination of cadmium in an air-acetylene flame with a high-frequency lamp yielded a detection limit of 10^{-12} g.

The graphite microprobe used to introduce the sample into the flame can also, at the same time, be heated by passage of an electric current.[166,167,169] The probe is heated by currents of up to

50 A at a 10 V potential difference.[170] With very non-volatile elements, such as aluminum, erbium, molybdenum, and vanadium, heating of the probe improves the absolute detection limit by an order of magnitude or more.[170] Table 8 contrasts the detection limits obtained for these elements in a nitrous oxide-acetylene flame with and without electrical heating of the microprobe.

With careful sampling and very accurate introduction of the probe into the same point in the flame, the error is primarily determined by fluctuations in the vaporization time of the element. Both the very rapid vaporization of the volatile elements and the slow vaporization of the non-volatile elements often result in pronounced curvature of the calibration curves of signal intensity versus amount of element. Clearly, with the volatile elements, going to a quicker response detection system (response time much less than 1 s) would help to straighten the calibration curve, but for the less volatile elements, integration of the signals is necessary. Self-absorption begins to be detected for elements like sodium and potassium at levels as low as 10^{-7} to 10^{-8} g, and naturally affects the linearity of the calibration curves. Matrix effects are negligible for cases where the matrix itself is very volatile, but non-volatile matrices can severely distort the analytical signal and must be closely reproduced in preparing the standards.[170]

Compared to continuous nebulization into the flame, pulse vaporization from microprobes offers better detection limits and also allows analysis of very small samples. Thus, a 1-mg sample may suffice to detect elements present at concentrations of 10^{-3} to 10^{-5}%. The combined use of a

TABLE 7

Detection Limits by Flame Emission for Pulse Vaporization from a Microprobe*

Element	Wavelength, nm	Detection limit, g
Ag	328.1	1×10^{-11}
Al	396.1	3×10^{-10}
Ba	553.6	1×10^{-11}
Ca	422.7	2×10^{-12}
Co	345.4	2×10^{-10}
Cr	425.4	5×10^{-12}
Cs	852.1	1×10^{-13}
Cu	327.4	5×10^{-12}
Dy	404.6	3×10^{-10}
Er	400.8	1×10^{-8}
Eu	459.4	2×10^{-11}
Fe	372.0	5×10^{-11}
Ga	417.2	5×10^{-12}
Gd	440.2	1×10^{-8}
Ho	405.4	1×10^{-10}
In	451.1	5×10^{-12}
K	766.5	1×10^{-12}
La	545.5	1×10^{-9}
Li	670.8	1×10^{-14}
Mg	285.2	1×10^{-10}
Mn	403.1	2×10^{-12}
Mo	390.3	1×10^{-8}
Na	589.0	1×10^{-12}
Nd	492.4	1×10^{-8}
Ni	341.5	5×10^{-11}
Pr	493.9	5×10^{-8}
Rb	798.1	1×10^{-13}
Sm	476.0	1×10^{-10}
Sr	460.7	2×10^{-12}
Tl	535.0	1×10^{-11}
V	437.9	1×10^{-9}
Yb	398.8	1×10^{-11}

*Nitrous oxide-acetylene flame.

(From Prudnikov, E. D., *Zh. Anal. Khim.*, 27, 2327 (1972).)

TABLE 8

Effect of Electrically Heating the Microprobe upon Detection Limits*

		Detection limit, g	
Element	Wavelength, nm	Electrically heated microprobe	Unheated microprobe
Al	396.1	1×10^{-10}	3×10^{-10}
Er	400.8	1×10^{-10}	1×10^{-8}
Mo	390.3	1×10^{-9}	1×10^{-8}
V	437.9	3×10^{-10}	1×10^{-9}

*Nitrous oxide-acetylene flame.

(From Prudnikov, E. D. and Shapkina, U. C., *Zh. Anal. Khim.*, 28, 1055 (1973).)

high-temperature flame and an electrically heated probe is a novel and interesting development.

2. *Sampling Rod*

Another simple device for mechanically placing the sample in the flame was shown to be suitable for direct atomic absorption analysis of solid samples, and was used to determine concentrations of rubidium,[172] lithium,[173] and cesium[174] in powdered rock. An iron screw rod is held in a horizontal position by a pivoting support attached to one side of the burner stand and can be easily positioned in the air-acetylene flame burning on a triple slot burner. The rod is 3 mm in diameter and 13 cm long, and is positioned parallel to the slots, about 1 cm above the burner head.

The rod is impregnated with a powdered mixture of the rock sample with sodium carbonate which plays the role of the radiation buffer. To take up the sample, a clean rod is immersed in acetone and then inserted several times into a container with the powdered sample and shaken. The authors state that after this treatment the rod retains about 80 mg of powder with a standard deviation of only 1.5 mg. Particle sizes below 100 μm have no effect on sensitivity, but grain sizes above 150 μm tend to give low results. When the rod is placed in the flame, the absorbance of the analytical beam passing just above it is recorded until the signal decays to the background, and the integrated area under the absorption peak is used for evaluation. Analysis of a series of geochemical standards for cesium yielded rather good agreement with values reported by neutron activation and by other methods. The relative standard deviation for the method was 10 to 15% and the detection limit for cesium in rock was 1.0 ppm.[174] Rubidium and lithium were detectable down to concentrations of 10 ppm.

The technique is clearly lacking in analytical sophistication. The manner of sample uptake is inadequate, the precision is rather poor, and the technique cannot be recommended except for obtaining a rough first estimation of the element of interest in a powdered sample.

Another method of sample introduction into the flame was described by Belcher et al.,[175] who called the technique "molecular emission cavity analysis." The sample is deposited in a small cavity at the end of a metal rod, the rod is introduced into the flame with the cavity aligned with the detector, and the intensity of molecular emission from the cavity is recorded. A schematic drawing of the set-up is indicated in Figure 19.

The cavity is approximately 5 mm in diameter at the end of a stainless steel screw 3 cm long. The volume of the cavity is 45 μl. The cavity is placed in the flame with a downward pitch of 7° because a more nearly horizontal orientation decreases the emission intensity, while a much larger angle decreases the precision. Incandescent emission of the stainless steel cavity itself is small in cool hydrogen diffusion flames when measured below 400 nm.

The investigators[175] applied the technique to the determination of sulfur, based on the molecular emission of S_2 measured at 384 nm. The limit of detection for sulfur was in the range of a few nanograms. Molecular emission arising from the S_2 species excited in cool hydrogen-rich flames in contact with a cool surface has been known for a long time and has been the basis of several recent reports.[177-179] Elements like phosphorus and boron also emit useful molecular spectra from cool flames, while direct determination of chlorine, bromine, and iodine can be based on indium halide emissions from cool flames.[180] All these elements can, in principle, be determined by the cavity technique.

The cavity technique has also been shown to be feasible for the determination of tellurium and selenium,[176] for which the detection limits were reported to be approximately 0.5 and 50 ng, respectively. Selenium was separated from all interfering species (large amounts of arsenic, antimony, sulfur, and many metal ions) by reduction to elemental selenium and its separation by filtration. The glass-fiber filter was then placed directly in the cavity for analysis.

The presence of the cavity enhances molecular emission from cool flames and the technique has the advantage of requiring only a few microliters of sample. However, some of the claims made in the literature for this technique are unjustified and, in the opinion of this reviewer, its weaknesses outweigh its strengths. For instance, with sulfur not only the intensity of emission from the cavity, but also the time it takes for different sulfur compounds to reach their maximum emission intensities differ from one compound to another, as illustrated in Figure 20.[175] The length of time required for maximum emission is determined by the volatility and thermal stability of the compound, by physical and chemical interferences,

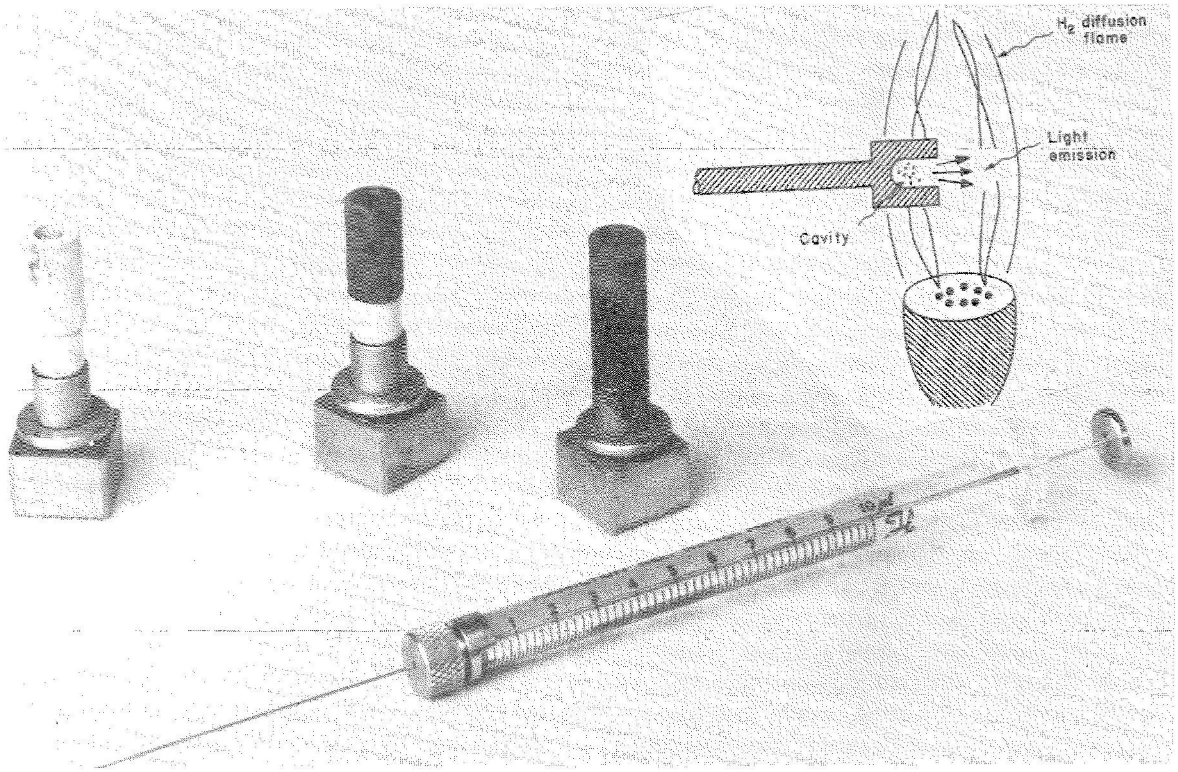


FIGURE 19. Schematic diagram of the position of the MECA cavity in the flame and examples of cavities. (Courtesy Anacon, Inc.)

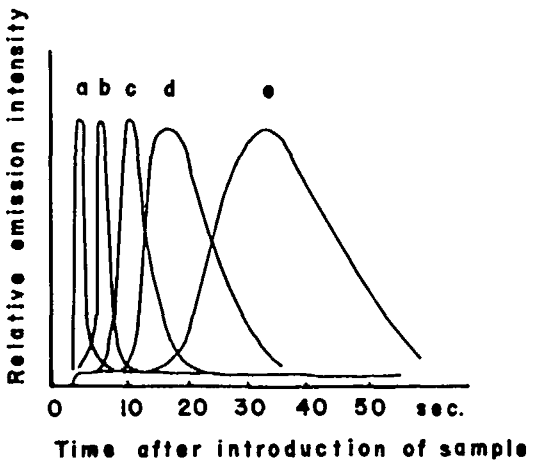


FIGURE 20. Effect of the nature of the compound on the rate of S_2 emission from the MECA cavity. S_2 emission at 384 nm is indicated for: (a) thiourea; (b) sulfuric acid; (c) ferrous sulfate; (d) manganous sulfate; (e) sodium sulfate (intensities not to scale). (From Belcher, R., Bogdanski, S. L., and Townshend, A., *Anal. Chim. Acta,* 67, 8(1973). With permission.)

and by the fact that the cavity becomes heated only gradually and the decomposition temperatures of the different compounds are reached after different intervals. About 40 s after introduction into the flame are required for the cavity temperature to reach a constant value of 850°C in a typical flame.[175] The ranges of linearity of the calibration curves for sulfur are limited and variable for different compounds. In addition, it was shown that the appearance of the emission-time trace, like those illustrated in Figure 20, does not retain the form of a single smooth peak, but spreads out at higher concentrations into a series of irregular maxima which persist for a considerable time. Thus, S_2 emission from 32 μg of thiourea exhibited continuously varying emission intensity for at least 80 s after introduction into the flame.[175] Each organic sulfur compound appears to exhibit a different emission-time curve. In addition, organic solvents affect both precision and emission intensity unfavorably. Clearly, the direct determination by this technique of an element such as sulfur in a real sample is not feasible under these conditions. It would be necessary to reproduce scrupulously the exact composition of the sample in preparing the standards, or to undertake separations to remove all the matrix prior to analysis. The technique is neither practical nor convenient and is unlikely to gain much popularity. A flame emission instrument modified for the cavity technique of sample introduction is offered by Anacon, Inc.

3. *Tantalum Boat*

The tantalum sampling boat technique for atomic absorption spectrometry has been introduced by Kahn et al.[181] and by Ringhardtz and Welz.[182] The tantalum boat and associated hardware are available from at least one commercial manufacturer (Perkin-Elmer Corp.). An aliquot of sample solution is pipetted into the boat, dried by gentle heating, and then atomized rapidly by pushing the boat into the flame in a reproducible manner. The position of the tantalum sampling boat over a burner is illustrated in Figure 21.

The boat is placed in the air-acetylene flame approximately 1 cm above the triple slot burner and directly below the analytical beam. The volume of the boat is about 1 ml, although smaller sample aliquots are usually used. The transient absorption signal which is recorded has a duration of about 1 s. The presence of the boat affects the absorption of the analytical beam by the flame itself by obstructing the natural flow path of the reacting gases, and therefore the absorption reading obtained with an empty boat in the flame is taken as the background and absorption of samples is measured relative to this baseline.

The signals are evaluated by measuring the area under the absorption peak. However, peak heights can also be used for analysis provided that concentrations are low and an even distribution of the sample over the boat is achieved during the drying step.[183] Errors caused by the sagging and stretching of the original tantalum boats may be obviated by bending the ends of the boat.[184,185] Another source of error, apparent as a gradual reduction in peak heights, is due to the formation of a crust on the boat. This delays the atomization of the sample, and may be avoided by the use of only dilute solutions.[183] When using a fresh boat in the determination of traces of cadmium and lead in foods, Holak[184] found it necessary to place the boat in the flame several times to eliminate absorption due to cadmium and lead emitted by the boat itself.

The detection limits of several metals obtained by the tantalum boat technique are contrasted with those obtained by conventional spraying-nebulization in Table 9.[186] The tantalum boat results are given for 1-ml aliquots. The use of the boat improves the atomic absorption detection limits for many elements by factors greater than ten. Aidarov and Aleksandrova[186] also reported improvements in atomic fluorescence detection limits with use of the tantalum sampling boat.

A variety of materials has been analyzed with convenience and sensitivity, albeit with occasional lack of precision, by the sampling-boat technique. Lead[181,187] cadmium,[187] and thallium[188] were determined in blood, and thallium was determined in urine.[188] Hauser et al.[187] took 0.5-ml aliquots of whole blood for analysis, dried them in the oven, and ashed them at a low temperature without addition of any reagents. They observed complete recovery of added cadmium and lead and reported a 25-fold improvement in detection limit for these elements in blood over the solvent

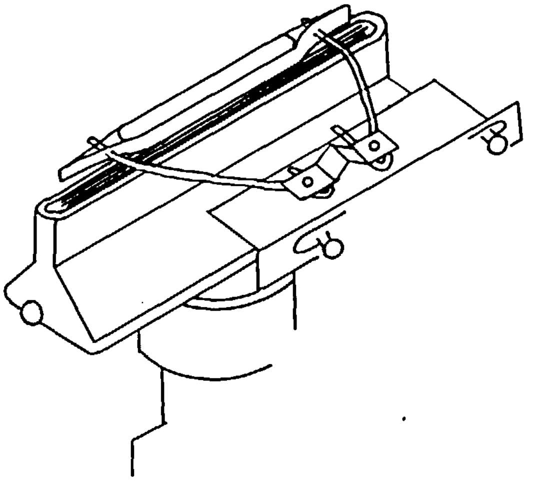


FIGURE 21. Sampling boat in position over the burner. (From Holak, W., *A. A. Newsletter*, 12, 63(1973). With permission.)

TABLE 9

Detection Limits Obtained with the Tantalum Boat

Element	Detection limit, ppm With Ta boat	With nebulizer
Ag	0.0001	0.005
As	0.02	0.1
Bi	0.003	0.05
Cd	0.0001	0.002
Hg	0.02	0.5
Pb	0.001	0.03
Se	0.01	0.1
Te	0.01	0.3
Tl	0.001	0.02
Zn	0.00003	0.002

(From Aidarov, T. K. and Alexandrova, L. G., *Zh. Anal. Khim.*, 28, 998 (1973).)

extraction procedures coupled with conventional atomic absorption. Absolute limits of detection were 0.1 ng of cadmium and 1 ng of lead. Although the procedure is very simple and sensitive, it suffers from poor reproducibility. For concentrations of 3.5 ppb in blood, the relative standard deviation of repeated analyses is 26%; with concentrations of 213 ppb, the relative standard deviation is 17%.

Curry et al.[188] used 0.05- to 0.2-ml aliquots of blood or urine and found it necessary to treat the blood sample with 3 drops of nitric acid prior to atomization and determination of thallium. The detection limit for thallium was 3 ng. Typical results are represented in Figure 22. For the blood samples illustrated in the figure, only the second peak of each trace is due to thallium. The method of standard additions had to be employed in order to overcome interelement interferences.

The determination of lead and cadmium in foods also seems to require very little sample preparation.[184] The food sample is blended to make it homogeneous, diluted with water, and a 0.2-ml aliquot is pipetted into the boat. The sample is dried, ashed in a muffle furnace at 500°C for 5 to 10 min, and pushed into the flame. The signal is recorded until the pen returns to the baseline, at which time the boat is withdrawn from the flame. The analyses are completed by comparison of the peak heights or peak areas with those obtained with aqueous standards similarly dried and atomized. The complete analysis takes about 10 min per sample.

The sampling-boat technique for the determination of traces of tellurium in selenium dioxide, sphalerite, galena, telluride, selenium metal, and other materials has been studied by Beaty.[189] He described two procedures for treating the sample prior to its delivery into the boat. With some materials, tellurium was extracted directly into methyl isobutyl ketone from a solution in 4 *M* hydrochloric acid. The presence of nitrate, lead, zinc, or arsenic caused interference and significantly reduced tellurium recovery. With samples containing interfering species which affect the extraction process, tellurium was coprecipitated with selenium prior to the extraction step. Whereas large amounts of nitric acid interfered with the precipitation, the interference from lead, zinc, and arsenic was greatly decreased. The relative standard deviation rose from 5.0 to 6.6% with coprecipitation. A linear calibration curve extended over the range from 5 to 100 ng of Te, and the limit of detection was 5 ng.

Soils have been treated with acids and the extracts used to determine lead, zinc, silver, and cadmium.[183,190] The detection limits were 2 ng for lead, 0.3 ng for silver, 0.1 ng for cadmium, and 0.06 ng for zinc,[183] but the precision was only moderate.

Burrell and Wood[191] determined zinc in seawater directly and found the sensitivity of the

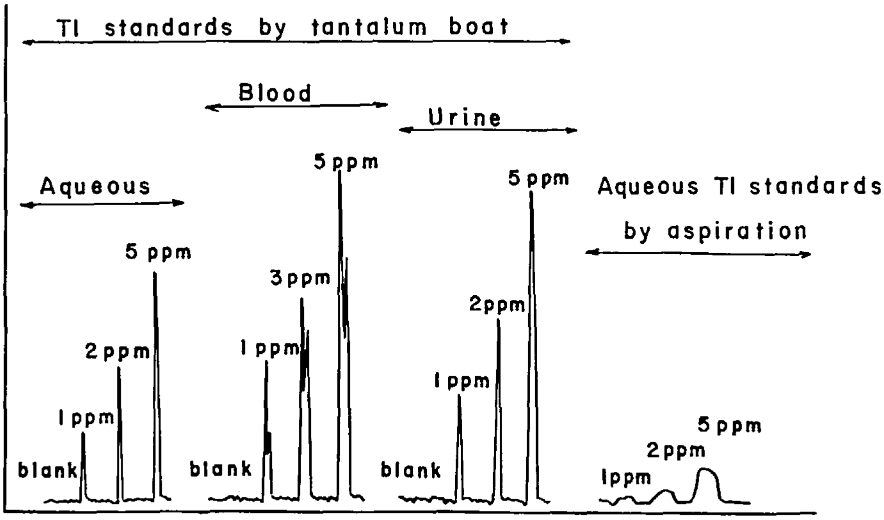


FIGURE 22. Typical results for thallium by atomic absorption with the tantalum boat and with the nebulizer. With the tantalum boat, 100-μl aliquots; with the nebulizer, 1 to 2 ml. (From Curry, A. S., Read, J. F., and Knott, A. R., *Analyst*, 94, 748(1969). With permission.)

boat to be adequate (detection limit of 2×10^{-4} μg Zn) for analysis without any preconcentration steps. Chao and Ball[192] used the sampling-boat technique to determine silver in suspended particles in streams. The procedure involved filtration of stream water through a 0.45-μm pore membrane which retained all the Ag associated with suspended particles, dry-ashing the membrane filter, digesting the residue with nitric acid, extracting the Ag into a mixture of tri-*o*-totyl phosphate and methyl isobutyl ketone, back-extracting into 0.3 *M* hydrochloric acid, and finally subjecting an aliquot of the extract to atomization in the tantalum boat. Although the procedure is quite time-consuming, the relative standard deviation in replicate analyses was only 3 to 5% with 1 to 10 ng of silver. When 2.5 l of sea-water was subjected to filtration and a 0.2-cm^3 aliquot of the final extract was placed into the boat for analysis, the detection limit for Ag in water was 2 ng/l^{-1}.

4. Delves Cup

The Delves Cup sampling technique combines the idea of mechanically introducing the sample into the flame in a sampling boat with that of collecting atomic vapor in an absorption tube where it is subjected to excitation from the source. Absorption tubes have been used previously by investigators who sought to enhance the sensitivity of atomic absorption by increasing the path length of the exciting beam through the atomic vapor.

a. Absorption Tubes for Flame Work

Absorption tubes used by earlier workers were either T-shaped or consisted simply of an open-ended tube with the flame entering one end and the mantle and the burnt gases leaving through the other. The latter arrangement was developed by Fuwa and Vallee.[193] The effectiveness of the absorption tubes is very dependent on the cooling that the atomic vapor suffers as it travels along the tube, which results in reactions and condensation on the tube walls. To prevent such cooling, absorption tubes have been protected by being placed inside other tubes of larger diameters,[194] or by being heated electrically.[195-199] The behavior of several elements and the memory effects in the absorption tube have been studied.[200,201] Iida and Nagura[200] described a ring-shaped total-consumption burner which fitted into one end of a 0.9-cm diameter quartz absorption tube in a manner that did not obstruct the excitation beam. For 12 elements they reported sensitivities that represented improvements over conventional flame atomic absorption by factors up to one order of magnitude.

The tube serves to protect the flame from entrainment of room air and thus enhances its reducing character and decreases turbulence. The effect is very similar to that achieved with vertically split flames,[202] with the exception of the additional advantage of elongating the absorption path through the shielded atomic vapor. Although the sensitivity of atomic absorption flame photometry is enhanced by such use of the absorption tube, the effects of background absorption also tend to become more serious than with conventional flames.[197]

The need for maintaining the absorption tube at a high temperature can be fulfilled by placing the tube in the flame along the length of a slot burner. Although this eliminates the electrical heating, it also shortens the useful length of the tube to the length of the burner slot. White[203] first reported the use of an absorption tube, coupled with the use of a platinum-wire loop as a means of sample introduction into the flame in the determination of lead in blood. However, he encountered severe overlap of nonspecific background absorption with the analytical atomic absorption signals, which did not become eliminated until an almost complete pre-oxidation of the sample.

b. Delves Cup Technique

Delves[204] proposed the technique as a means for the detection of lead poisoning in patients by direct analysis of samples of whole blood. As a diagnostic tool, the technique has the advantages of being rapid and very sensitive, and of requiring only 10-μl samples. The small sample size required for analysis is especially important in the treatment of children, among whom lead poisoning is not uncommon. A single determination takes about 5 min.

The instrumental set-up is illustrated in Figure 23. An air-acetylene flame burns on a Boling 3-slot burner and an absorption tube made from nickel foil 0.015 cm thick rests on nickel supports which are fastened to the burner and which hold the absorption tube in the flame about 20 mm above the burner and parallel to the slots. The sample is contained in a nickel cup, 10 mm o.d. and 5 mm

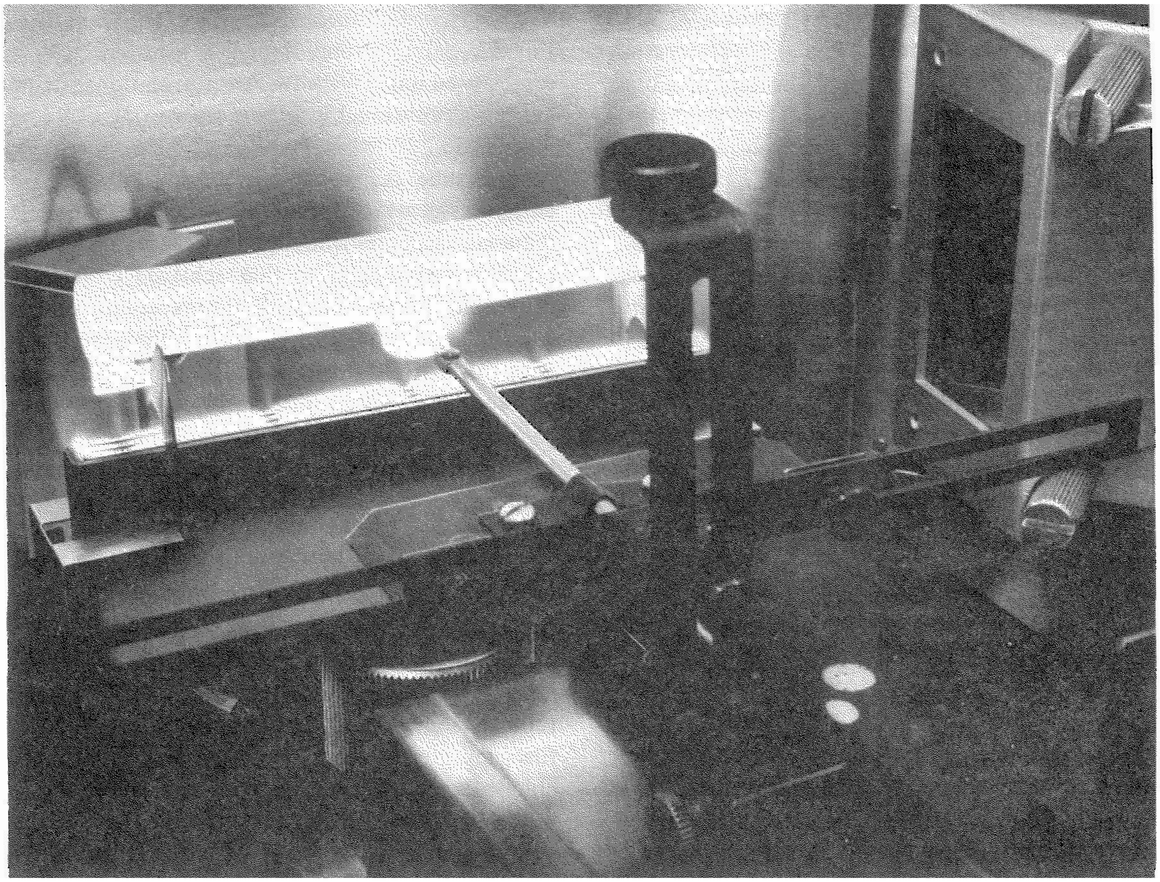


FIGURE 23. Delves Cup and the absorption tube in position over the burner. (From Fernandez, F. J. and Kahn, H. L., *A. A. Newsletter*, 10, 1(1971). Courtesy of Perkin-Elmer Corporation.)

tall, fashioned of the same nickel foil, and the cup is positioned in the flame quickly and reproducibly by means of a special mechanical assembly in front of the burner.[205] The cup rests in a wire loop made of platinum,[204] Nichrome, or Inconel.[206] The sampling cup is positioned exactly under and about 2 mm below the circular 9.5-mm diameter entrance port in the middle of the absorption tube. Some lead atomic vapor and flame gases flow into the tube, which is traversed by the 283.3-nm exciting line from the lead hollow-cathode tube, and diffuse out through the open ends of the tube.[204,205]

The sample is prepared for analysis as follows. A 10-μl aliquot of blood is pipetted into the nickel cup and dried on a hot plate at 140°C for about 30 s. Then, 20 μl of a dilute solution of hydrogen peroxide is added and the sample is returned to the hot plate for about 2 min. After this, the cup is placed in the holder and moved into the flame for analysis. The absorbance at 283.3 nm is recorded as a function of time. The resulting spectrum is illustrated in Figure 24, and exhibits the characteristic series of three peaks. The first peak corresponds to the introduction of the cup into the flame and seems to be due to the volatilization of the excess hydrogen peroxide; the second peak must correspond to absorption or scattering by the products of combustion of the residual organic matter; and the third peak is the analytical absorption due to lead vapor. Although treatment with peroxide oxidized the blood sample only partially, it can be seen from Figure 24 that lead is not vaporized until after the products of the combustion of the organic matter have had time to diffuse out of the absorption tube, thus allowing a convenient measurement of peak height from the baseline established after the peak. For further convenience, the nonspecific absorption peaks can be eliminated by the use of a

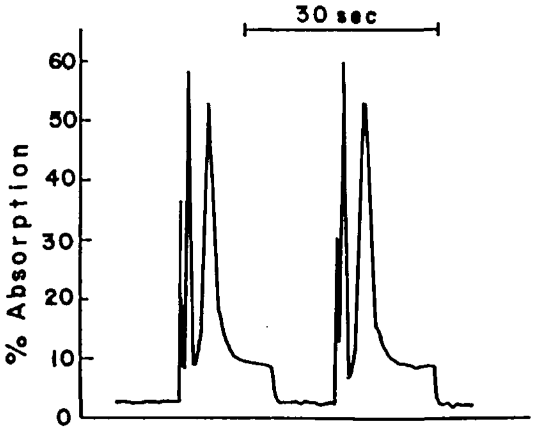


FIGURE 24. Absorption signals at 283.3 nm obtained with duplicate 10-μl samples of blood containing 1 ppm of Pb. (From Delves, H. T., *Analyst,* 95, 434(1970). With permission.)

background corrector, as discussed elsewhere in this review.

A time-delay circuit has been described which eliminates the nonspecific absorption peaks in the blood lead determination by the Delves Cup technique.[207] It simply does not record absorption for a preselected length of time prior to the appearance of the lead atomization peak. Although the device does have the effect of simplifying the appearance of the recorded data, its usefulness is very limited because it can eliminate irrelevant signals only when they are already well resolved from the lead peak and cannot correct for any nonspecific absorbance simultaneous with the analytical signal.

The detection limit of the Delves Cup technique is 1 X 10^{-10} g of Pb, which corresponds to 1 μg of Pb per 100 ml of blood (based on the 10-μl sample). This is more than an order of magnitude lower than the normal levels of lead in blood.

With a complex sample like blood, it is to be expected that matrix interference effects should be considerable. The rates and efficiency of volatilization and atomization are affected by concomitants, and consequently, analysis should be carried out by means of calibration curves prepared by spiking known blood samples with lead standards. Randomly selected nickel cups can cause large variations in sensitivity[204,205] and have to be matched by replicate determinations of a standard lead solution. Careful matching cuts the variability down to 5 to 8%.[205] For repeated analyses, Delves reported a standard deviation of 4% at the 3-ng level and of 15% at the 1-ng level.[204]

Metal absorption tubes have been replaced with fused silica,[206,208] quartz,[209] or fused alumina[210] tubes by several investigators, who claimed a better sensitivity for lead and an improved lifetime of the tube. Ediger and Coleman[206] have found that nickel tubes could be destroyed after 4 hr of operation, while a silica tube could last for 2 to 3 weeks of almost continuous use. For the manufacture of sample cups, nickel is the metal preferred over platinum or tantalum because of best precision, low cost, and an extended lifetime, unlike the limited life of the tantalum boat, which suffers oxidation in the flame. The nickel sample cups wear out only after about 50 to 100 uses, mainly by becoming misshapen and losing precision. In several reports[210,211] the nickel sample cup was successfully replaced by a carbon cup. One investigator[211] claimed a lifetime of 100 to 200 runs with the carbon cup before it began to lose sensitivity. Cups made of fused quartz have also been employed.[209]

The original Delves Cup procedure for the determination of lead in blood has been modified[206,208,209,212] in several reports. It has been shown that the already rapid procedure can be further shortened by omitting treatment with hydrogen peroxide prior to atomization.[206] After drying the 10-μl aliquot of blood on the hot plate, the sample cup is placed 11 mm away from the center of the burner in order to burn off most of the organic matter. When the flame inside the cup goes out, the cup is pushed to the center of the flame and into position under the entrance port of the absorption tube. This treatment decreases considerably the amount of molecular absorption observed at 283.3 nm and eliminates all nonspecific background at the 217.0-nm lead line which can be used with comparable detection limits.[206] Instead of oxidation with peroxide, the blood sample may also be wet-ashed with aqua regia.[209] A 10-μl sample of whole blood digested with 0.80 cm^3 of aqua regia yields negligible smoke signals but an undiminished lead signal. Barthel et al.[212] substituted 0.5% nitric acid for hydrogen peroxide as the oxidizing agent. The samples treated with nitric acid were first dried for 15 min in an oven at 200°C and then charred for 15 min on a hot plate at 450°C in order to minimize the nonspecific matrix signal. The workers reported good precision and satisfactory results, although a charring temperature of 450°C seems rather high for an element as volatile as lead.

Another simplification of the technique has enhanced its usefulness as a tool of mass screening for lead poisoning in children.[208] A droplet of blood from a lanced finger is spotted directly onto filter paper. After the blood dries, a disc having a diameter of exactly ¼ in. is punched out from the spot, placed in a Delves Cup and pushed into the flame without any pretreatment. Although this approach results in a standard deviation on replicate analyses of 10%, the method is still eminently suitable for the purposes of rapid screening.[208] The degree of spread which occurs when a drop of blood is placed on filter paper is not significantly affected by such conditions as anemia or by the actual levels of blood lead. It is, however, affected by the exact volume of the drop placed on the paper, which causes a variation of 7%.[211] Naturally, blood must not be allowed to undergo any clotting prior to paper spotting because this would affect its spreading ability. The burning filter paper disks tend to contribute to the slow deterioration of the nickel cups by gradually broadening and shortening the recorded absorption peaks.[211]

The Delves Cup technique has been extended to elements other than lead[189,210,213-216] and to materials other than blood. Lead was also determined in urine,[217] in evaporated milk,[218] and in paint.[219] Lead, copper, cadmium, and zinc were determined in kidney, liver, lung, muscle, and bone; and copper was determined in plasma.[215] The analysis of biological tissues required only grinding and homogenizing the sample with water and diluting to volume prior to delivery of aliquots into the Delves cup. An acid digestion step could also be included. The determination of cadmium in urine, plasma, and whole blood involved chelation with ammonium l-pyrrolidinecarbodithionate and extraction into methyl isobutyl ketone.[216]

The detection limits and sensitivities for several elements measured by the Delves Cup technique are given in Table 10.[210] Aqueous solutions of pure salts were used to evaluate the sensitivity of the technique and 5-μl aliquots were taken for analysis. For most elements the absolute detection limits are seen to be good. For tellurium, 1% absorption was estimated to arise from only 0.5 ng of the element when it was first extracted into methyl isobutyl ketone and the extract was atomized in the Delves Cup.[189] However, a reagent blank on order of magnitude higher than this was also observed.

TABLE 10

Detection Limits and Sensitivities Obtained with the Delves Cup

Element	Wavelength, nm	Sensitivity (absorbance for 1 μg)*	Detection limit, ng	Flame type
Ag	328.1	10	0.05	Air/C_2H_2
As	197.2	0.8	5	N_2/H_2
Bi	223.1	0.9	5	Air/C_2H_2
Cd	228.8	40	0.2	N_2/H_2
Co	240.7	0.1	20	Air/C_2H_2
Cu	324.7	1	2	Air/C_2H_2
Ga	287.4	0.005	300	Air/C_2H_2
Hg	253.6	2	0.5	N_2/H_2
Pb	283.3	40	–	Air/C_2H_2
Sb	231.2	0.4	2	Air/C_2H_2
Se	206.3	0.4	20	N_2/H_2
Sn	224.6	0.6	1	Air/C_2H_2
Tl	276.8	6	0.5	Air/C_2H_2
Zn	213.8	40	0.005	Air/C_2H_2

*The sensitivity is defined, in accordance with an IUPAC recommendation, as the slope of the calibration curve. In order to estimate the amount of material which corresponds to 1% absorption, divide 0.0044 by the listed sensitivity value.

(From Clark, D., Dagnall, R. M., and West, T. S., *Anal. Chim. Acta,* 60, 219 (1972). With permission.)

West and co-workers^{210} investigated the applicability and sensitivity of the Delves Cup technique for 14 elements and reported an interesting observation of multiple absorption peaks for several of the elements. It was assumed that the multiple peaks were not due to molecular absorption by the matrix because absorption persisted at several different atomic lines. Thus, lead, silver, selenium, bismuth, and gallium each exhibited one peak; zinc, copper, cadmium, thallium, tin, and cobalt each exhibited two peaks; mercury and antimony each exhibited three peaks; and arsenic gave four peaks. Attempts to volatilize aluminum, barium, calcium, germanium, magnesium, vanadium, and tungsten by the Delves technique were unsuccessful.^{210} The approach is clearly applicable only to elements of relatively high volatility.

In general, the methods that have been described for the mechanical placement of samples in the flame for analysis appear to have few unqualified advantages. Possible exceptions seem to include the suggested electrical heating of a microprobe simultaneous with its placement in the flame for the determination of very non-volatile elements, and the convenience of the rapid, though somewhat imprecise, diagnostic determination of lead in blood by the Delves Cup.

B. Tantalum Ribbon and Other Electrically Heated Devices for Flameless Atomization

1. Tantalum or Tungsten Ribbons and Filaments

a. Description and Properties

i. Donega and Burgess Atomizer

The elimination of the flame and the substitution of electrical heating is a natural development of the tantalum boat sampling technique. Donega and Burgess^{220} used boats 50 mm long and 6 mm wide made of 25-μm tantalum or tungsten foil or of 125-μm graphite sheet as atomization vessels for atomic absorption spectrometry (Figure 25).

The tantalum and tungsten boats had a depression capable of holding 100 μl of solution; the graphite boats accommodated up to 50 μl. The boat was enclosed in a quartz envelope, which could be raised to pipet the sample onto the boat. The sample was first dried by applying a low current. Then, the envelope was evacuated, filled with nitrogen, hydrogen, or argon at 1 to 300 torr pressure, and heated by application of an electrical current up to a temperature of about 2,200°C in less than 0.1 s. The maximum atomization signal was observed in a fraction of a second and was examined by means of an oscilloscope. The elements tested included aluminum, chromium, copper, manganese, molybdenum, nickel, platinum, silicon, sodium, and vanadium and detection limits on the order of 10^{-12} g were observed for several of the elements.

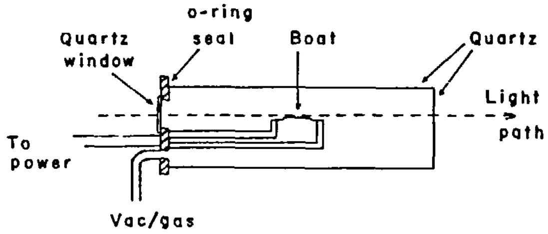


FIGURE 25. Flameless tantalum-boat atomizer developed by Donega and Burgess. (Reprinted with permission from Donega, H. M. and Burgess, T. E., *Anal. Chem.*, 42, 1522(1970). Copyright by the American Chemical Society.)

The following five parameters affected the intensity of the absorption measurements: the temperature of atomization, the boat material, the nature of the sample, and the nature and pressure of the filler gas. The temperature of atomization determines the rate at which the sample is vaporized and the rate at which ground-state atoms are generated. Since it is desirable to have as large a proportion as possible of the ground-state atoms of the sample present in the light path at the same time, an atomization temperature must be reached rapidly and must be carefully selected experimentally for each element in each type of matrix. Figure 26 illustrates the effect of boat temperature on the atom population of silicon, added as sodium silicate. It is always important to remember that an optimum atomization temperature of the tantalum strip, or any other non-flame atomization device, may be imposed in a given experimental situation, not by the nature of the sample, but by the speed of response of the detection and the read-out systems. For a true representation of the atomization process, these systems should be able to respond faithfully to transient signals that persist for 0.1 s or even less. The nature of the compound of which the element of interest is a part clearly affects the ease of volatilization and atomization. Thus, the presence of refractory compounds would decrease absorption, while the presence of very volatile compounds may result in error due to loss during the drying step.

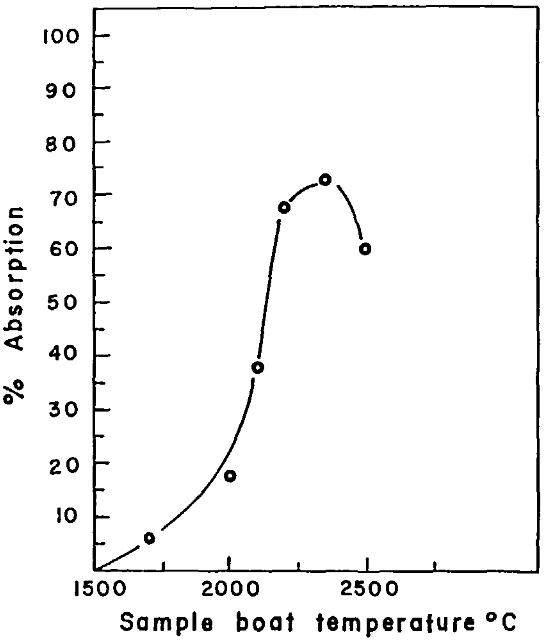


FIGURE 26. Effect of sample boat temperature on the absorption of silicon at 251.6 nm. (Reprinted with permission from Donega, H. M. and Burgess, T. E., *Anal. Chem.*, 42, 1523(1970). Copyright by the American Chemical Society.)

The requirements on the boat material are those of a high melting point, reasonable conductivity, and inertness toward the sample, all of which are well fulfilled by tantalum, tungsten, and graphite. Takeuchi et al.[221] compared tantalum with platinum, nickel, and tungsten, and judged tantalum to be superior because of its high melting point and ease of fabrication.

Donega and Burgess[220] observed significant effects on absorption of changes in the composition and pressure of the gas which was used to fill the absorption chamber prior to atomization. The different effects of hydrogen, nitrogen, and argon on the absorption of sodium are indicated in Figure 27. The initial rise in absorbance with increasing gas pressure may be attributed to the decrease in the rate of diffusion of the atomic vapor of the sample caused by the presence of the foreign gas. The reason for the decrease of absorption at higher pressures of the filler gas is unclear.[220]

ii. Other Tantalum Strip and Filament Devices

Hwang et al.[222] simplified the apparatus proposed by Donega and Burgess by eliminating the vacuum system and employing a high speed recorder in place of the oscilloscope. A later model of their flameless atomization cell is offered by Instrumentation Laboratory Inc. as model 355 Flameless Sampler. The tantalum-ribbon atomizer is also offered by at least two other commercial manufacturers (Jarrell-Ash and Barnes Glomax). The sample, up to 100 μl, is placed in a small depression in a strip of tantalum ribbon. The cell is aligned very carefully to ensure that the analytical beam passes directly over the center of the tantalum ribbon at a height of about 2 mm. The tantalum ribbon is clamped firmly into place but can be replaced quickly. The instrumentation also includes a power supply with a precise current selection for the drying and the atomization processes, and a source of purge gas which circulates through the absorption cell during the operation of the cell. After the sample has been dried, the current may be increased moderately at first to ash the sample, if necessary. The high atomization current is applied until a sharp peak is obtained on the recorder and the signal returns to the baseline.[222]

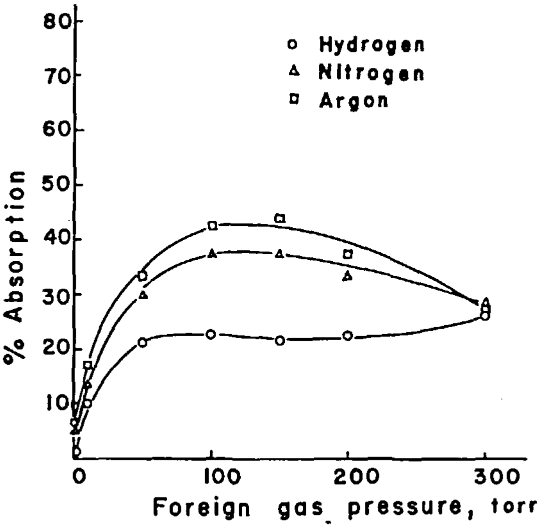


FIGURE 27. Effect of foreign gas pressure on the absorption of sodium at 589.0 nm in a flameless tantalum-boat atomizer. (Reprinted with permission from Donega, H. M. and Burgess, T. E., *Anal. Chem.*, 42, 1523(1970). Copyright by the American Chemical Society.)

A simple atomizer employing an electrically heated tantalum strip was also described by Takeuchi, Yanagisawa, and Suzuki,[221] and a similar atomizer employing a tantalum filament was described by Maruta and Takeuchi.[223] The latter apparatus is illustrated in Figure 28.

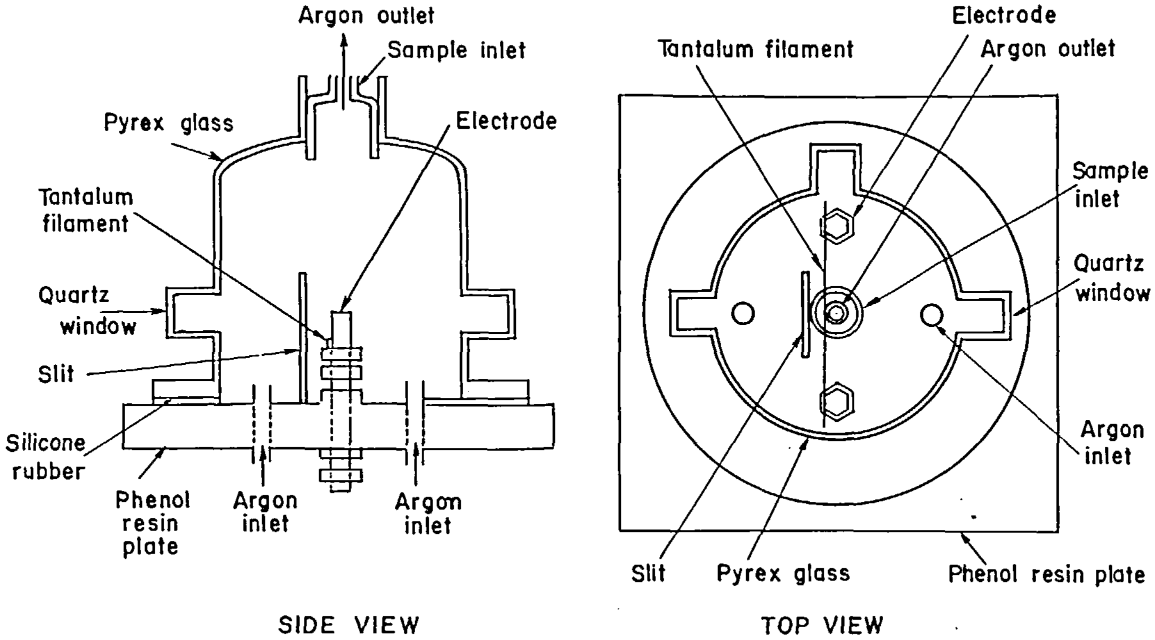


FIGURE 28. Tantalum-filament atomizer and chamber. (From Maruta, T. and Takeuchi, T., *Anal. Chim. Acta*, 66, 6(1973). With permission.)

Cantle and West[224] employed a cylindrical tungsten filament 60 mm long and 2.2 mm in diameter in the center of which was ground a small depression to accommodate 1-μl samples. As with all ribbon and filament atomizers, the incident radiation was allowed to pass just over the center of the filament. Comparing the characteristics of the tungsten- and carbon-filament atomizers of equal dimensions, the tungsten filament was found to have a much lower resistance and thus to require a much lower voltage to reach the same temperature. It was also stronger and had a longer lifetime than the carbon filament, which must be changed after every 100 to 200 runs. Argon and nitrogen served equally well as sheath gases and their rate of flow was not critical. The following amounts of elements caused 1% absorption signals: 0.78 pg of zinc, 14 pg of lead, 7.5 pg of copper, and 4.4 pg of silver.

The absorption signal falls off rather rapidly as the height of measurement is raised several millimeters above the tantalum strip. Unlike with flame atomization, the metallic vapor recombines rapidly as it rises above the tantalum ribbon and travels through a rapid temperature gradient into the cool atmosphere above the ribbon.[225] Comparing helium, argon, and nitrogen as purge gases, no significant effect on the atomic absorption of copper was detected. Reproducibility was not affected by working at atmospheric, instead of reduced, pressures.[221] The rate of flow of the purge gas must be neither too high, which would flush the sample vapor through the absorption chamber too rapidly for maximum response, nor too low, which would broaden and shorten the absorption peaks, due to slow diffusion, and may result in incomplete flushing of oxygen from the absorption cell.[225] Takeuchi et al.[221] observed that the rate of flow of the inert gas had different effects on the atomization peak heights of different elements. The absorption of iron decreased, while that of chromium increased, when the argon flow rate was changed from 2 to 7 l/min. With argon, helium, or hydrogen, but not with nitrogen, the sensitivity was better when the gas was not interrupted during the absorption measurement.[225] The desirable qualities of the purge gas include low thermal conductivity and low specific heat, which allows minimum cooling of the Ta ribbon. With some elements, however, hydrogen is the gas of choice due to its reducing character.

b. Sensitivity

The sensitivity of flameless atomic absorption with a tantalum-ribbon atomizer is presented in Table 11.[225] Sensitivities reported for tantalum and tungsten filaments are of rather similar magni-

TABLE 11

Sensitivities and Detection Limits for the Electrically Heated Flameless Tantalum-Ribbon Atomizer

Element	Wavelength, nm	Temperature, °C	Sensitivity (absorbance for 1 ng)*	Detection limit, g
Ag	328.1	1200	2×10^{-1}	4×10^{-12}
Al	309.3	2000	5×10^{-3}	3×10^{-10}
As	193.7	2400	7×10^{-3}	3×10^{-10}
Au	242.8	2400	4×10^{-2}	2×10^{-11}
Ba	553.6	2000	1×10^{-1}	1×10^{-11}
Be	234.9	2400	6×10^{-1}	2×10^{-12}
Bi	223.1	2200	4×10^{-2}	4×10^{-11}
Ca	422.7	2200	1×10^{0}	1×10^{-12}
Cd	228.8	700	6×10^{-1}	2×10^{-12}
Co	240.7	2000	5×10^{-3}	3×10^{-10}
Cr	357.9	2400	1×10^{-1}	2×10^{-11}
Cs	852.1	1800	6×10^{-2}	7×10^{-11}
Cu	324.8	1800	2×10^{-1}	1×10^{-11}
Eu	459.4	2000	6×10^{-2}	3×10^{-11}
Fe	248.3	2400	2×10^{-2}	1×10^{-10}
Ga	287.4	1800	1×10^{-2}	1×10^{-10}
Hg	253.7	900	6×10^{-3}	2×10^{-10}
In	303.9	1800	1×10^{-2}	1×10^{-10}
K	766.5	1800	1×10^{0}	1×10^{-12}
Li	670.8	2000	6×10^{-1}	2×10^{-12}
Mg	285.2	1400	$2 \times 10^{+1}$	1×10^{-13}
Mn	279.5	1800	2×10^{-1}	7×10^{-12}
Na	589.0	1600	1×10^{0}	1×10^{-12}
Ni	232.0	2400	1×10^{-2}	2×10^{-10}
Pb	217.0	1400	1×10^{-1}	1×10^{-11}
Pd	247.6	2400	2×10^{-3}	7×10^{-10}
Rb	780.0	2200	2×10^{-1}	1×10^{-11}
Sb	217.6	2400	6×10^{-2}	2×10^{-10}
Se	196.0	2000	6×10^{-2}	7×10^{-10}
Si	251.6	2300	1×10^{-4}	1×10^{-8}
Sn	286.3	2400	1×10^{-2}	1×10^{-10}
Sr	460.7	2200	1×10^{-1}	1×10^{-11}
Te	214.3	2000	7×10^{-3}	3×10^{-10}
Ti	364.3	2300	1×10^{-3}	1×10^{-9}
Tl	276.8	1400	2×10^{-2}	7×10^{-11}
V	318.4	2300	4×10^{-3}	4×10^{-10}
Zn	213.9	1200	1×10^{0}	1×10^{-12}

*The sensitivity is defined, in accordance with an IUPAC recommendation, as the slope of the calibration curve. In order to estimate the amount of material which corresponds to 1% absorption, divide 0.0044 by the listed sensitivity value.

(Reprinted with permission from Hwang, J. Y., Mokeler, C. J., and Ullucci, P. A., *Anal. Chem.*, 44, 2018 (1972). Copyright by the American Chemical Society.)

tude. In Table 11, the sensitivity is defined as absorbance per nanogram of element (rather than as weight for 1% absorption), while the detection limit is the weight which yields a signal equal to twice the standard deviation of the noise, calculated from 10 consecutive readings. The height of the measurement was 0 mm. The precision of the technique corresponds to a relative standard deviation of 2 to 4% at the nanogram level.

c. Interferences

Several interferences have been reported in work with electrically heated tantalum-strip[221,226] and -filament[223] atomizers. The mechanisms of interference are probably similar to those responsible for many of the interferences observed with heated graphite-tube furnaces and especially with carbon-rod and -filament atomizers.

Magnesium signals were depressed by greater than tenfold excesses of phosphate.[221] The presence of copper salts did not affect absorption due to magnesium but the absorption due to copper was changed by magnesium.[221] Maruta and Takeuchi[226] studied the effects of 0.05 to 0.2 *M* hydrochloric, perchloric, nitric, and phosphoric acids on the absorbances obtained with a few nanograms of copper, iron, and chromium, and concluded that acid interferences observed with the tantalum-strip atomizer are significantly different from those observed for these metals in conventional flame atomic absorption. Some of the results are indicated in Figure 29. Hydrochloric acid had no effect on the absorption due to copper, iron, or chromium. Perchloric acid did not affect the absorption due to copper, but it enhanced that due to chromium. The effect of perchloric acid on iron was eliminated at higher power levels of heating. Nitric acid depressed the signal due to chromium, while affecting those for copper and iron very little. Phosphoric acid enhanced the copper signal and depressed the iron and chromium signals, but the latter effects decreased at higher power levels.

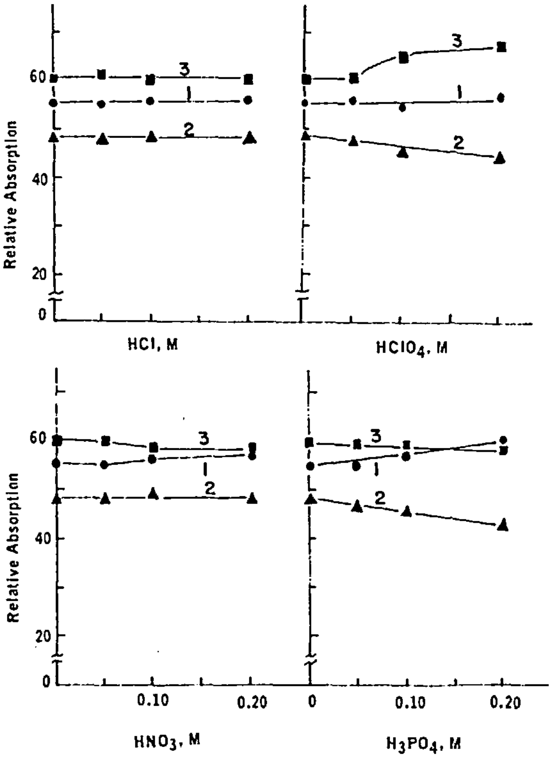


FIGURE 29. Effects of hydrochloric, perchloric, nitric, and phosphoric acids on the atomic absorptions of copper, iron, and chromium with a tantalum-strip flameless atomizer. (1) 1 ng of copper; (2) 1.5 ng of iron; (3) 2 ng of chromium. (From Maruta, T. and Takeuchi, T., *Anal. Chim. Acta*, 62, 253(1972). With permission.)

Maruta and Takeuchi[223] investigated the effects of 100-, 50-, and 10-fold weights of 12 different metals, present as chlorides, upon the atomic absorption signal of chromium in a solution containing 6 ppm of this element. Iron, copper, manganese, aluminum, and sodium did not interfere, while calcium, strontium, and vanadium interfered quite severely. As would be expected, the degree of interference decreased with increasing temperature of atomization. It is interesting to note that vanadium and molybdenum enhanced the signal due to chromium, although the effects disappeared at high temperatures. The use of high atomization temperatures appears to be necessary for the suppression of interferences, but may lead to some loss of sensitivity if the resulting increase in the rate of atomic vapor formation leads to signal distortion due to inadequate speed of the response system.

d. Applications

The technique of flameless atomic absorption with a tantalum ribbon and similar atomizers has been applied to trace determination of several metals in materials of biological origin. Lead in blood was determined both with an extraction step[227] and directly.[228] Hwang et al.[227] complexed blood lead by chelation with ammonium 1-pyrrolidinedithiocarbamate and extracted it into methyl isobutyl ketone. A 20-μl aliquot of the extract was pipetted onto the boat and dried for about 30 s at a low current to evaporate the solvent, and then atomized at a higher current. The relative standard deviation of the analysis was 5% at the 1.2 X 10^{-9} g level. A background correction was unnecessary because the pyrrolidinedithiocarbamate appeared to be charred away along with the evaporating methyl isobutyl ketone. When the blood of patients on EDTA or penicillamine therapy is tested, low results are obtained due to incomplete extraction of lead. Hwang et al.[228] also described a direct determination of lead in blood. In this procedure a 25-μl aliquot of whole blood, diluted 1:10 with water, was placed on the tantalum atomizer. It was dried, charred at about 400°C, and atomized at 1,500°C. A small residue of carbon which builds up on the atomizer is brushed off. The atomizer is also periodically heated up to 2,000°C in hydrogen gas to ensure its usefulness for more than 200 analyses before replacement becomes necessary.[228] Background correction was carried out by use of the reference beam from a hydrogen continuum lamp.

Chromium and manganese were determined[229] in serum by 1:4 dilution with water and subjection of a 25-μl aliquot to analysis by the flameless tantalum-ribbon technique. Nickel was similarly detected by using undiluted serum.[229] Precision of analysis is reflected in a relative standard deviation for manganese of 8%, for chromium of 30%, and for nickel of 4%, at approximately the 2.5×10^{-10} g level. Magnesium was determined in serum after a 400-fold dilution with water and injection of 2-μl aliquots.[221]

The determination of cadmium in blood, hair, nails, and biopsy samples by the tantalum-ribbon technique· was described by Ullucci and Hwang.[230] Blood samples were taken through an adaptation of the pyrrolidinedithiocarbamate—methyl isobutyl ketone extraction procedure, while solid samples were decomposed by acid treatment and treated with hydrogen peroxide. Copper and manganese were determined in brain tissues by a similar treatment.[231]

An aluminum alloy was analyzed for magnesium and yielded slightly high results (0.77 to 0.80%, as against an expected value of 0.74%) and the deviation was tentatively attributed to interference by aluminum.[221] Chromium in steel was determined by dissolution of 0.1-g samples in hydrochloric and nitric acids, dilution to 200 cm^3 with water, and atomization of 0.5-μl aliquots at 2,150°C.[223] For a series of 9 steels having chromium contents between 0.36 and 1.10%, the method was shown to be precise and free from any matrix effects.

In the determination of cadmium, lead, silver, and indium in rainwater and stream water,[232] cadmium could be evaluated by direct comparison with aqueous standards, but matrix effects were detected with lead, silver, and indium. To eliminate matrix interference, lead was extracted with dithizone and chloroform after adding citrate to the sample and adjusting the pH to 9 to 11 with ammonia. Silver was extracted with dithizone and carbon tetrachloride from an acidified sample, and indium was extracted with 8-hydroxyquinoline and chloroform from the sample buffered at pH 3.5.

The tantalum-ribbon atomizer has been used in determination of lead in atmospheric aerosols.[233] Concentrations of lead in air as low as 0.01 μg m^{-3} could be determined with samples even as small as 105 l, the air being allowed to impinge upon a tantalum ribbon in a special impact sampling device. The tantalum ribbon was then subjected to analysis. A limit of detection of 10^{-11} g of lead was reported and reproducibility of measurement was in the range of 6 to 10% with 4.0 ng of lead.

e. Advantages

The advantages of the electrically heated tantalum boat as the atom reservoir in atomic spectrometry are similar to those of other flameless sampling devices. The sensitivity is improved by a factor up to 10^5, compared to conventional flame atomic absorption, and microsamples can be employed. By controlling the chemical environment in which the atomic vapor is generated, the most favorable conditions can be selected. Enclosure of the atom reservoir and selection of the pressure and nature of the filler gas allow operation in the vacuum ultraviolet.

As with other flameless sampling techniques, direct solid sampling may be employed. It would shorten the time consumed by an analysis because it eliminates the dissolution and pretreatment steps. However, a serious problem arises from the necessity of taking a tiny representative sample from material which may not be perfectly homogeneous. Thus, it is likely that solid samples will continue to be put into solution prior to analysis.

2. Wire Loop Atomizer

a. Description and Performance

An electrically heated wire loop atomizer has been used for flameless atomic fluorescence[234-237] and atomic absorption studies.[238,239] Bratzel, Dagnall, and Winefordner[236] replaced the flame cell of the atomic fluorescence spectrophotometer with a loop fabricated from tungsten or platinum.

The sample solution was placed on the loop by a dipping procedure which took up about 2 μl of the solution. The loop was irradiated by electrodeless discharge lamps and fluorescence was measured immediately above the loop. The loop had a diameter of 1/32 in. and was protected by a double sheath of argon. Peak heights and integrated signals varied slightly with varying argon flow rate. Gas flows of 15 l min^{-1} were found to be best for both sheaths.

The nature of the anion affected the fluorescence signal of mercury, as indicated by the following relative signal intensities for chloride, cyanide, sulfate, nitrate, and bromide: 1.00, 1.07, 1.09, 0.99 and 0.82. Thousandfold excesses of several metals and anions suppressed the cadmium signal to varying degrees. Clearly, the effect must be related to changes in volatility and stability of the various compounds and should be sensitive to changes in atomization temperature. The following detection limits were reported: 0.02 pg of cadmium; 2 pg of silver; 20 pg of mercury or zinc; 40 pg of bismuth; 0.2 ng of calcium; 2 ng of thallium; 4 ng of magnesium, lead or beryllium; and 20 ng of gallium.[236]

An electrically heated spirally looped tungsten-filament atomizer was used by Williams and Piepmeier.[240] The filament was taken from a commercial light bulb. The heated filament is positioned in the center of a vertical quartz tube, where it is protected by continuously flowing argon. The sample is placed on the filament with a syringe through a small hole in the quartz tube. The excitation beam traverses the quartz tube just above the filament. Scattering from the tungsten filament at wavelengths above 330 nm was corrected by measuring broad band absorption at a nearby wavelength. The following weights of elements resulted in 1% absorption signals: 3 pg of calcium; 20 pg of chromium or copper; 70 pg of magnesium; 0.2 ng of iron; 0.3 ng of manganese; and 20 ng of tin. Double peaks observed for copper and manganese at atomization were tentatively attributed to nonuniform heating of the filament.

Goode et al.[237] fully automated the delivery of microliter droplets to the platinum-loop atomizer, heating of the atomizer, data acquisition, and analysis and systematically studied the effects of different experimental parameters on the atomic fluorescence of Cd.

Chauvin et al.[238] used loops fabricated by twisting 80-mm lengths of a 97% tungsten-3% rhenium alloy wire, 250 μm in diameter, around a needle. The alloy has a high melting point (about 3,200°C) and is more pliable and resistant to oxidation than 100% tungsten. Different loops gave sensitivities that were reproducible within 5%. Each loop could be used about 100 to 200 times. Nitrogen or argon, at a flow rate of 2 to 3 l min^{-1}, served as the sheathing gas. Two-microliter aliquots of sample solutions were pipetted for analysis. The detection limits for nickel and lead were 2 and 0.1 ng, respectively.

The interference effects of 10-, 100-, and 1,000-fold excesses of 20 cations and 16 anions upon the atomic absorption signal of lead were tested.[238] Many species appreciably enhanced or suppressed the absorption signal. No straightforward correlation was found between the extent of interference and any one physical property of the analyte or the interfering material. It was postulated, however, that the interferences may be the effect of differences in the rate of production of free lead atoms from compounds of different volatility and of the thermal stability of the salt matrix surrounding the lead. With a slow response detection system, a significant increase in the rate of vaporization becomes registered as a depression, while a slight decrease in the atomization rate can cause enhancement by giving the detector system more time to respond. Formation of very nonvolatile compounds can, of course, lead to incomplete atomization and therefore a depressed atomization signal.

The main limitation of the loop atomizers is the relative imprecision of sampling resulting from the extremely small volumes (10 μl or less) that can be accommodated. In addition, the signal intensity is very dependent upon careful optimization of conditions, such as the rate of sheath gas flow.

b. Indirect Methods

Interference of foreign chemical species upon the atomic absorption signals of some elements determined with the wire loop atomizer was put to use by Newton and Davis[239] as an indirect method of determination of cyanide, lanthanum, and zirconium. A loop of a tungsten-rhenium alloy wire is soaked in a solution of an element which can be determined with good sensitivity by atomic absorption spectrometry. Cadmium is well suited for this purpose, although other elements, such as lead or magnesium, can also be used. The metal is concentrated upon the wire by an apparent ion-exchange process.[241] When this wire is then immersed in the sample solution, certain ions from the solution replace or remove the cadmium on the wire. The degree of decrease of the cadmium atomization signal from the loop prepared in this manner is a measure of the concentration of the interfering ion found in the sample solution. Monovalent cations in the sample do not affect the cadmium signal, except when they are present in high concentrations. However, most other cations do replace cadmium from the wire to some degree and would, therefore, interfere with the indirect determination of cyanide, lanthanum, or zirconium unless they are removed or masked.

The effect of the length of time during which the wire loop was soaked in a solution containing 10 ppm of lanthanum nitrate on the change in cadmium absorbance is illustrated in Figure 30a, and a calibration curve showing how the cadmium absorbance depends on the concentration of lanthanum nitrate in the sample solution is illustrated in Figure 30b. Similar results were obtained with zirconium and cyanide.

Such indirect analyses are of interest only from an academic point of view and lack any promise of practical usefulness. The dependence of the signal upon the length of soaking is an inconvenience, and interferences from other ions present in any realistic sample can fairly be expected to be overwhelming.

V. CHEMICAL VAPORIZATION

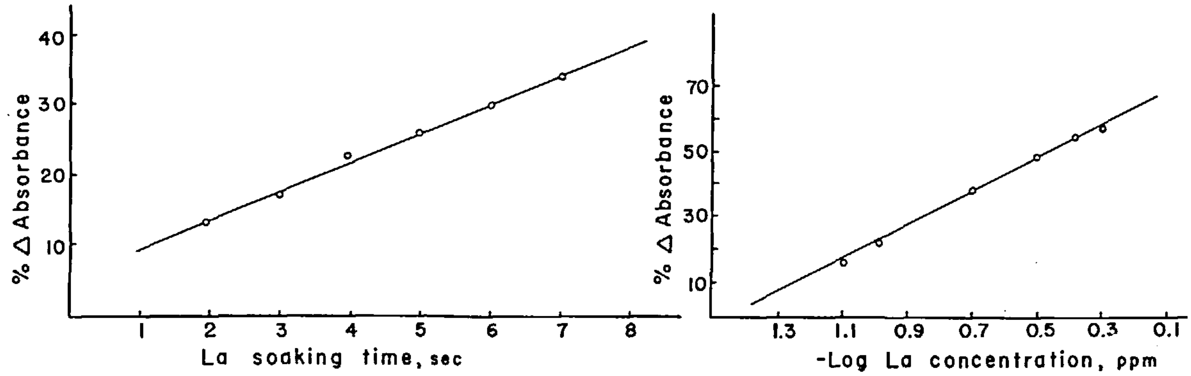
The technique of chemically treating the sample to generate a volatile product to be subjected to analysis by atomic absorption spectrometry has been applied to a series of elements which form volatile hydrides and, most notably, to the analysis of mercury. Chemically generated hydrides are carried into a flame, where they are atomized and subjected to excitation from the source. Chemical evolution of mercury vapor does not require the use of a flame for analysis. This technique for the atomic absorption determination of mercury has been described in a large number of papers since it was first reported by Poluektov in 1964.[242] Kits for quickly adapting conventional atomic absorption units to the determination of volatile hydrides or mercury are available from several commercial manufacturers. The necessary apparatus can also be put together easily in the laboratory. The results of chemical vaporization analysis are generally quite satisfactory, providing good sensitivity and considerable freedom from interferences.

A. Generation of Volatile Hydrides

Several elements in groups IVA, VA, and VIA of the periodic table may be evolved as hydrides from sample solutions upon treatment with suitable reducing agents. The evolved gas is collected and allowed to enter the flame in a reproducible manner. The elements that can be determined by this method include arsenic, antimony, bismuth, selenium, tellurium, germanium, and tin.

1. Arsine

Holak[243] was first to suggest the conversion of arsenic to arsine by the conventional arsine generation method[244] prior to introduction into the flame for analysis. The arsine evolution method



(a) (b)

FIGURE 30. Indirect determination of lanthanum with a flameless metal loop atomizer. (a) A calibration plot of percent change in the absorbance signal of cadmium as a function of soaking time in a solution containing 10 ppm of lanthanum nitrate (b) A calibration plot of percent change in the absorbance signal of cadmium as a function of the logarithm of the concentration of lanthanum nitrate, with a 50-sec soaking time. (Reprinted from Newton, M. P. and Davis, D. G., *Anal. Lett.*, 6, 927 and 929(1973) by courtesy of Marcel Dekker, Inc.)

consists mainly of treating the sample with hydrochloric acid to establish an acidic environment of around 4 *N*, adding potassium iodide, prereducing with stannous chloride, and finally adding granular zinc to initiate evolution of the hydride. The reaction was carried out[243] in an erlenmeyer flask closed with a rubber stopper fitted with glass tubing, from which the generated gas flowed through a calcium chloride drying tube and then into a U-shaped section of glass tubing filled with glass beads and immersed in liquid nitrogen in a Dewar flask. Arsine condensed in the U-tube, while most of the hydrogen generated by the reaction escaped through the other end of the U-tube. After about 30 min, when the conversion of arsenic to arsine was deemed to be complete, the U-tube trap was closed with pinch clamps and removed from the liquid nitrogen bath. After the collected sample came to room temperature, nitrogen gas, preset at a flow rate of 50 cm^3 min^{-1}, was connected to one end of the U-tube while the other end was connected to the aspirator capillary of the conventional premix burner via a needle of small diameter. To allow the sample to enter the flame, both pinch clamps were removed simultaneously. The absorbance was recorded as a function of time and the peak height was plotted against the weight of arsenic to establish a working curve. Holak used an air-acetylene flame and reported a detection limit of 0.04 μg of arsenic.[243]

Several modifications of this method for arsenic have been suggested by other investigators.[245-249] The freezing of the evolved arsine in a liquid nitrogen bath was omitted in favor of bubbling the gas through a small volume of silver nitrate trapping solution.[245] The following reaction takes place in the trapping solution:

$$AsH_3 + 6Ag^+ + 2H_2O \rightarrow 6Ag + AsO_2^- + 7H^+$$

The solution was then aspirated in the conventional manner into a hydrogen-argon-entrained air flame and absorption at the 193.7-nm arsenic line was measured.

The chemical trapping step may also be eliminated, and the generated arsine may be led to the flame directly[246,250] or be swept into the flame from a collection reservoir by a carrier gas.[247,251,252] The reaction flask itself may serve as the collection reservoir,[252] or can be equipped with an adapter carrying an expandable balloon and another adapter to allow flushing the flask with the carrier gas, usually argon.[251] After the sample in the reaction flask has been treated with hydrochloric acid, potassium iodide, and stannous chloride solutions, the system is flushed with argon. Then, zinc metal is introduced and the collection balloon is immediately attached. At the end of a 4 to 5-min interval, a multiway stopcock is turned to divert argon from its direct path of flow to flush out the collected arsine from the balloon and the flask and carry it to the hydrogen-argon-entrained air flame.[251] A valve system for introducing zinc into the reaction vessel without admitting air has been described.[247] Elimination of oxygen from the reaction vessel is helpful, since oxygen tends to inhibit the reaction in which arsine is generated. A detection limit of 0.02 μg was reported for arsenic, and a similar detection limit for selenium was also shown possible by this method.[251]

Other modifications of Holak's method for arsenic include several flameless applications.[248,249,253,254] In one report,[248] the chemically generated arsine gas is carried by a flow of argon into an electrically heated absorption tube traversed by the exciting beam from the arsenic hollow cathode tube (Figure 31). The temperature of the absorption tube is 700°C, which is sufficient to cause effective atomization of the vapor. The flameless approach eliminates almost all background absorption signal which is observed in the hydrogen-argon-entrained air flame, for which the background is already low, and allows a further increase in sensitivity by a factor of about two.

Other investigators have used the arsine generation process to introduce sample into a microwave-induced plasma.[249] Although the usual method for arsine generation takes several minutes to ensure complete conversion of arsenic, the system described by Lichte and Skogerboe[249] effects this within about 30 s. It consists of a column of granular zinc through which the carrier gas flows and into which sample solution is injected by means of a syringe introduced through the septum at the top of the column. The sample is made strongly acidic and prereduced with stannous chloride prior to injection. With optimized conditions for the plasma, the detection limit was reported to be 5 ng of arsenic, and even that was attributed mainly to the reagent blank. The configuration of this arsine generator is not limited to use with plasma and should prove quite suitable for use with the flame.

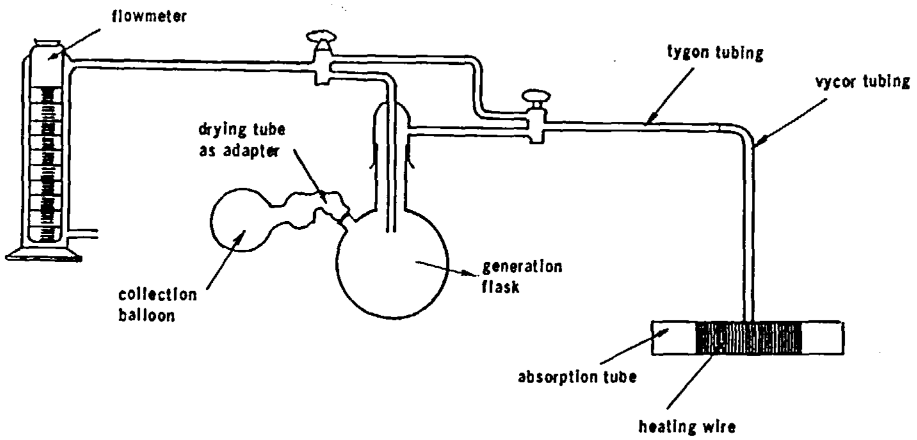


FIGURE 31. Arsine generation apparatus and the electrically heated absorption tube. (Reprinted with permission from Chu, R. C., Barron, G. P., and Baumgarner, P. A. W., *Anal. Chem.*, 44, 1477(1972). Copyright by the American Chemical Society.)

By means of the arsine evolution technique, As was determined in soils at the ppm level and in natural water at the ppb level.[250] Arsenic was also determined in sewage,[255] contaminated natural water,[249,253,255,256] and in blood, hair, and plant leaves.[249] Several automated procedures were reported.[253,254,257] One of the automated procedures[254] describes the determination of arsenic in atmospheric particulates. The air is filtered through glass fiber filters and trapped arsenical particulates are subsequently dissolved by acid digestion. After treatment with sodium borohydride, the evolved arsine flows into a quartz cell, heated to 800 ± 20°C, in which absorption by arsenic atoms is measured.

2. Other Volatile Hydrides

Treatment with potassium iodide, stannous chloride, and metallic zinc, successful in the generation of arsine, was also shown to be effective for the generation of the hydrides of selenium and antimony by some workers,[252,258] but failed to produce stibine, SbH_3, in another report.[259] However, it was found that titanium (III) chloride, either in hydrochloric acid alone or in a mixture of hydrochloric and sulfuric acids, does serve for the evolution of SbH_3 upon treatment with zinc or magnesium.[259] As in the arsine procedure, stibine was collected in a balloon, which was later deflated suddenly to release the gas into the hydrogen-argon-entrained air flame. The same investigators also applied the titanous chloride-magnesium method to the evolution and determination of the hydrides of arsenic, antimony, bismuth, selenium, and tellurium.[260] They found the use of a background corrector to be preferable with arsenic and selenium, and also found that careful control of acid concentrations and time sequences during gas collection was vital to the success of the determination of tellurium.

Gaseous hydrides may also be generated for atomic absorption analysis with the aid of sodium borohydride as the reducing agent.[255,260,261] After treating the sample with acid and purging the reaction flask with argon, a pellet of sodium borohydride is introduced through the dosing stopcock,[255] and after a 15-s interval the hydride collected in the collection balloon is allowed to empty into the flame. The borohydride reagent works for arsenic, antimony, selenium, bismuth,[255,261] germanium,[260,261] tin, and tellurium.[261] It has the advantages of reacting more rapidly than the zinc-hydrochloric acid system and of causing low arsenic blanks. It does not, however, extend the method to the determination of either silicon or lead, which do not absorb although they are in the same group of the periodic table as germanium,[260] or to the determination of gallium.[261] The concentration of hydrochloric acid in the reaction mixture with sodium borohydride has a large effect upon the sensitivity of the Sn determination, which is only about 1/5 as large in 2 *M* as in 0.5 *M* acid. Of the remaining 6 elements, selenium and germanium are somewhat affected by the concentration of hydrochloric acid over the range from 1 to 6 *M*, while bismuth, antimony, tellurium, and arsenic remain essentially unaffected.[261] Some reported detection limits are indicated in Table 12.[260]

In the automated technique for the determination of antimony, arsenic, and selenium in water,[253] arsenic and selenium were determined simultaneously by means of a dual-channel atomic absorption spectrophotometer, while somewhat different conditions proved to be optimal for the determination of antimony. The automated apparatus can analyze up to 40 samples per hour.

3. Advantages of the Hydride Evolution Method

Introduction of the sample into the flame in the form of the hydride of the element of interest offers several advantages over the conventional pneumatic solution aspiration method. Firstly, the separation process inherent in the evolution step serves to eliminate practically all matrix effects by leaving the matrix materials behind in the reaction vessel. Secondly, a very efficient use is made of the sample because the entire amount of the element of interest present in the sample reaches the flame in a form very suitable for efficient atomization, whereas with pneumatic nebulization a large fraction of the aspirated solution is wasted because of the formation of large droplets. Thirdly, the method allows a sensitivity improvement by factors from 50 to 200. Whereas aspirating a solution into the flame maintains a constant signal which lasts during the period of aspiration, introducing the hydride into the flame all at once, as a pulse, yields a much more intense, though briefer, signal.

Several disadvantages of the technique can also be mentioned. It is, of course, more complex than direct aspiration into the flame. The sudden introduction into the flame of large quantities of hydrogen, which is evolved along with the hydrides, causes a change in the background absorption in several wavelength regions, making the use of background correctors helpful. Finally, hydride evolution has been applied with success only to seven elements, and is not likely to be applicable to many others.

Chemical evolution of the element of interest from the sample in the form of a gaseous compound need not be limited to the evolution of hydrides. For instance, sulfur has been determined by chemical evolution of sulfur dioxide,[262] which flowed through an unheated absorption tube and whose molecular absorption was measured employing a continuous excitation source.

B. Cold Vapor Technique for Mercury

1. Development of the Method

a. Open-ended Mercury Evolution System

While investigating means of improving the limited sensitivity to mercury of the conventional flame atomic absorption, Poluektov and coworkers[242] noted a significant increase in absorption upon addition of stannous chloride to the sample solution. Further work showed that nebulization alone, with the flame extinguished, generated appreciable atomic absorption by mercury vapor (after correction for background absorption and for scattering by the aerosol droplets). These

TABLE 12

Detection Limits for the Hydride Evolution Technique*

Element	Detection limit, μg†	Detection limit in solution, ppm
As	0.001	0.00008
Bi	0.003	0.0002
Ge	0.05	0.004
Sb	0.004	0.0003
Se	0.002	0.0001
Sn§	0.004	0.0002
Te	0.004	0.0003

*Ge and Sn by $NaBH_4$ method, the rest by $TiCl_3$-Mg method. Rounded off to 1 significant figure.

†Detection limits are based on 15-ml sample volumes.

§From Reference 261.

(From Pollock, E. N. and West, S. J., *A.A. Newsletter,* 12, 6 (1973). With permission.)

observations led to the formulation of the cold vapor evolution technique for mercury. The apparatus used by Poluektov[242] and by many later researchers is essentially similar to the set-up schematically illustrated in Figure 32.

The carrier gas, such as air, nitrogen, or argon, enters the reaction flask through a gas dispersion tube. The dispersion tube is immersed in the reducing solution of stannous chloride. The carrier gas next flows through a water trap, then through a tube filled with a dessicant such as anhydrous magnesium perchlorate, and finally through a quartz-ended glass absorption tube. The addition of a two-way stopcock at the start of the train allows bypassing the reaction flask. After establishing a baseline on the recorder with only the carrier gas flowing through the absorption cell, the Hg-containing sample is introduced and, after an interval of about 2 min or less, the gas is directed through the reaction flask. A convenient way of introducing the sample quickly and accurately is by injecting it with a syringe through a septum on a side arm of the reaction flask. Mercury is reduced to the metallic state and due to its great volatility is rapidly carried through the absorption cell by the carrier gas. The absorption of the 253.7-nm line from the hollow cathode lamp may be recorded against time, resulting in a typical curve illustrated in Figure 33. The exact shape of the curve and the length of time required to purge the system sufficiently are clearly determined by the rate of flow of the carrier gas. Lower gas rates allow an increase in recorded peak height due to lowered dilution of the mercury vapor, but they also require an increased waiting period between sample injections. Analysis is completed by measuring peak heights above the baseline and comparing them with a calibration curve of peak heights plotted against weight of mercury injected.

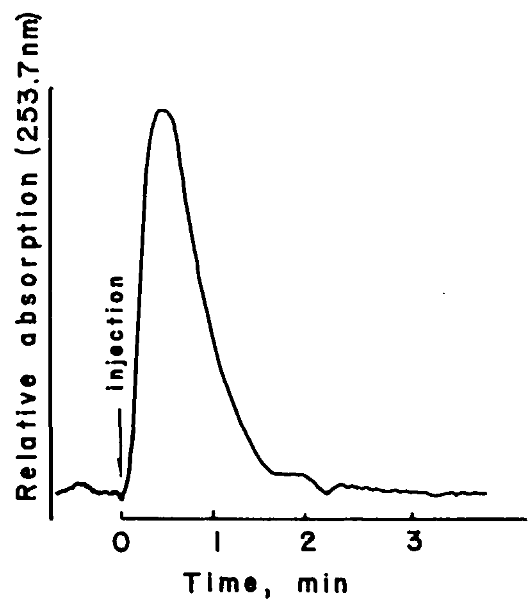


FIGURE 33. Absorption signal of the chemically evolved mercury as a function of time. Injected: 4 ml of a solution of 10 ppb of mercury. Air flow rate: 2.2 l min.$^{-1}$

Although the peak is observed to be directly proportional to the total weight of mercury as long as low amounts are involved, the sensitivity of analysis can be slightly affected by the volume of the injected sample. Several workers found that with sample volumes larger than a few cubic centimeters, the absorption signal for a constant amount of mercury decreases with increasing volume.[263,264] Raising the concentration of the reducing solution does not eliminate this effect.[263]

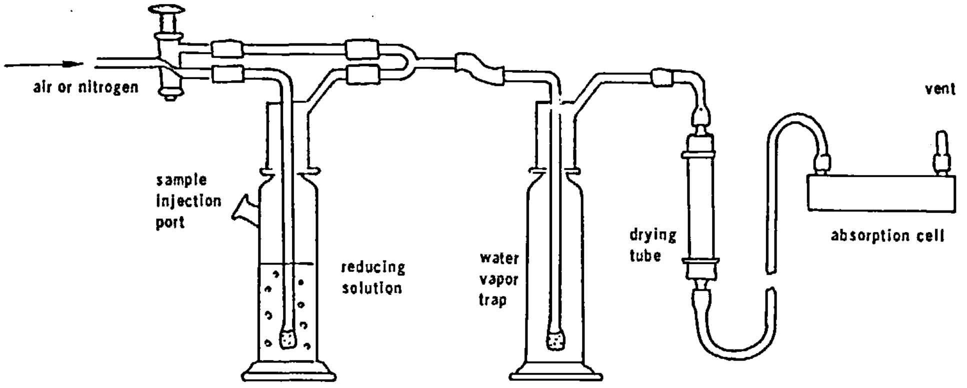


FIGURE 32. Apparatus for cold vapor atomic absorption determination of mercury.

Essentially the same apparatus has also been used with several modifications. The internal volume of the train was reduced and the purging efficiency of the carrier gas was improved by designing a reaction vessel which is basically a Pyrex Büchner-type funnel with a fine frit.[264] Carrier gas enters through the bottom of the funnel. Sample and reductant are introduced through ports in a rubber stopper fitted tightly at the top of the funnel. The carrier gas is vented through a third port in the stopper and flows through a drying tube and the absorption cell. The substitution for the entire bottom of the reaction vessel of a large fritted-glass gas disperser and the decrease of the internal volume lower the extent of dilution of the mercury vapor and improve sensitivity. The removal from this system of 25 μg of mercury, contained in a 10-cm^3 sample, is complete after about 40 s of purging with a nitrogen flow rate of 6 cm^3 s^{-1}.[264]

An automated version of the equipment has been described, capable of testing 22 samples per hour. When applied to the concentration range of 0.001 to 0.01 ppm, a reproducibility study resulted in a relative standard deviation ranging from 7.6% at the 2-ppb level to 1.6% at the 8-ppb level.[265]

b. Cyclic Mercury Evolution System

Whereas the above procedure employs an open-ended system, with the mercury vapor being vented into the hood after passage through the absorption cell, the apparatus described by Hatch and Ott,[266] and adopted by many workers, represents a closed system where the vapor is cycled between the reaction flask and the absorption cell until a steady maximum absorption value is obtained. With a given internal volume of the system, it takes approximately 3 min for maximum absorption by the 1.1 μg of mercury injected to be reached at a circulation rate of about 2 l min^{-1}.[266] When an equilibrium value of absorbance is reached, only a part of the mercury present in the system is found in the vapor state, the exact proportion being dependent on the internal volume of the system and the volume of the reaction mixture. Evaluation of results can be based on the absorbance values exhibited during the first equilibrium,[266-268] or absorbance values of several successive equilibrations with the same sample may be summed.[269] In the latter case, the generated vapor is expelled from the system after each cycling period and equilibrations are continued until no more mercury can be evolved. The extra time spent in carrying out successive equilibrations does not seem to be justified by small gains in sensitivity. The method is considerably less rapid than the open-ended system.

c. Detection Limits

Reported detection limits for mercury have ranged from a few tenths of a nanogram to about 10 ng.[242,264,266,269-272] The cold vapor evolution method for mercury is eminently suited to measurement by atomic fluorescence[267,272-274] and offers equally good detectability.

d. Interferences

The cold vapor evolution method for Hg is essentially free from interference by common inorganic species, as long as large amounts of reducible species are absent. Among anions, while chloride and bromide have no effect on the evolution of mercury from the stannous chloride medium, iodide, present at a concentration of 10 ppm, suppressed the mercury signal by as much as 70%.[263] The substitution of hydrazine hydrate for stannous chloride as the reductant eliminated this interference.[263]

Broad band non-atomic absorption is occasionally a source of interference in the cold vapor atomic absorption method for mercury, similar to the non-atomic background absorption often observed with other flameless methods, such as the heated graphite-tube atomizer. When the mercury vapor generated from the sample is carried directly into the absorption cell, the possibility that traces of some volatile organic compound may also be evolved cannot be disregarded with some types of samples. Absorption of the analytical mercury 253.7-nm line by such vapors would cause an erroneously high reading for mercury, a problem which obviously cannot be solved by employing a double-beam instrument because both the desirable and undesirable absorptions affect only the sample beam. The problem of broad band absorption interference was recognized early[43] and several methods for alleviating it have been suggested. A blank containing the same matrix may be used, but is inconvenient because a thorough knowledge of the nature of the sample is necessary. The amalgamation step of isolating evolved mercury vapor on gold or silver prior to analysis is effective but increases the overall time of analysis.

A correction for nonspecific absorption may be made by measuring absorbance at a nearby wavelength where mercury does not absorb but where any molecular absorption would still be present. An iron line at 253.7 nm is convenient for this purpose, as is the hydrogen continuum lamp, but in either case the need for changing lamps can more than double the time of analysis on some instruments.

One good method of correcting for background absorption involves incorporation into the instrument of a continuum source,[43,263,275] the radiation from which travels the same path as the analytical beam from the mercury lamp. Electronic comparison of the two signals allows the reading out of only truly atomic absorption. Such background correctors are widely used in other non-flame methods.

Another means of background correction, applicable specifically to the cold vapor mercury analysis, can be constructed easily and quickly in the laboratory.[276] Into the closed system, where the vapor is cycled between the reaction flask and the absorption cell, is introduced a two-way stopcock, shown in Figure 34. Into one arm of the stopcock is placed a plug of glass wool dipped in a 1% solution of palladium (II) chloride. During operation, the absorbance is first measured with vapors cycling through the bypass position of the stopcock. Then the stopcock is turned to send the vapors through the palladous chloride plug, which stops all the mercury vapor very selectively while allowing any interfering volatile species present to continue to exhibit absorbance. Subtraction of the signals yields the true value of mercury absorbance. The removal of mercury takes about 1 min, depending on the amount of mercury present and on the rate of pumping.[276]

2. Sample Preparation

Preparation of many types of samples for the cold vapor mercury analysis involves pretreatment which breaks down organomercury complexes and releases all the mercury in the form of mercuric or mercurous ions. The sample may then be kept in the solution form until analysis time, when it is treated with a reducing agent and the evolved mercury vapor is swept directly into the path of absorption by a flow of the carrier gas. Or, the evolved mercury vapor may be carried over an amalgamator where mercury is quantitatively collected, and subsequently released by heating at the time of analysis.

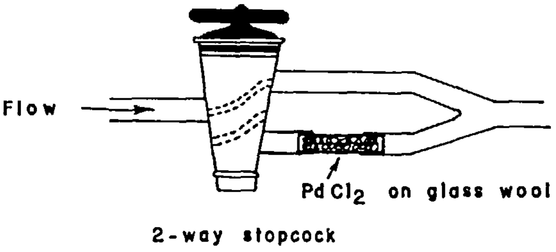


FIGURE 34. Palladium chloride absorber for mercury. (Reprinted with permission from Windham, R. L., *Anal. Chem.*, 44, 1334(1972). Copyright by the American Chemical Society.)

Samples containing organic compounds are usually first decomposed by digestion in an oxidizing acidic environment. In addition to the commonly used treatments with nitric, hydrochloric, and sulfuric acids, potassium permanganate, and hydrogen peroxide, the following digestion methods have also been used in the cold vapor technique. Soils were decomposed without heating by treatment with acid and potassium persulfate,[268] or by the combined action of permanganate and persulfate.[267] Water samples were treated with potassium persulfate and phosphoric acid.[277] Samples of many organic materials were oxidized at room temperature with chromic acid, alone or combined with red fuming nitric acid.[278] Coal was combusted and the products caught in an acidic, strongly oxidizing solution.[279,280] Aqueous solutions containing organomercury compounds were oxidized by bubbling through them a stream of oxygen mixed with ozone.[281] The investigators of the latter approach did not claim complete destruction of organic matter by the ozonization procedure and emphasized the need for a strong and rapidly acting reducing agent to free the mercury. For a series of organomercury compounds, treatment with ozone followed by reduction with sodium borohydride was found to be very effective.

Several workers[282,283] have described a preconcentration step in the preparation of sea-water samples for analysis. A large sample of sea-water is reduced with stannous chloride and aerated into a small volume of an absorbing solution that contains permanganate and sulfuric acid. The latter is then reduced to release the absorbed mercury.

Collection of mercury by amalgamation on silver prior to a flameless atomic absorption or atomic fluorescence finish has been successfully employed by several investigators.[272,284-289] The amalgamator is presented for reaction in the form of silver foil, wire, screen, or wool. Gold amalgamators have also been found effective.[271,280,286,290,291] Although chemical digestion followed by reduction is quite adequate,[272,287] the simplest procedure for treating the sample in preparation for collection of mercury by amalgamation is combustion in a furnace or in a combustion flask.[271,272,288] Products of combustion in a furnace, of samples like wheat flour,[272] were carried by argon through a 180-mm long silica tube packed with a Ag wire. Products of combustion in a combustion flask of some biological samples[288] were dissolved in dilute HCl and mercury was extracted 'from solution by amalgamation on a Ag wire. When air is being tested for mercury,[289] it can be drawn directly through a plug of silver wool. By employing 24-hr sampling periods, mercury concentrations in air in the range of 15 ng m^{-3} to 10 μg m^{-3} have been determined.[289] Soils have been shown to release mercury vapor upon heating;[286,291] however, low results may be expected due to the presence of volatile organomercury compounds.[291]

Relatively low temperatures suffice for the quantitative release of collected mercury from the amalgamator. While at 80°C only 1 to 2% of mercury is released, at and above 260°C the release from a silver collector approaches 100% completeness.[289]

Materials other than gold and silver have been employed for the collection of mercury prior to the measurement step. Asbestos pads impregnated with cadmium sulfide presented one alternative.[271] Amalgamation on a copper wire has also been reported.[292] Both organic and inorganic forms of mercury can be determined in an environmental water sample by electrolyzing an aliquot of the sample between a copper-coil cathode and a platinum-wire anode.[293,294] Electrolysis for 90 min was required for the quantitative deposition of 50 ng of Hg from a 50-cm^3 sample.[294] Mercury was separated from a sample of fish, after digestion with nitric acid at an elevated temperature and pressure, by electrolysis with two platinum electrodes.[270] For analysis, mercury was released from the cathode as a vapor by subjecting the electrodes to a potential difference of 6 V.[270] Mercury in air is determined following filtration of known volumes through fine filters. One technique[295] involves filtration of air through activated charcoal contained in a Vycor tube. After sampling, the tube is sealed until it is ready to be placed into the analytical train in the laboratory. Then the charcoal is heated, mercury compounds are released and decomposed by heat, and mercury vapor is collected by amalgamation on silver. The analysis is completed by subjecting the amalgamator to a temperature of 300°C to release mercury. The precision of the technique is reflected in a relative standard deviation of 2.6%, and accuracy of the determination allows a recovery of at least 95% of mercury from synthetic atmospheric samples in the range of 0.15 to 1.5 μg m^{-3}..

There are clear advantages in amalgamating or plating out mercury on a collector rather than leaving it in a solution until the analysis is performed. Solutions tend to deteriorate by adsorption on container walls, by volatilization, and by desorption of contaminants from container walls. Even though such problems are minimized through scrupulous care, greater effort than with the preservation of the solid amalgam is required from the operator. Furthermore, the amalgamation step tends to improve sensitivity by allowing all of the mercury to enter the absorption cell essentially simultaneously upon a rapid application of heat to the collector. And most important, amalgamation represents a reliable separation of mercury from any potential volatile interferents capable of causing broad band absorption at the analytical line.

Whereas only heating is required to release mercury from an amalgam, a strong reducing agent is needed to evolve mercury from an oxidizing digestion medium. Stannous chloride, the reductant used by Poluektov in the original procedure,[242] is usually still used, alone or in conjunction with hydroxylamine or other reducing agents. Stannous sulfate, of course, plays an identical role.[266,278,296,297] Mixtures of stannous chloride with cadmium chloride have also been used.[298] Sodium borohydride was shown to be an effective reducing agent[281] for aqueous solutions of organomercury compounds first partially oxidized by ozone. Attempts to use ascorbic acid and araboascorbic acid as reductants for these solutions proved unsuccessful.[281]

3. Preservation of Mercury Standards

The ability to preserve mercury solutions at concentration levels of 10 ppb and lower is important in order to properly preserve dilute samples such as natural waters during the interval between collection and analysis, and in order to free the operator from constantly having to prepare fresh dilutions of standards.

The instability of aqueous solutions of inorganic mercury salts is widely recognized. An untreated solution containing 50 ppb of mercury, added as mercuric chloride, in distilled water stored in a polyethylene container loses 20% of its strength within the first hour and 90% of its strength after 2 days.[299] Attempts to stabilize such solutions have resulted in several somewhat conflicting reports in recent literature. The use of acidic potassium permanganate as a preservative has been suggested by some investigators,[300,301] while others found nitric acid to be the only effective preservative.[299,302] The choice of the former preservative is rather surprising in view of the limited stability of acidic permanganate and the danger of precipitation of manganese dioxide. Preservation with hydrochloric acid, sulfuric acid, or phosphoric acid, or with a mixture of acetic acid and formaldehyde was found to be quite ineffective.[299] Acidification with nitric acid down to pH 0.5 was observed to prevent any loss of mercury from a solution containing 25 ppb of mercury for a period of about 5 days, and the loss was less than 2% after 16 days of storage.[302] In addition, it was observed that acid had to be present in the container before water and mercury were added; when the acid was added last, the rate of loss was significantly increased.[299] A comparison of the suitability of polyethylene, polyvinyl chloride, and glass containers revealed that the loss of mercury was much more rapid from solutions stored in polyvinyl chloride,[302] while glass appeared to be either slightly[302] or significantly[303] superior to polyethylene.

Good stability of solutions containing from 0.1 to 10 ppb of mercury was provided by 5% (v/v) nitric acid plus 0.01% dichromate.[303] These solutions remained at full strength for as long as 5 months when stored in glass containers. Storing them in polyethylene containers required that the dichromate content be increased to 0.05%, which made them stable for at least 10 days. The same investigator[303] found that there were substantial losses of mercury during the first 10 days from solutions preserved with nitric acid, with sulfuric acid and potassium permanganate, or with potassium dichromate alone.

Thus, the most reliable method of stabilizing solutions of dilute mercury standards and samples seems to be treatment with nitric acid and potassium dichromate and storage in glass containers.

Dry gelatin spiked with known amounts of mercury presents a feasible method for preserving mercury for flameless atomic spectrometry standards.[304] It is especially attractive as a reference material in determining mercury in biological materials because of the relatively similar nature of the matrix. A portion of such a reference material can be prepared for analysis by any of the methods discussed earlier for the preparation of unknown samples. It can be combusted and the mercury vapor can be collected on an amalgamator for subsequent release by heating. Or it can be digested with hot concentrated nitric acid for subsequent evolution of mercury vapor by treatment with a reducing agent. Digestion breaks down the amino acids in gelatin which chelate mercury and which would otherwise prevent quantitative reduction. Gelatin spiked with mercuric sulfate to contain 2 ppm of mercury was shown to yield constant mercury values for over a year.[304]

4. Applications

The very good sensitivity offered by the cold vapor technique has allowed a rapid and accurate determination of trace levels of mercury in a wide variety of materials which previously often required lengthy pretreatment and concentration steps. The technique has been applied to the analysis of fish[263,265,270,271,278,296,305-307] and other foods,[269,271,305,308] of water,[263,265,267,277,284,285,287,294,301,309,310] air,[263,271,274,289,295] coal,[265,271,279,280,311] rocks, soils, and sediments.[266-268,274,287,291,312-314] Also analyzed by the cold vapor technique have been urine, plasma and other biological materials,[263,265,270,271,278,288,298,308,315-317] vegetation,[278] wood,[271] pulp and paperboard,[318] standard reference materials,[319] metals,[266] and other substances.

The several papers referred to in this section are far from representing a complete list of the applications of the cold vapor technique for mercury which have appeared in the literature since Poluektov[242] and Hatch and Ott[266] described the technique several years ago. The popularity of this technique is not surprising in view of the fractional nanogram detection limits, the relative freedom from interferences, and the very easy adaptability to any available atomic absorption instrument at very small additional cost.

VI. ADDITIONAL MODIFIED METHODS OF SAMPLE INTRODUCTION INTO THE FLAME

A. Modulated Injection

In the modulated injection technique, the sample enters the flame at periodic intervals and the analytical signal is obtained at the modulation frequency. Modulation of sample aspiration into the flame was described in several papers a few years ago.[320-323] The researchers observed a considerable suppression of the flame background emission signal, but rather small improvements in detection limits.[322,323] Recent reports have described novel modulation approaches which allow larger gains in detection limits[324-326] by suppression of low frequency noise components.

Marinkovic and others[324,325] employed a modulation device illustrated in Figure 35a. The aerosols of the sample solution and the pure solvent, generated by two separate nebulizers, enter the flame through two channels. The sample solution is aspirated continuously, but the flow of the solvent aerosol is interrupted by a rotating disk. When the disk obstructs the solvent aerosol flow, only the sample reaches the flame. When the disk does not shut off the solvent flow, the paths of the two aerosols are deflected, as illustrated in Figure 35a. As a result, only the solvent aerosol reaches the flame. The rate of flow of gas has to be carefully adjusted to allow the desired deflection of the aerosol streams. Modulation frequencies of 70 Hz[324] and 40 Hz[325] were used.

The significant improvement which this device offers over the modulation methods employed by the earlier workers is in the use of two separate nebulizers to supply the aerosols alternately to the flame. When a single aerosol flow is modulated, the alternating presence and absence of the solvent in the flame causes fluctuation of the flame temperature. Some researchers have attempted to eliminate this background modulation by using an organic solvent,[322] but found this approach inadequate, and used, in addition, a phase-lock amplifier which was controlled by the emission intensity of an internal standard line. Using two nebulizers allows a constant amount of solvent to be present in the flame at all times, and thus allows effective suppression of noise and background emission.

An improved design of the modulation system was described by Bojovic and Antic-Jovanovic,[326] and is illustrated in Figure 35b. In this version, both aerosol streams are alternately interrupted by one chopper with four slots. A 70-Hz chopping frequency is used. The design of the chopping disk

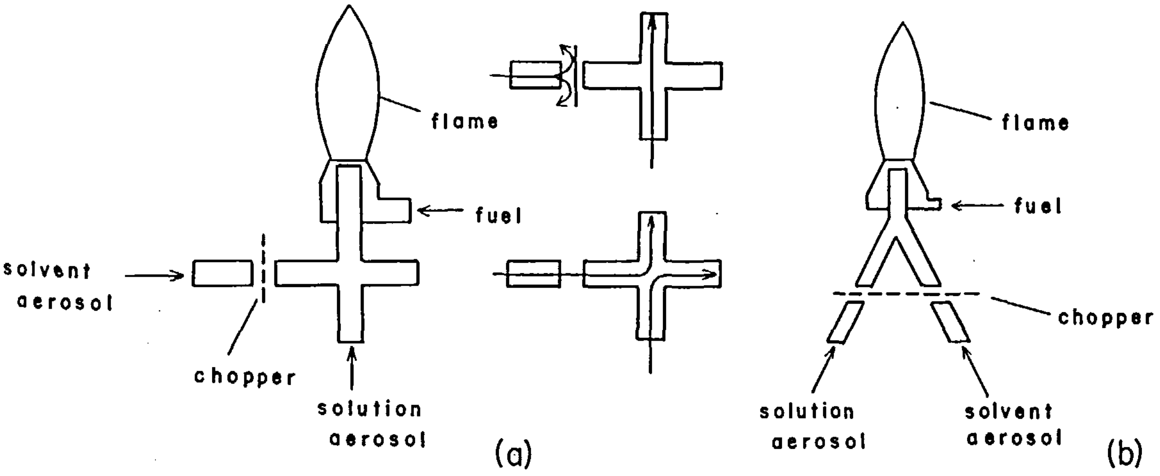


FIGURE 35. Devices for modulation of the aerosol. (a) One aerosol stream is chopped. (From Antic-Jovanovic, A., Bojovic, V., and Marinkovic, M., *Spectrochim. Acta,* 25B, 405(1970), Pergamon Press. With permission.) (b) Both aerosol streams are chopped. (From Bojovic, V. and Antic-Jovanovic, A., *Anal. Chim. Acta,* 27B, 385(1972). With permission.)

is such that a constant total quantity of aerosol enters the flame, although, at different instants of time, the solvent alone, the sample alone, or different proportions of the two aerosols are actually reaching the flame. The amplifier is tuned to the chopper frequency. Line-to-background intensity ratios and detection limits attained with the two modulation systems are similar, but the performance of the device in which both aerosol streams are chopped is independent of the gas flow rate. The gas flow rate may be varied to adjust the rate of sample consumption and to optimize flame conditions, which cannot be done with the original design.

The results in Table 13, where modulated injection is contrasted with continuous injection (with light chopping), indicate a considerable increase of the line-to-background emission intensity for the several lines tested. The desirable effect on the appearance of a typical atomic emission spectrum is also illustrated in Figure 36. The strong OH-band emission of the oxygen-hydrogen flame in the vicinity of the 285.2 nm Mg line is effectively eliminated. The relative intensities of the lines are the same with continuous and modulated sample supply. But improvements in the detection limits are in the vicinity of the factor of 20. The fact that the improvement in detectability is smaller than that in the line-to-background ratio is attributed to the noise spectrum of the flame emission.[325]

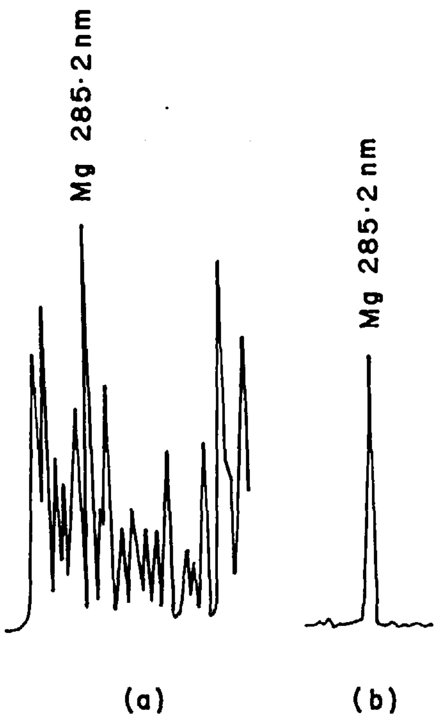


FIGURE 36. Flame emission spectrum in the vicinity of the 285.2-nm line of magnesium. (a) Steady supply of aerosol. (b) Modulated supply of aerosol. (From Bojovic, V. and Antic-Jovanovic, A., *Spectrochim. Acta,* 27B, 385(1972), Pergamon Press. With permission.)

Mossotti et al.[327] described the design and performance of two modulation devices for flame emission and atomic absorption. The techniques use a piezoelectrically induced deformation of one or two solution streams entering the nebulizer. The solution flow to the flame is modulated in such a manner that the alternating signal produced by the modulation is almost independent of the net constant rate of uptake of solution. In the dual-channel technique, the alternating component in the flame spectrum reflects the differences of composition between the sample and the blank solutions.

Hieftje and Malmstadt[328,329] described a system of sample injection which introduces isolated droplets of sample solution into the flame. The system was originally devised for the purpose of studying the sequence of events that take place when a droplet of solution travels through the flame. Studies included the desolvation and vaporization processes and chemical and spectral interferences.[328] The droplet generator used by these workers is illustrated in Figure 37. The droplets are generated by forcing a jet of liquid from a capillary which is mechanically vibrated by a bimorph electromechanical transducer. The size of the droplets can be varied from 10 to 200 μm and is determined by the vibration frequency and the diameter of the capillary. The frequency of droplet introduction may be varied from 0.1 to 2 X 10^5 s^{-1}. The variation of frequency over this wide range is achieved by a periodic application of a negative pulse of 350 V to an auxiliary pulsing electrode. This pulse results in the detachment from the capillary of a droplet which is positively charged. When this droplet passes between two highly charged deflection plates, it is deflected and becomes directed into the flame, while the remaining undeflected droplets strike a stream trap and are eliminated from the system.[328] The trajectory of the droplets in the flame is very reproducible and is controlled by a micromanipulator which allows three-dimensional positioning.[329]

TABLE 13

Effect of Aerosol Modulation on Line-to-Background Ratios and Detection Limits

Element	Wavelength, nm	Concentration, ppm	Line-to-Background ratio		Improvement factor	Detection limit,† ppm		Improvement† factor
			Continuous	Modulated		Continuous	Modulated	
Mg	285.2	100	2.4	210	88	5	0.3	20
Ni	305.1	100	4	96	24	9	0.8	10
Cu	324.7	50	2	64	32	5	0.3	20
Sr	460.8	5	1.8	92	51	0.2	0.008	20
CaOH	625.0	5	1.2	58	48	0.2	0.008	20
Li	670.8	1	1.2	66	55	0.02	0.0006	30
Sr*	460.8	2	1.6	88	55	0.2	0.008	20
CaOH*	625.0	2	2	125	62	0.3	0.01	30
Li*	670.8	1	3.8	205	54	0.01	0.0006	20

*These results are for an air-hydrogen flame. The rest are for an oxygen-acetylene flame.

†Detection limits and corresponding improvement factors are rounded off to 1 significant figure.

(From Bojovic, V. and Antic-Jovanovic, A., *Spectrochim. Acta*, 27B, 385 (1972), Pergamon Press, With permission.)

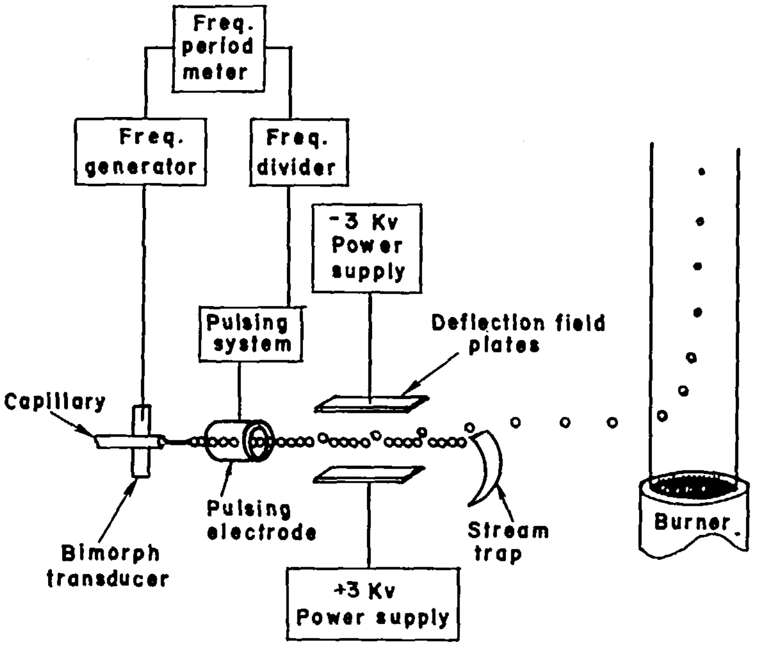


FIGURE 37. System for introducing isolated droplets into the flame. (Reprinted with permission from Hieftje, G. M. and Malmstadt, H. V., *Anal. Chem.*, 40, 1863(1968). Copyright by the American Chemical Society.)

When the isolated droplet enters the flame, the solvent evaporates and solute particles become vaporized very efficiently in a small and well-defined region of the flame, producing a concentrated cloud of atomic vapor in a small volume. Only this very small region of the flame is viewed by the instrument, which has the effect of significantly reducing the flame background. At a known point in the flame, the efficiency of desolvation is essentially unity, and with the sample introduced at a constant rate, the degree of vaporization at a given height in the flame is very reproducible. The relative standard deviation of flame emission signals from isolated droplets over periods of time of several hours in only 0.17%. In addition to good stability and precision, the sensitivity of the technique compares favorably with conventional pneumatic aspiration. The relative detection limits for calcium and sodium improve by a factor of 5, and the absolute detection limits for the isolated droplet technique are 7×10^{-16} g for Na and 3×10^{-14} g for Ca. The applicability of the technique was illustrated by a flame emission determination of sodium and calcium in serum samples without any sample pretreatment other than dilution.

Aside from emission, the technique is also applicable to atomic absorption and especially atomic fluorescence.[329] Since the atomic vapor is present in a small volume in the flame, the exciting beam must be focused on this small area in order to prevent illumination of large areas around the atomic vapor, which would only serve to increase the background, increase noise, and bend the calibration curves in atomic absorption. In atomic fluorescence, on the other hand, if the source is not focused on just the analytical point of the flame, no disadvantages result because the exciting beam is not viewed by the detector.

The droplet-generating equipment was used[330] to describe a "null-point" technique for flame spectrometric analysis. To achieve the "null," the rate of introduction of droplets of the standard is varied until a signal having the same intensity as that for the sample is obtained. It is assumed that at the "null-point," the number of atoms of interest present in the flame is the same for standard and sample. The simple application of the relationship $f_{sample} \times C_{sample} = f_{standard} \times C_{standard}$, where f denotes the rate of introduction of droplets and C denotes the concentration of the solution specified by the subscript, enables the analyst to calculate the concentration of the unknown.

The advantages of this technique can be considered to include the following. A range of sample concentrations can be matched with a single standard merely by changing the rate of droplet introduction slightly. Since at the "null-point" the atomic concentrations in the flame are the same for both the sample and the standard, the effect of any nonlinearities in the optical and electronic read-out systems is somewhat minimized. The technique lends itself to automation.[330] However, the technique requires rather involved instrumentation and promises little usefulness for practical analysis.

At high concentrations the accuracy of the technique becomes limited by self-absorption, just as in the conventional flame methods. At high rates of droplet introduction, overlap of atomic vapor clouds may occur and lead to inaccuracy.[330] When applied to the determination of calcium and sodium in blood, the precision was good, the relative standard deviation being less than 1% for calcium at a concentration of 100 ppm and approximately 0.1% for sodium at a concentration of 3,200 ppm.

B. Controlled Injection into the Aspiration System

Rohleder et al.[331] optimized burner operation by force-feeding solutions to the total consumption burner by means of a piston pump.

Jones[332] described the following aspiration system. A solution is force-fed into the premix chamber of the burner by means of a motor-driven infusion pump. By varying the infusion rate, a calibration curve relating the signal to the calculated "dynamic concentration" is prepared by using a single standard solution. The sample is then fed at such a rate as to put its signal in the range of the curve. To eliminate the variation in the total amount of liquid entering the chamber at different feed rates, a T-connection is used, where a diluent, such as water, is mixed with the force-fed sample to assure a natural constant aspiration rate by the capillary. The obvious advantage of the technique is in the time saved by not having to make up series of standard concentrations or to dilute the unknown appropriately. The results indicate the same precision and accuracy as those obtained by conventional nebulization.

Sarbeck et al.[333] combined the idea of injecting the sample into the aspirated stream with the principle of pulsed introduction of discrete sample aliquots into the flame. The capillary of the total consumption burner was connected to an elevated reservoir of the carrier liquid, such as water, which caused a continuous flow of the blank into the flame. The discrete aliquots of the sample were injected into the flow of the blank by means of a microliter syringe. The momentary increase in the total flow rate during injection of the sample was eliminated by placing a constriction between the injection port and the burner capillary. Essentially, the sample was injected as a small plug of constant concentration, but it became diluted by mixing with the carrier liquid as it traveled to the flame. As a result, the atomic emission, absorption, or fluorescence signal recorded as a function of time emerged as a sharp peak followed by exponential tailing. When samples of different volume were injected, the duration of injection necessarily changed, and thus the shape of the signal peak became affected. This necessitated measurement of peak areas rather than peak heights in evaluating the signals. The limits of detection offered by this technique were about 100 times worse than those obtained with similar instrumentation but with conventional sample aspiration. A relative standard deviation of only 2.2% was obtained by flame emission when successive 2-μl aliquots of solution containing 40 ppm of potassium were injected, and that was primarily determined by the precision of the microliter syringe. The technique requires only small volumes of sample solution and is potentially amenable to automation,[333] but its lack of sensitivity is a serious drawback.

C. Heated Nebulizer Chamber

The improvement of vaporization efficiency due to heating the walls or interior of the nebulization chamber has been recognized for a long time and has been discussed in the literature.[334-337]

Heating can be achieved by an electric heating coil, by infrared radiation, or by high-frequency energy. Although vaporization efficiency is increased by heating, the technique presents several disadvantages.[337] The forced vaporization of the large droplets results in an increased concentration of analyte reaching the flame, but with lesser uniformity than with the nonheated chamber. Also, more solvent enters the flame, which may adversely affect the temperature of the flame. Since nebulization is not carried on continuously, a temperature variation in the nebulization chamber is present following the stop of nebulization and following the start of nebulization, and may lead to poor reproducibility of the analytical signal. The introduction of larger solute particles into the flame may increase the seriousness of some interference effects.[337]

Many heated nebulizers include a condenser.[334,335,338,339] A cooled surface is imposed in the path of the vapor and serves to condense a significant portion of the solvent vapor, while essentially all of the solute particles go into the flame. This approach reduces noise and improves sensitivity. Venghiattis[334] reported that both the sensitivity and the limit of detection were improved by about an order of magnitude for each of the 12 elements tested. Uny et al.[339] described a heated nebulizer, including a condenser, for which sensitivity and detection limit improvements of 10 to 30 times were possible and for which absence of increased noise was claimed.

D. Direct Injection of Solids

1. Continuous Introduction

Although the usual practice with solid samples is to put them into solution for aspiration into the conventional aspirator-burner, the preliminary decomposition, ashing, and dissolution steps tend to be the most time-consuming steps of the total analysis. Several methods for direct sampling of solid materials for direct introduction into the flame have been devised. Gilbert,[340] for instance, suspended finely ground soil in 50:50 isopropanol-glycerol for aspiration into a total consumption burner and determined 10 elements by flame emission spectrometry. The early work in direct introduction of solid samples into flames has been reviewed elsewhere.[341] Since then, several interesting systems have been reported. Shipitsyn et al.[342] placed powdered sample into a container underneath the burner. The metal bottom of the container was struck by a pulsating hammer, which sent the sample powder into the burner through a small orifice in the top of the container. The technique was applied to the determination of potassium in solids. Panichev and Turkin[343] subjected powdered samples to ultrasonic vibrations, which caused particles to be detached from the surface and carried by a stream of oxygen into the flame.

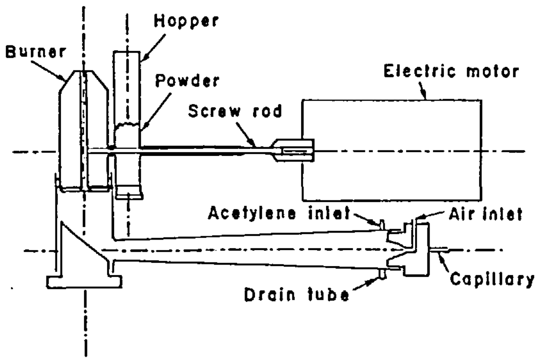


FIGURE 38. Cross-section of burner and feeding device for powders. (Reprinted with permission from Coudert, M. A. and Vergnaud, J. M., *Anal. Chem.*, 42, 1303(1970). Copyright by the American Chemical Society.)

Coudert and Vergnaud[344] employed the device illustrated in Figure 38 to introduce powdered solids directly into the flame. The motor-driven screw rod fed the sample at a constant rate into the burner, from where it was carried by the gas mixture into the flame. The workers applied the technique to the determination of palladium in activated carbon, alumina, and a molecular sieve material. The sample powder was diluted by a factor of about 100 with calcium carbonate. A Pd mass flow of less than 2 μg min^{-1} was sufficient to cause 1% absorption and allowed the detection in the above materials of less than 10 ppm Pd.

Kashiki and Oshima[345] mixed solid powders with a solvent and agitated the mixture by vibration of a dispersion blade. The end of the plastic tubing attached to the aspirator of the nebulizer was immersed in the agitated mixture and a low flow of the oxidant was adequate to carry the powder into the flame. The set-up is illustrated in Figure 39. Agitation of the aspirating tube and the dispersion blade was provided by the electro-

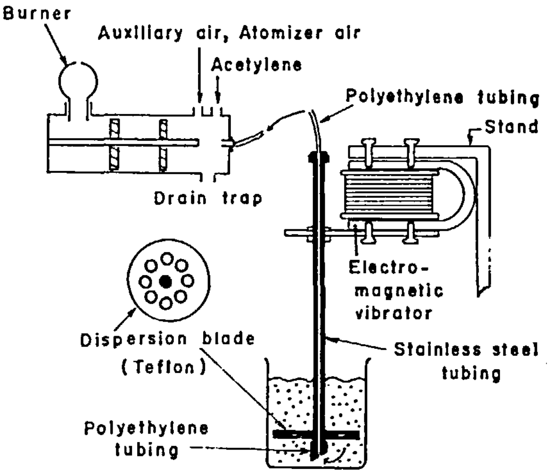


FIGURE 39. Assembly for feeding solid powders into the burner. (From Kashiki, M. and Oshima, S., *Anal. Chim. Acta*, 51, 388(1970). With permission.)

magnetic vibrator. The workers determined cobalt and molybdenum in alumina. The samples had to be ground at least to 200-mesh to assure stable and constant absorption readings. Although many solvents yielded satisfactory results, methanol was selected because of largest signal enhancement. The rate of sample introduction into the flame was controlled both by the rate of vibration and by the rate of oxidant flow.

Jones et al.[346] developed a device for solid sampling which produces metal particles in the micrometer size range directly from a solid metal sample, and Winge et al.[347] showed the applicability of the technique to flame spectrometry. The solid metal sample serves as the cathode, the end of a small copper tube serves as the anode, and a low-current DC arc is struck across the electrodes. The cathode spot moves continuously over the sample surface of a few square centimeters and allows a uniform sampling of a relatively large area. The arc discharge causes the ejection of droplets of molten metal from the sample surface. This aerosol of metal is carried by argon to the nitrous oxide-acetylene flame. The technique has been applied to chromium, manganese, and nickel in steel with satisfactory results. The approach is clearly limited to the sampling of electrically conducting sample materials.

2. Pulse Introduction

Methods of introducing solid samples directly into the flame are not limited to those relying on a continuous mode of injection and pneumatic aerosol transfer. Discrete portions of solid samples have also been subjected to flame analysis.

Venghiattis[348] mixed solid samples with a solid mixture of a fuel and an oxidizer. The burning temperature of the fuel was 3,400°K, and when small portions of the mixture were burned in the optical path of the instrument, an enhanced atomic absorption signal was observed. Pressing the mixture into a pellet and placing it within a stainless steel or graphite sheath gave more reproducible signals than burning loose powder.[349] In another technique, the metal to be determined was adsorbed from solution onto a flammable powder which was then subjected to combustion to release atomic vapor of the metal.[350]

Some of the techniques presented in Section IV.A of this review are applicable to direct introduction of discrete solid samples into the flame. Thus, the graphite microprobe[165-171] enhances the flame atomic analysis of solid as well as liquid samples. The sampling rod[172-174] introduces a mixture of powdered rock and Na_2CO_3 directly into the flame. The Delves Cup and the Ta boat could be applicable to solid sampling as well.

E. Ultrasonic Nebulization

Although pneumatic nebulization of the sample prior to or simultaneous with its arrival into the flame is by far the most common method of sample injection, ultrasonic nebulization offers a feasible alternative which is potentially as widely applicable as pneumatic nebulization and which possesses some unique characteristics. At the present time, however, ultrasonic nebulization has not become generally employed. This is due mainly to the gain of only small improvements in sensitivity and to unavailability of specially designed commercial ultrasonic nebulizer-burners.

The theory of ultrasonic nebulization, like that of pneumatic nebulization, is quite complex, and only tentative explanations of the mechanism of droplet formation have been offered. It has been suggested that under the influence of ultrasound, standing waves are formed on the surface of the liquid and that droplets break away from those areas of the surface which are bound by the nodal lines. Equations have been postulated to describe how droplet size decreases with increasing frequency of the ultrasound. Ultrasound frequencies ranging from 20 kHz to 5.4 MHz have been used in the generation of solution aerosols, but only frequencies above 500 kHz are capable of generating droplets of smaller diameter than the most frequent size of the pneumatically generated droplets.[350]

In an ultrasonic nebulizer, power is transmitted from the transducer to the sample solution by a coupling liquid with a focusing device or by a velocity transformer.[351] The former approach was employed in some of the earlier reports of ultrasonic nebulization in flame work.[352-355] These systems, however, required a relatively large volume of sample, were not as reproducible, and were less convenient for sample changing than the ultrasonic nebulizers with a velocity transformer which are fed by a continuous flow of sample into the nebulizer chamber through a capillary.[351, 356-358] Noncontinuous, or pulse, introduction of small samples has also been described recently.[359,360]

1. Continuous Operation

An ultrasonic nebulizer with a velocity transformer is illustrated in Figure 40.[351] The sample entered the nebulization chamber through a capillary tube and the sample flow rate could be controlled by varying the length of the capillary tubing or by using a peristaltic pump. No improvement in sensitivity for magnesium was observed because ultrasound frequencies of only 70 kHz and 115 kHz were used, whereas frequencies in excess of 500 kHz are needed to generate aerosols in which the diameters of the droplets are below 5 μm. A similar nebulizer has been used by other investigators.[356]

Figure 41 reproduces a diagram of a typical premix burner modified for ultrasonic nebulization by addition of a radiofrequency-powered ultrasonic crystal in a vertical position.[357] A similar set-up was used earlier by Stupar and Dawson.[358] The vertical configuration of the transducer had the advantage of being able to handle faster sample flow rates without becoming overloaded, and allowed a faster changing of samples because the preceding solution became cleared from a vertical surface much more rapidly than from a horizontal one. The performances of the unmodified pneumatic nebulizer and of the one modified for ultrasonic nebulization were contrasted for silver, cadmium, magnesium, lead, and zinc. Flame conditions were optimized separately for each element and for each nebulizer. Ultrasonic frequency was carefully controlled at 1.4 MHz. The sample feed rate was controlled at the optimum value of 3.0 ± 0.1 cm^3 min^{-1} for both the pneumatic and ultrasonic mode. Under these conditions, detection limits were improved by factors ranging from 0.7 for lead to 4 for silver. The poorer detection limit for lead is attributed not to lesser sensitivity, which actually increased, but to a poorer precision.

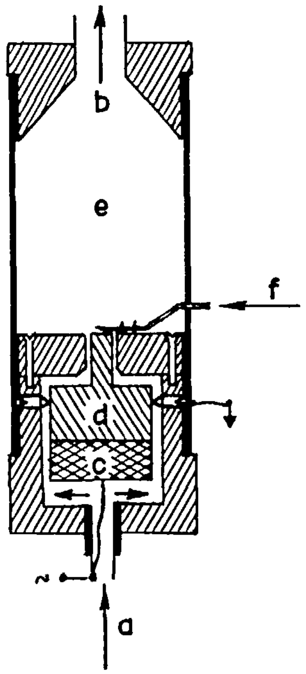


FIGURE 40. Ultrasonic nebulizer with a velocity transducer; (a) air, (b) aerosol, (c) ceramic crystal transducer, (d) velocity transformer, (e) spray chamber, (f) sample solution. (From Stupar, J. and Dawson, J. B., *Appl. Optics,* 7, 1351(1968). Copyright by the Optical Society of America. With permission.)

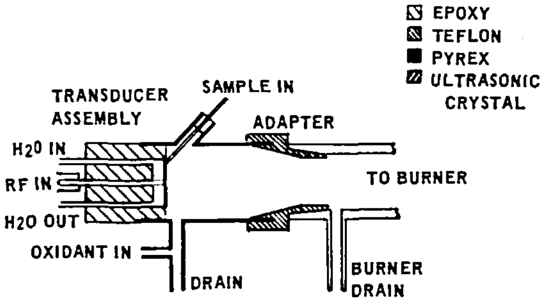


FIGURE 41. Ultrasonic nebulizer coupled with the premix burner. (Reprinted with permission from Copeland, T. R., Olson, K. W., and Skogerboe, R. K., *Anal. Chem.,* 44, 1471(1972). Copyright by the American Chemical Society.)

Ultrasonic nebulization overcomes several limitations of pneumatic nebulizers. It generates sample solution droplets of controllable and more uniform size. Thus, at ultrasonic frequencies of 3 MHz, most droplets have a diameter of 1.8 μm, at 115 kHz most are 17 μm in diameter, and at 70 kHz most are 23 μm in diameter, while with a pneumatic nebulizer droplets are generated in a wide range of diameters, with the majority of droplets having a diameter in the vicinity of 5 μm.[351] Obviously, small droplet size makes condensation less efficient, and thus causes more efficient utilization of the sample as well as more efficient vaporization and atomization. Nebulization efficiencies of typical ultrasonic and pneumatic devices were compared by Stupar and Dawson.[358] They used the same premix burner, whose aspirator and spray chamber could be converted to the ultrasonic mode, and calculated the relative efficiency by measuring the amount of sample which was passing to waste, subtracting this from the total rate of consumption of sample, and calculating what fraction of the total rate of flow of sample corresponded to the portion that was usefully consumed. To allow a valid comparison, in both modes of operation the sample was delivered to the nebulizer by means of a peristaltic pump, and flow rates of air and acetylene were held constant during the experiments. The results obtained at several sample solution delivery rates are indicated in Table 14.[358] The efficiency of sample utilization is consistently superior with the ultrasonic nebulizers. The efficiency of nebulization decreases most rapidly with increasing sample flow rate in the case of the pneumatic nebulizer. However, the ultrasonic nebulizer in which the transducer face is horizontal fails to function at sample flow rates above 1.6 cm^3 min^{-1} due to overloading of the transducer. The nebulizer in which the transducer is mounted vertically, as in Figure 40, is not subject to such a limitation because the sample solution flows over its surface instead of flooding it.

In pneumatic nebulization, the rate of sample aspiration is inextricably connected to the character of the flame because the gas flow rates required for efficient nebulization limit the range of possible flow rates and resulting flames. Ultrasonic nebulization, by contrast, is largely independent of gas flow rates and allows the operator a greater freedom in selecting optimum flame conditions for the given analysis.

2. *Pulse Operation*

In contrast to nebulizers which are fed sample solution continuously, several recent reports have dealt with the one-shot, or pulse, sample delivery for ultrasonic nebulization.[359,360] Two such systems are illustrated in Figures 42[359] and 43.[360]

Denton and Malmstadt[359] concluded that simply coupling an ultrasonic nebulizer with a conventional burner does not necessarily improve sensitivity, but a burner designed especially to accommodate low rates of flow of gas can improve sensitivity by more than an order of magnitude. The advantage of low gas flow rates is, of course, in the decreased dilution and in the longer residence of the atomic vapor in the flame. The authors designed 4 burners and compared them to the performance of the Beckman total consumption burner and the Jarrell-Ash 10-cm slot burner. The specially designed burners, operating at a rate of gas flow of 3 l min^{-1} and coupled with the ultrasonic nebulizer, improved sensitivities of copper, iron, zinc, and lead by a factor of more

TABLE 14

Variation of Nebulizer Efficiency with Sample Flow Rate

	Percent efficiency		
Flow rate, cm^3 min^{-1}	Pneumatic	Ultrasonic with transducer face horizontal	Ultrasonic with transducer face vertical
0.1	36.7	58.7	50.0
0.2	31.7	56.7	46.7
0.4	23.3	48.3	47.5
0.6	20.0	33.4	40.6
0.8	17.5	36.7	31.7
1.0	15.3	45.0	25.7
1.5	12.9	32.2	24.4
2.0	11.0	x	24.7
2.5	9.6	x	24.0
3.0	8.6	x	23.6
3.5	7.5	x	24.5
4.0	6.8	x	25.0
4.5	6.1	x	21.9

x Failure of nebulization at flow rates above 1.6 cm^3 min^{-1}.

(From Stupar, J. and Dawson, J. B., *A.A. Newsletter*, 8, 38 (1969). With permission.)

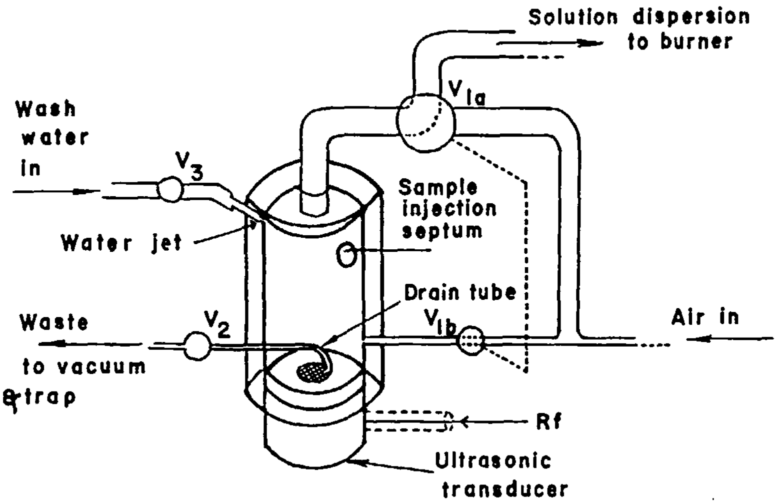


FIGURE 42. Ultrasonic nebulizer for pulse sample injection. (Reprinted with permission from Denton, M. B. and Malmstadt, H. V., *Anal. Chem.*, 44, 242(1972). Copyright by the American Chemical Society.)

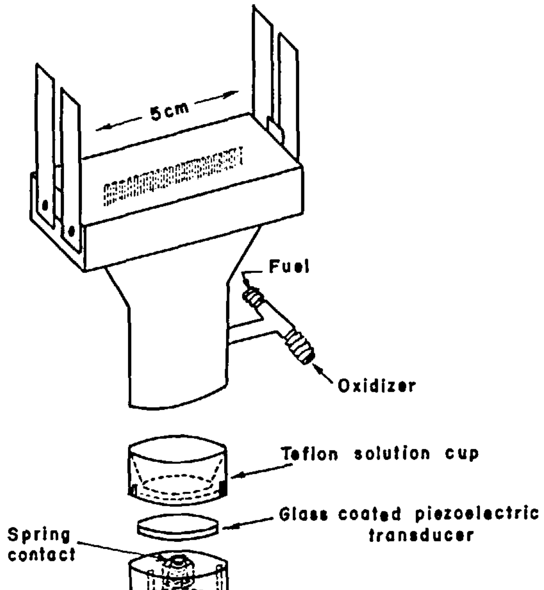


FIGURE 43. Ultrasonic nebulizer-burner with a removable sample cup. (Reprinted with permission from Korte, N. E., Moyers, J. L., and Denton, M. B., *Anal. Chem.*, 45, 530(1973). Copyright by the American Chemical Society.)

than 10. The ultrasonic nebulizer system used by Denton and Malmstadt is illustrated in Figure 42. The piezoceramic transducer is a glaze-covered barium titanate crystal having a diameter of 1 in. In order to light the flame, valve V_1 is turned to allow direct flow of air to the burner. The sample is injected through the septum by means of a 50-ml syringe. Valve V_2 is set so as to allow vapor to flow to the burner. The radiofrequency generator is switched on, and after about 15 sec, when the vapor flow to the burner comes to a constant rate, the atomic absorption signal is recorded. Between injections the power is switched off, V_1 is set for direct air flow to the burner, vacuum suction is applied through valve V_2, and valve V_3 is opened briefly several times to permit a jet of deionized water to flush out the residual sample. Two rinsings with water are sufficient in most cases, and five rinsings are used when a concentrated sample is to be followed by a very dilute one in order to avoid cross-contamination.

The system used by Korte et al.[360] is presented in Figure 43. The sample cup, piezoelectric transducer, and power source, shown separately in the diagram, snap into the bottom of the burner. The power is supplied by a 3-MHz radiofrequency source. The surface of the transducer is coated with glass to eliminate any possible interaction of the sample with barium titanate, of which the transducer is fabricated. The burner head is 5 cm wide and carries a row of 33 holes, 0.813 mm in diameter, at 1.52-mm intervals. In using this nebulizer-burner the following procedure is followed. A 0.2-ml or smaller aliquot of sample is pipetted into the cup and the cup and nebulizer are snapped into the bottom of the burner. The nebulization timer is usually set at 1.5 s, at the end of which time an absorption peak is recorded. The reproducibility of the technique is rather good, yielding an average deviation from the mean of less than 2% for a series of replicate analyses. It is also of interest to note that no signal is observed from the injection of pure solvent, which offers predictable evidence that vaporization of tiny droplets in the flame is very efficient.

The amount of sample used for each run with this nebulizer-burner has an effect upon both sensitivity and reproducibility of analysis. It is clear from Figure 44 that maximum sensitivity is reached when only 200 μl of sample is placed on the transducer, which is an amount just sufficient to cover the entire surface of the crystal with solution. When a larger volume of sample is used, even if nebulization time is also increased, sensitivity does not improve. When volumes larger than 350 to 400 μl are used, large drops start being generated and clog up the burner. With a 200-μl sample, which seems about optimum for sensitivity, a nebulization time of 1.5 s achieves an essentially 100% complete nebulization. Reproducibility suffers somewhat when volumes much smaller than 200 μl are employed, and this is probably due to difficulties in handling small volumes.

This integral burner-ultrasonic nebulizer, although designed especially for this mode of sample introduction, as opposed to modifications of existing models of premix burners used by prior workers, still does not exhibit any particularly significant effects on sensitivity. For the elements silver, cadmium, mercury, nickel, and manganese, sensitivity improves only by an average factor of 4, compared to pneumatic nebulization. This does not, however, diminish the significant advantages of low sample size, nearly 100% efficient sample nebulization, and the possibility of independent selection of gas flow rates appropriate to the most efficient atomization and excitation processes.

3. Conclusion

At this stage, ultrasonic nebulizers still require more time and manipulation during changing of samples and naturally cost considerably more than pneumatic nebulizers. Although the small sensitivity improvement alone may not justify the replacement of a good pneumatic system with an ultrasonic nebulizer, the lower sample volume requirements, the very rapid vaporization of the fine sample fog, and especially the possibility of using low rates of flow of gas may offer valuable advantages in some cases. For instance, when cool flames are used, pneumatic nebulization suffers a loss of sensitivity and an increase in noise due to incomplete vaporization of large droplets and to light scattering, which would not occur with an ultrasonic nebulizer. The decrease in scattering

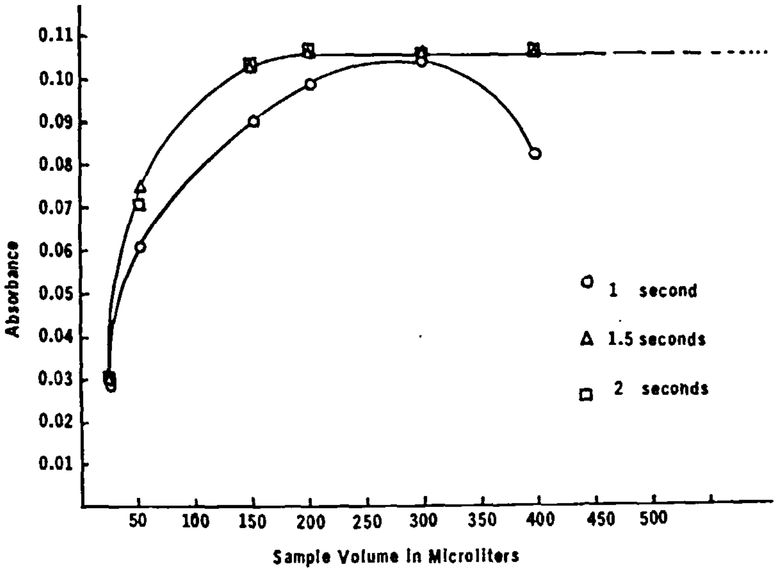


FIGURE 44. Effect of sample volume on the atomic absorption of manganese, at a concentration of 0.9 ppm, with the ultrasonic nebulizer-burner. Pulse times: 1 s, 1.5 s, and 2 s. (Reprinted with permission from Korte, N. E., Moyers, J. L., and Denton, M. B., *Anal. Chem.*, 45, 530(1973). Copyright by the American Chemical Society.)

noise can also affect some atomic fluorescence methods very favorably.

VII. CONCLUSION

Although conventional flame emission and atomic absorption continue to serve as reliable and convenient methods of analysis at low concentrations, considerable research efforts, notably the development of non-flame atomizers, have extended atomic spectrometry into the range of trace and ultratrace analysis. Relatively few other analytical techniques are useful at concentration levels of 1 ppb or less, and none is as inexpensive, rapid, and readily available to most laboratories as atomic spectrometry.

With increased sensitivity come increased possibilities of error. The analysis of every new kind of sample constitutes a new research problem. Matrix effects are often quite pronounced. The matrix may be responsible not just for background molecular absorption, but also for changes in volatility and atomization efficiency. Light scattering is a common problem and can cause serious error. The preparation of appropriate standards must naturally be carried out with great care and their stability to storage must be tested.

It is certain that research into methods of sample injection and atomization in atomic spectrometry will continue and that application papers will continue to appear in larger numbers. The design of apparatus will improve and sample introduction will be made more convenient. With most non-flame atomizers, an inordinately large amount of power is expended to atomize tiny amounts of material. It is reasonable to expect that atomizers which are more efficient will be designed. More automated procedures will probably be devised.

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