



Instrumentation and techniques for the direct analysis of inorganics in solid matrices by nonflame atomic absorption spectroscopy
by Donald Alan Bath

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemistry
Montana State University
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Abstract:

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ANALYSIS OF INORGANICS IN SOLID MATRICES BY
NONFLAME ATOMIC ABSORPTION SPECTROSCOPY

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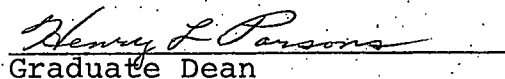
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ABSTRACT

The problem of analyzing solid samples directly without chemical pretreatment was studied. Samples were inserted into the Woodriff graphite furnace utilizing a new pedestal style injection system developed for use in the analysis of solids.

Elimination of effects from the presence of large amounts of matrix material was approached in two ways. A system utilizing sequential pulsed hollow cathode tubes was developed to correct for molecular absorption or light diffraction due to the presence of the matrix. Data which suggests that background problems may be minimized or eliminated by the proper choice of operating temperature coupled with the peak area mode of measurement is presented.

GENERAL INTRODUCTION TO THE PROBLEM

The analyst is usually faced with the problem of obtaining the most accurate, precise data possible. In addition, he must obtain the data in the fastest and cheapest way. Any new method must provide a significant improvement in one of these considerations in order to be a success. When, in 1955, Walsh (1) in Australia and Alkemade and Milatz (2) in Holland demonstrated the advantages of absorption methods over emission methods of quantitative spectrochemical analysis, they opened a new world of possibilities for the improvement of analytical technique. Much of this world remains to be explored.

Traditionally, samples to be analyzed by atomic absorption spectroscopy have been treated to get the element of interest into solution. This requirement is the result of several considerations. Among these are: a) the need to nebulize the sample into the atomizer, b) the inability of the system to handle large amounts of matrix material, c) a need for preconcentration due to high detection limits, and d) the inability to correct for the scattering or absorption of light by matrix material. A need to pretreat the sample introduces several sources of error. It is not uncommon, particularly when attempting analysis

of ultratrace levels, to find that any reagent used introduced amounts of the analyte element greatly in excess of those found in the sample. It is also not uncommon to find oneself at the mercy of complex equilibria or unknown extraction efficiencies when attempting to bring the element into solution. It is common to see these problems ignored or dismissed. The ideal answer is to do away with all sample pretreatment.

With the advent of nonflame methods of sample atomization (3,4,5,6), detection limits were lowered and it became possible to work with samples which previously had been analyzed by other methods or had not been analyzed at all.

Nonflame atomizers have no inherent requirement for sample dissolution (7), however, they do suffer from the effects of nonspecific interferences due to molecular absorption and light scattering to a much greater degree than flame atomizers (8).

It is then the purpose of this work to suggest possible improvements in instrumentation and in techniques of sample handling and data analysis which make it possible to analyze for trace inorganics in matrices such as glass without chemical pretreatment. A system capable of

correcting for large background signals is described which may be used with any of the currently available nonflame atomizers. The techniques described are most clearly applicable to constant temperature atomization systems such as the Woodruff furnace but may have value when applied to pulse heated systems.

BACKGROUND CORRECTION

Introduction

Atomic absorption spectrochemical methods had been in use for some time before the problem of background interference due to molecular absorption and light scattering was noted and systematically studied. Willis, David, and Allan (9,10,11,12,13) each independently observed effects which they attributed to light scattering caused by salt particles. They made no attempt to justify this conclusion.

Billings (4) presented data showing the effects of background interferences on the determination of a number of elements. He assumed that light scattering by salt particles in the flame caused the interferences noted. Slavin, in a note appended to Billings' paper, maintained that the experimental conditions chosen were sufficiently nonstandard to raise doubt as to the validity of some of the determinations. Although he offered no evidence of this claim, it is probable, in light of later results, that molecular absorption and scatter due to the character of the flame may have been of considerable importance.

Koirtzyohann and Pickett (15) were the first researchers to attempt a systematic investigation of

background interference. It was their conclusion that most background interferences in flame spectroscopy were the result of molecular absorption. They proceeded to undertake a theoretical investigation in which they presented strong evidence against any large scattering contribution to background signals (16). They did not address themselves to nonflame systems.

L'vov (17), in his work on the heated cuvette, discovered that as NaCl passed from the cuvette a cloud of particles was formed by condensation which was capable of scattering light. He later found that the interference was essentially independent of wavelength in certain parts of the spectrum indicating not only that particles were present, but also that their diameter was large compared to the wavelength. He also attributed some of the interference, especially that in the 200-300 nm. region, to molecular absorption.

When organic matter is introduced into a pulsed non-flame system, it is usual to ash the sample by applying a low current to the atomizer for a few seconds (18). This disposes of the organic and prevents light scatter due to a "smoke" of carbon particles. In many cases it may also lead to the loss of analyte element.

Once the problem of background interference was realized, work was begun in an attempt to eliminate the problem. Koirtyohann and Pickett (19) devised a system which allowed the light from either a hydrogen lamp or a hollow cathode to be directed through the absorption cell by manually repositioning a mirror. The theory was that background scatter or absorption would be broad-band and would block either the hollow cathode light or the hydrogen continuum to an equal extent. Successive samples are analyzed using the hollow cathode with one and the hydrogen lamp with the next. The absorbance noted from the hydrogen lamp is then used to correct the value obtained using the hollow cathode. This and all similar systems make use of the assumption that the spectral slit width of the instrument is much wider than the absorption lines for the elements. If this were not true either a correction would have to be made for element line absorption from the continuum or the measurement for background absorption would have to be made at a different wavelength.

The main disadvantage of the system proposed by Koirtyohann and Pickett is that it does not provide simultaneous background correction. The analyst is forced to

assume that background levels will remain constant from one sample to the next.

Numerous methods have since been proposed which provide simultaneous background correction. A currently available commercial system uses a continuum source, an element line source and a rotating sector mirror which allows light from the two sources to pass alternately through the absorption cell (20). Another commercial system uses pulsed hollow cathodes and a half-silvered mirror to accomplish the same task (21,22). In addition to these methods, systems utilizing Zeeman effect (23), beam polarization (24,25) and dual wavelength spectrophotometers (26) have been used.

Any attempt to improve background correction methods must take into account the basic requirements of a good atomic absorption system. Since light source intensity and total light delivered to the absorption cell are of prime importance, the design of a good system requires consideration of light source configuration and placement. Basic hollow cathode tube design has received great attention over a period of years, since the hollow cathode is the preeminent atomic absorption light source.

Various demountable hollow cathode tubes have been described. Originally the demountable hollow cathode tube was designed for use as an emission source in high resolution spectroscopy (27,28). Goodfellow (29) and Rossi and Omenetto (30) described lamps for use as atomic absorption sources. Both listed impressive advantages for this type of source. Due to the ability to interchange cathodes, the demountable lamp can replace a number of single element sources. In addition, since this type lamp allows continuous gas flow, the outgassing steps necessary for the preparation of sealed lamps is eliminated and the lamp is less susceptible to self reversal caused by a lingering atomic cloud in the cathode. Since these early successes several variations based on these two designs have been attempted (31,32,33). Of these the design of Popham and Schrenk (32) deserves mention because of its simplicity and good performance without need for water cooling. A new dimension was added to the demountable hollow cathode lamp when Woodriff, Wheeler, and Ryder (34) described a double-ended model for which they claimed improved intensity and greater ease of optical alignment. This lamp in addition to having windows at both ends had anodes at both ends of the cathode, an arrangement which allows the

discharge to operate from both ends. A simplified version of the design has also been described (35).

Other schemes have been used to make hollow cathode tubes for more than one element. In order to achieve multi-element capability in a single sealed hollow cathode tube, it has been common practice to either coat the cathode with more than one element or make the cathode of an alloy of several elements. These lamps work well for certain combinations of elements and are simple to produce. They are, however, seriously limited in that optimum operating conditions can not be individually established for individual elements. In addition, lamps of this type suffer from gradual changes in resonance line intensity because the volatile elements vaporize first then condense on the cathode surface and keep the less volatile elements from being sputtered. Gillies and Yamanski proposed a design which minimizes these problems (36). Their lamp consists of a glass envelope containing two cathodes, one in front of the other. The power to each cathode is individually regulated. Woodriff et al. (37) have proposed a system of demountable see-through hollow cathodes in which each cathode is contained in a separate glass

envelope thus allowing each to be operated at precisely the optimum conditions.

In addition to study of the hollow cathode tube itself, considerable work has been done to determine optimum operating conditions. Dawson and Ellis (38), when faced with an optical system which passed very little light, overcame the problem by pulsing their hollow cathode tubes. When large currents of short duration were passed through conventional hollow cathode lamps, an intense emission was noted with no increase in line width or self reversal. Intensities many times those normally possible are possible while lamp life is extended. Mitchell and Johansson (39) applied this technique to atomic fluorescence as did Weide and Parsons (40). Since the light requirements of fluorescence methods exceed those for absorption methods, the immediate impact of the work of Dawson and Ellis on this field rather than on atomic absorption research is quite reasonable. At this time, a pulsed hollow cathode system for atomic absorption analysis is commercially available (22).

The present study represents an attempt to combine the best features of various component designs to obtain a

simple, precise unit for use in correcting for background scatter or absorption in atomic absorption spectroscopy.

Experimental

Since there are at present no hollow cathode tubes commercially available which meet the requirements of a system such as the one to be described, it was first necessary to design and build a hollow cathode tube for the system. The tube eventually used is shown in Figure 1. The envelope is a piece of pyrex tube 2.0 cm. in diameter and 9.0 cm. long. The ends of the tube are sealed and the quartz windows are held in place by two screw-type electrical conduit clamps and a series of washers and gaskets. Two ports are provided on the side of the pyrex envelope for connection to a vacuum pump and to a supply of inert gas. The cathode holder is a piece of steel tube 0.6 cm. in diameter open at both ends. A tungsten wire brazed to the tube and sealed through the glass envelope serves as a contact. The anode is a length of tungsten wire similarly sealed through the envelope. The hollow cathode tube as described emits an acceptable iron spectrum. In order to use it for other elements it is necessary to remove the end cap and insert a liner of metal foil containing the element of interest into the cathode holder.

Argon gas for the tube is supplied from a tap on the line used to supply flushing gas for the furnace. A

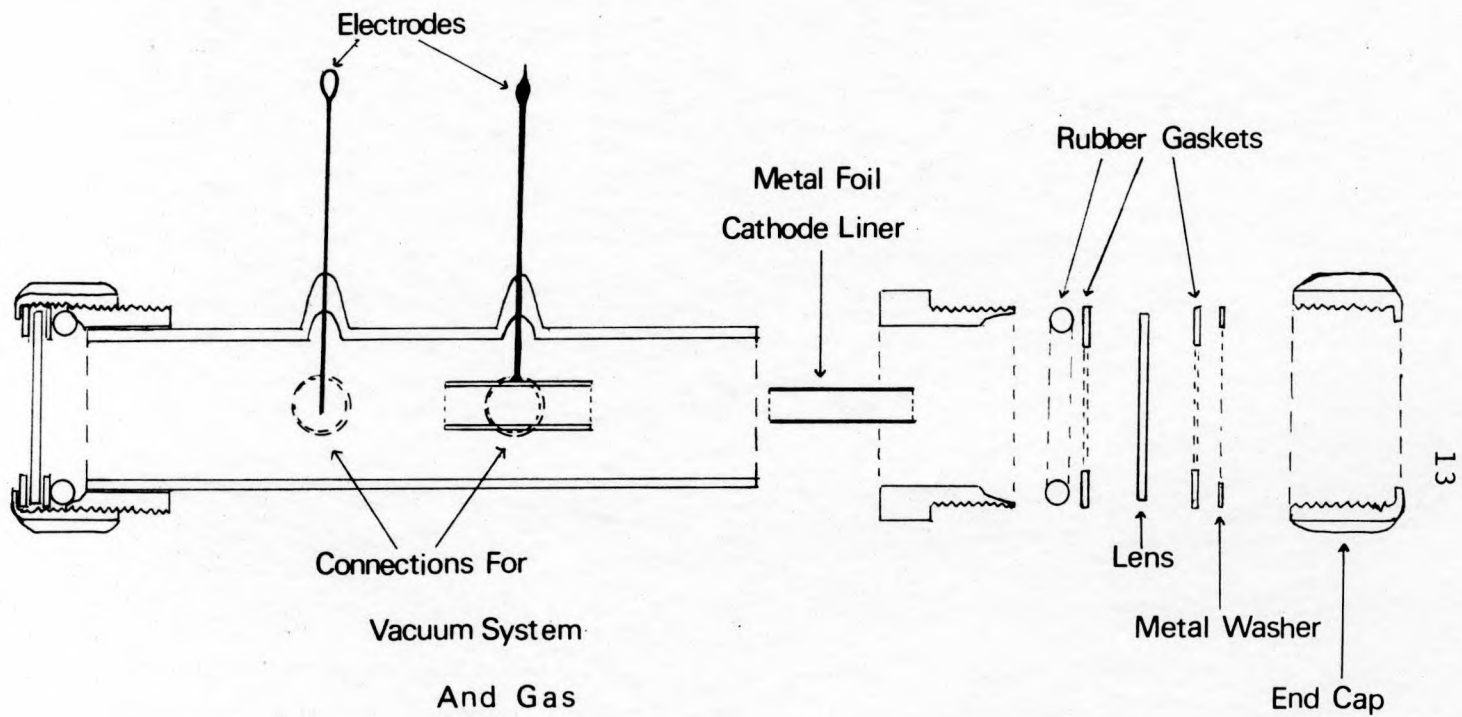


Figure 1. See-through hollow cathode tube

needle valve installed ahead of the gas inlet to the hollow cathode tube allows adjustment of the flow to the tube. A Welch Duo Seal mechanical vacuum pump operating continuously keeps the pressure to less than 1 torr as measured by a C.V.C. pressure gauge. A needle valve between the pump and the hollow cathode tube allows adjustment of the vacuum level. In operation the vacuum pump is used to evacuate the tube to less than 1 torr and then inert gas is admitted until a pressure of 1 torr is obtained with constant pumping.

A Varian Techtron hydrogen hollow cathode lamp was used as the continuum source. Both lamps were operated in the pulsed mode by a Spectrogram Corporation LPS-1D Dual Lamp Power Supply. This unit allows individual adjustment of the current to each lamp and also allows establishment of a constant idle current. A 400 Hz pulse was supplied to the dual lamp supply by a phase-sensitive (lock-in) amplifier, the model JB5 from Princeton Applied Research. The detected signal was fed to an Analog Devices 755P log amplifier and subsequently to the lock-in amplifier. A conventional optical set-up built around a Beckman D.U. monochromator was used. A modified Woodruff furnace, as

described in a later section, was used as the atomization cell. Figure 2 shows the whole unit.

Results and Discussion

The background correction system developed operates as shown in Figure 3. The element lamp is pulsed at 400 Hz (square wave) and exactly 180° out of phase with the hydrogen lamp pulse. With both lamps adjusted to give pulses of equal length and intensity, the signal coming from the photomultiplier tube is interpreted by the lock-in amplifier as a D.C. signal. The lock-in amplifier rejects this signal and gives no output. When a substance which either scatters the light or absorbs over a broad band is introduced the intensities of both signals are reduced by an equal amount. The lock-in amplifier again sees a D.C. signal and again there is no output. When a sample containing analyte element is introduced, light from the element lamp is absorbed and the difference between its signal and the undiminished signal from the hydrogen lamp gives an A.C. square wave which the lock-in amplifier detects and decodes. The introduction of the log amplifier between the phototube and the lock-in amplifier assures that the signals subtracted are absorbances rather than transmittances and thus that the output of the lock-in amplifier will be linear for all background values where absorbance is linear.

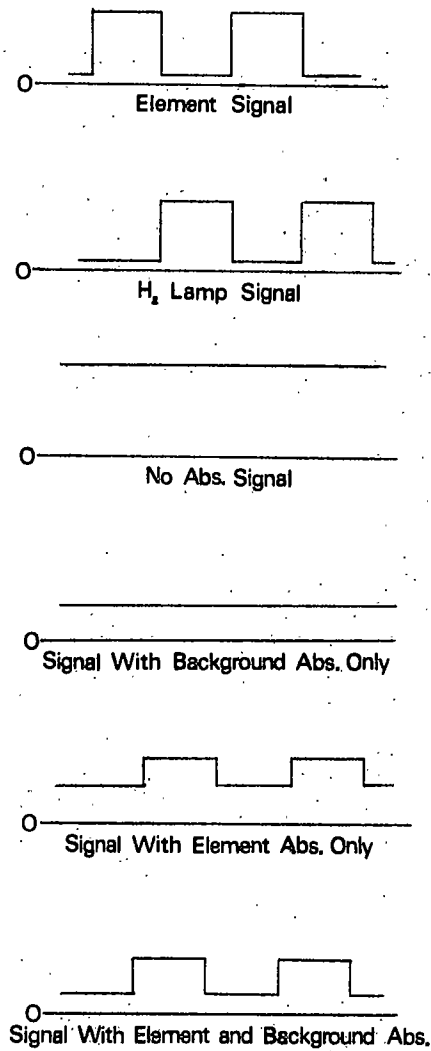


Figure 3. Schematic illustration of mode of operation of background corrector

An idle current of 0.7-1.0 ma. is maintained on both hollow cathodes at all times. The stability of the discharge in a hollow cathode operated in a pulsed mode should be greatly improved by maintaining an idle current which maintains the plasma discharge at all times (39). Indeed, with the demountable see-through hollow cathode it proved impossible to maintain a discharge at all without the presence of a D.C. component.

The operating conditions chosen are shown in Table I. All currents shown are average currents as displayed on panel meters and as such are approximately half the maximum pulse current. For purposes of judging maximum currents to be applied to a given hollow cathode, these meter readings may be used. The light intensity, however, is related to the peak current. Argon was chosen as the fill gas because of its ready availability in areas where the furnace is used. Work by L'vov (17) would indicate that Neon would be a better choice but the difference was not significant enough to warrant the inconvenience of using two inert gasses. Maximum intensity was obtained with a pressure of 1 torr or less. This is in agreement with the findings of L'vov. At pressures greater than 5 torr, the discharge could not be maintained.

Table I. Background Corrector Operating Parameters

<u>Type of operation</u>	- pulsed	<u>Rate</u>	400 Hz
<u>Continuum lamp</u>	- Hydrogen		
Current	7-30 ma (max 40)		
<u>Element lamp</u>	- see-through constant flow demountable		
Fill gas	- Argon	Pressure of fill gas	- less than 1 torr
Current	20 ma (Cu)	15-20 ma (Pb)	15-20 ma (Ag)
Time for out-gassing		15 min	
Warm-up time		12 min	
Stability	±2%		
D.C. component for both lamps (idle current)		0.7-1.0 ma	

satisfactorily. Initial experiments with the see-through hollow cathode showed the presence of significant band structure in the emission spectrum. This was found to be due to the presence of water vapor (or possibly acetone vapor) in the inert gas supply. A drying tube containing CaO desiccant was introduced into the gas line directly ahead of the hollow cathode tube. The presence of the drying tube reduced the intensity of band spectra to an acceptable level. Popham and Schrenk (32) reported similar difficulties but recommended the use of a liquid air trap. Such a drastic solution was fortunately not required in this case.

The use of hollow cathodes as absorption cells has been described (41). Their possible use as filters, although obvious, has not been mentioned. An advantage of the sequential arrangement is that the see-through element lamps should absorb the element line from the hydrogen continuum. Attempts at definitely establishing this action by monitoring the signals on an oscilloscope proved inconclusive. When a copper hollow cathode was used behind the see-through copper hollow cathode, a definite diminution (approximately 10% for the conditions shown in Table I) of the signal from the rear tube was noted indicating

that the front tube was acting as a filter even in the pulsed mode. How much of the element line would be removed from the continuum is a moot point. It can be said that some would be and that the background system would be improved to that extent. Since this would be a minor improvement at best, under these circumstances no further attempt was made to study the effect.

The principal advantage of the sequential arrangement is the improvement it shows in amount of light delivered to the rest of the system versus the amount delivered by presently available commercial systems. For example, in systems using a half silvered mirror (21,22), at least half of the light is lost due to the mirror. In the system utilizing sequential hollow cathodes the first cathode loses no light due to extra optics and the rear cathode loses only the amount subtracted by passage through the two quartz windows of the first cathode. For quartz windows of this thickness approximately 90% of the light would be transmitted through each (42). The second cathode should yield approximately 80% as much light in the sequential arrangement as it does with no windows in front. Actual determinations show that approximately 83% of the light got through. Slight differences in light reflection may

account for the additional light noted in the determination. Thus 1.7 to 2.0 times as much light would be delivered to the rest of the system versus a system using a half silvered mirror.

A prime consideration in testing any atomic absorption unit is the determination of the stability of the source and electronics. This is particularly true for the system studied since the log amplifier used does amplify as well as making the transmittance to absorbance conversion. Figure 4 shows the results of a stability study using a commercial Cu hollow cathode tube and the see-through hollow cathode. The commercial hollow cathode attained reasonable stability in approximately 3 minutes. The see-through hollow cathode required 12 minutes to reach the same degree of stability. In addition, it should be noted that approximately 15 minutes of pumping is required, with inert gas flow, to sufficiently clean the tube before ignition. The cleansing and additional warm-up time is probably necessitated by absorption of impurities on the cathode surface during periods when the tube is not in use. For the same current value, the see-through tube gives slightly lower light output. The curves in Figure 4 represent the intensities obtained for a current of

Hollow Cathode Stability

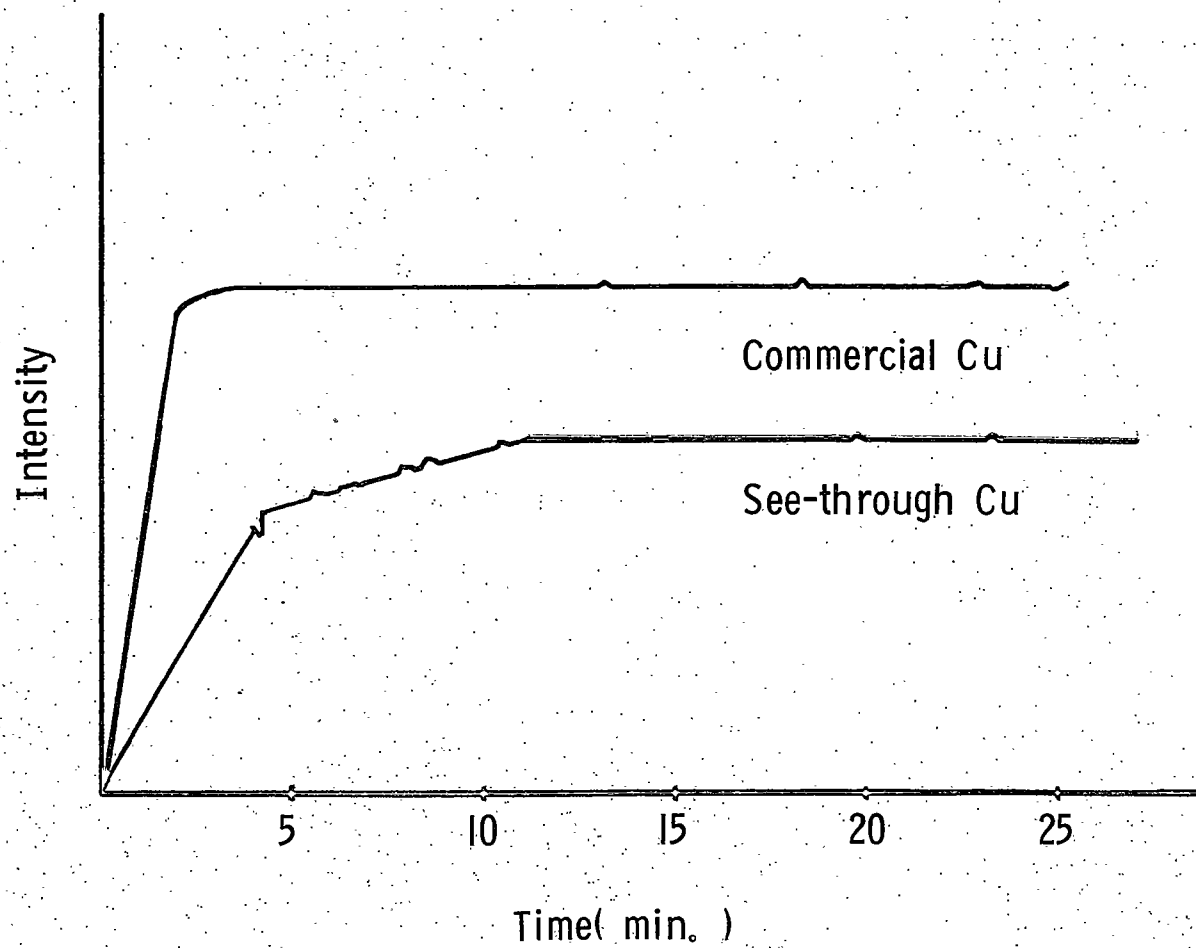


Figure 4. Hollow cathode stability

approximately 10 ma. The lower value for the see-through tube is probably due to the cooling effect of the constant gas flow. In addition, Dean and Rains (43) report that open-ended hollow cathodes give lower intensities than their closed counterparts. The maximum current rating for the commercial Cu tube is 12 ma. D.C. The flow-through tube can be run at 40 ma. D.C. or more when used as a Cu hollow cathode.

In terms of durability the see-through cathode is greatly superior to the commercial unit. With a Pb foil cathode liner in place, an attempt was made to determine maximum current rating. At values above 30 ma. absorbance for a standard solution declined and the cathode heated up markedly. At approximately 50 ma. the Pb foil melted. After the remains of the foil were removed from the tube and a new foil liner inserted, the tube was reignited. No apparent damage was noted and no decrease in capability was found. With a Cu liner, it was found to be advisable to replace the foil liner after approximately 100 hours of operation. The liner showed signs of pitting and surface oxidation and light output was beginning to decrease. Exact lifetime for a liner would, of course, depend on operating conditions and could vary significantly from one

time to the next. An advantage that should not be overlooked is the inherent increase in usable lifetime to be had with any flow-through hollow cathode tube due to the constantly renewable carrier gas supply. Degassing is probably the principal limiting factor in the life of sealed hollow cathode tubes.

In reference to Figure 4 it should be noted that after warm-up, a $\pm 2\%$ variation in signal was noted over a period of several hours for both the commercial and the see-through hollow cathodes. This variation represents total signal drift for the system and as such can not be broken down to give stability figures for individual components. It is obvious, however, that the see-through hollow cathode is not significantly different than the commercial tube.

With the see-through hollow cathode installed in the system, experiments were made to determine the ability of the overall system to correct for various types of background. First work was done without the log amplifier. While this method gives totally unusable results for real samples which give background absorbance greater than 0.01, it may be used to verify the validity of the basic system. When smoke producing organic matter was inserted into the Woodriff furnace, the output to the recorder showed no

variation indicating that the light from the two sources was being blocked and/or absorbed to an equal extent. With the log amplifier installed in the system, several determinations were attempted. Figure 5 shows the results of a study using copper standards and turpentine residue. One set of points represents system response to copper standards alone while the other set is for samples of the same concentrations with sufficient turpentine residue to give an absorbance maximum of 1.3 if uncorrected. The two sets of points are sufficiently indistinguishable to allow the use of one line to represent both sets. Turpentine was chosen as the background producing material since it gives an absorption or scattering characteristic of most organic matter such as blood, plant material or oil. This type of blockage would be noted for incompletely ashed samples or for wet samples. Figure 6 shows typical peaks. Peak A is the characteristic high spike seen when such material is inserted into the furnace. The lack of a peak shown in B is the signal obtained with the background correction system in operation. Peak C is a typical copper peak showing evidence of uncorrected interference from turpentine residue. Peak D is the same concentration sample with proper correction. Peak E represents an overcorrected

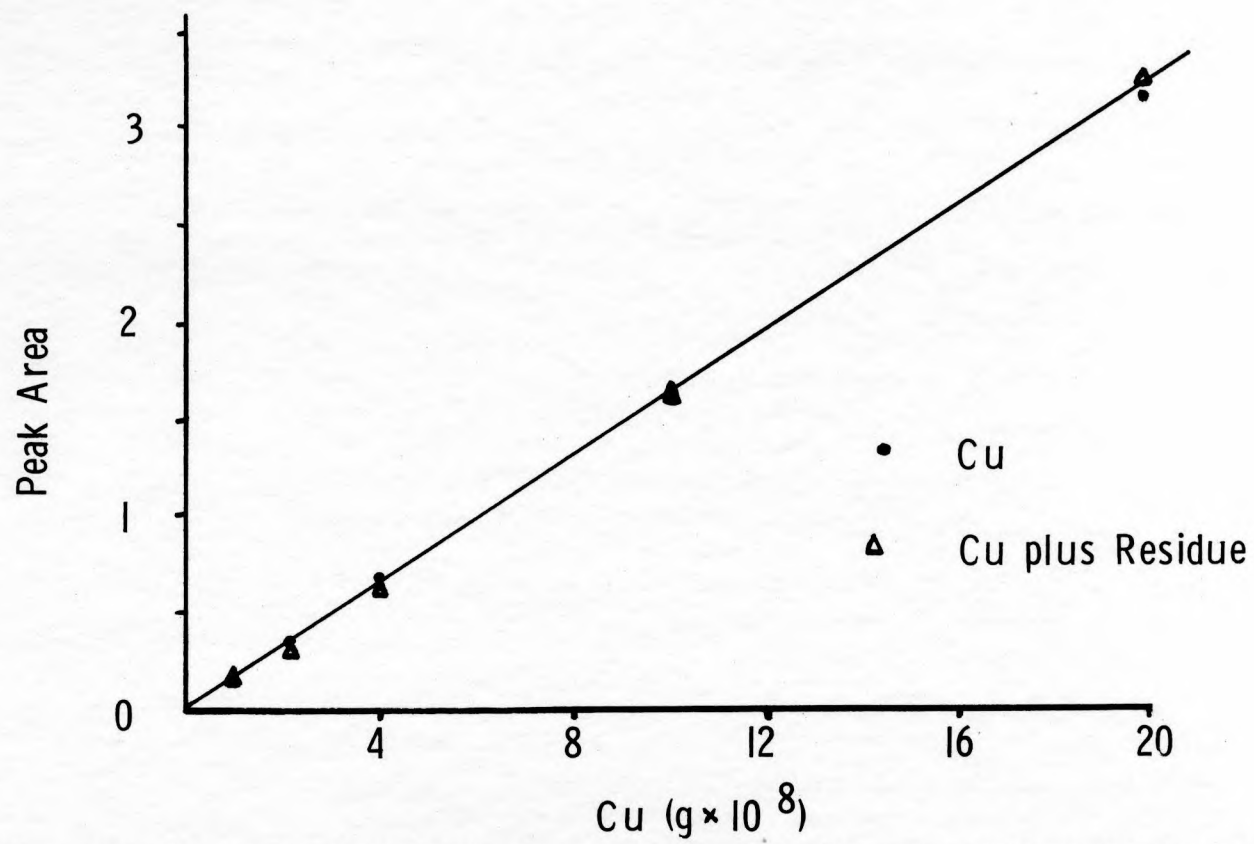


Figure 5. Standard curves obtained for copper with and without background

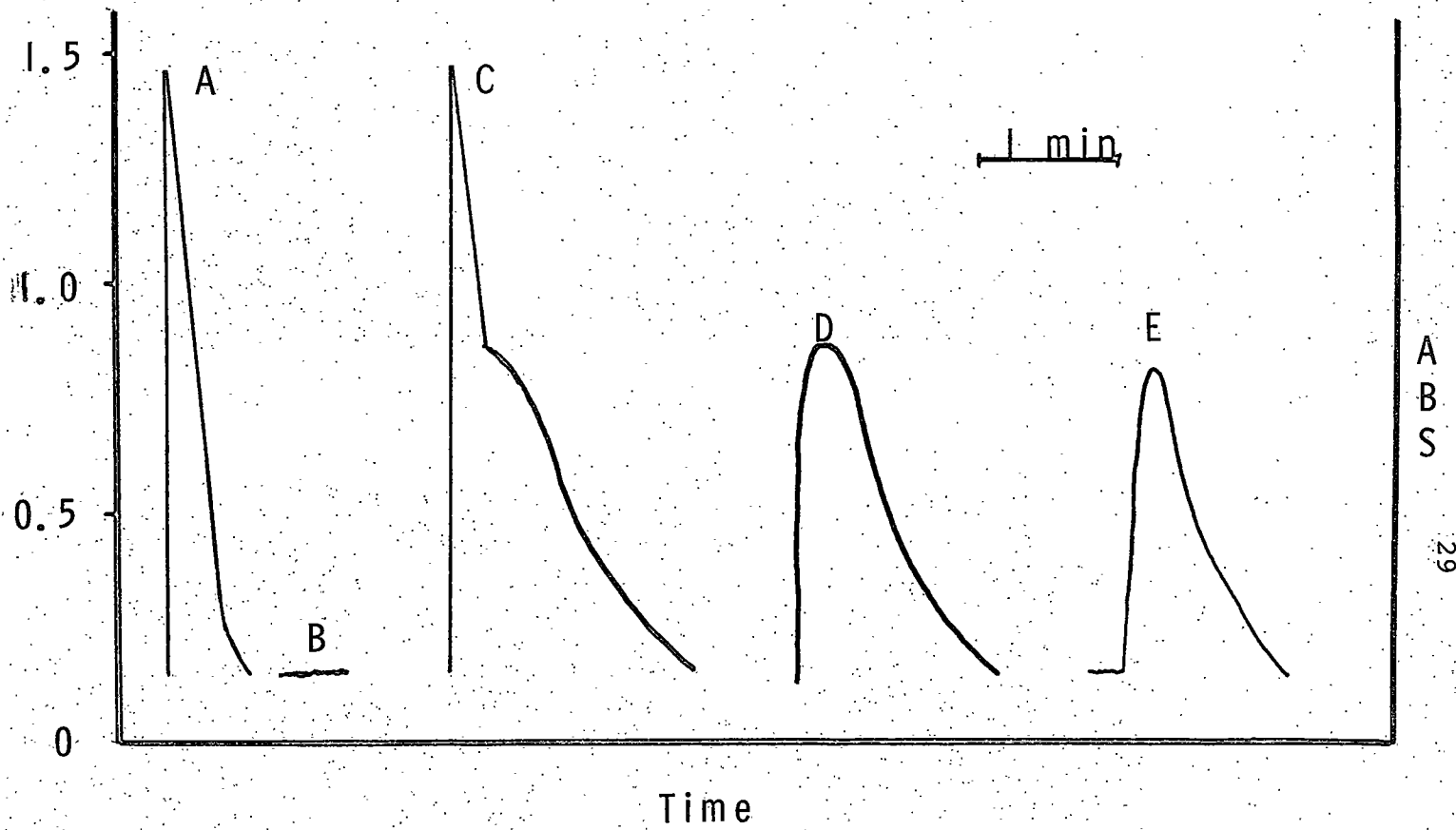


Figure 6. Typical copper peaks

copper peak. A flaw in this and similar systems is the problem of possible overcorrection. When a sample is introduced which contains sufficient background producing material to block all or most of the light, the unit maintains the initial baseline until enough of the background producing material has left the light path to allow a difference signal. In such a case the sample peak obtained will be either smaller than expected or nonexistent depending on the residence time or amount of the background material and on the rate at which the analyte element is vaporized. It is, therefore, advisable to determine approximate background levels when analyzing any unfamiliar type of sample and to recheck any determination where considerable delay in the appearance of a signal is noted. No diminution of element signal is noted and proper correction is possible up to background absorptions of 1.5 absorbance. This compares with claimed values for correction up to 1.0 absorbance for the Varian unit and 0.4 absorbance for the unit manufactured by Perkin-Elmer (22). Background material levels which may cause problems were determined. Amounts of water in excess of 5 microliters were unacceptable as was organic material in quantities normally

associated even with small unashed samples. The dried residue of up to 2 microliters of turpentine or similar material was acceptable.

Salts and other inorganic materials give a lower, longer duration signal which if ignored will lead to considerable error. This type of background interference is much more amenable to elimination by a system such as the one described since at any given time a considerable amount of light is being transmitted even with large amounts of the background producing material present. Techniques and requirements for the elimination of this type of interference for glass matrices are discussed in detail in the ensuing section. Table II illustrates the magnitude of error introduced by such a matrix and the improvement possible using proper background correction instrumentation. At no time did the absorption by the background exceed 0.7 absorbance for the values listed.

Table II. Effect of SiO₂ Background on the Determination
of N.B.S. S.R.M. 616

	Cu Determined* (ppm)	Range** (ppm)	95% C.L.**	% Recovery (max)
Without correction	6.1	±3.8	±3.3	763
With correction	0.82	±0.16	±0.4	103
Accepted value	0.80		±0.09 [†]	-

*Furnace temperature 2100°C 324.7 nm line

**5 or more samples

[†]N.B.S. reports range or 95% C.L. whichever is larger

SOLIDS ANALYSIS

Introduction

In a recent review article (44), Dinnen summarized the current methods for analysis of inorganic and geological materials. Since many of these materials are solids a considerable portion of the review was devoted to techniques for sample decomposition and to extraction techniques. It was noted that atomic absorption and flame emission spectroscopy particularly require sample dissolution.

The extent to which this premise is accepted is shown in an article by Welcher, Kriege and Marks (45). They describe a method using nonflame atomic absorption spectroscopy which they claim is a direct method. A check shows that only the customary separation steps are eliminated. The sample is dissolved. Dissolution is considered to be such an inherent requirement that no thought is given to its elimination.

Review of the literature does lead to the discovery of a few attempts at devising ways to eliminate sample dissolution and its attendant problems. Mavrodineanu and Boiteux (46) reviewed several novel ways of supplying solid samples to a flame. Included in these are methods

for entraining a fine powder in an air stream with subsequent introduction into the flame, automatic feeding of ashless filter paper containing the sample into a flame, and sample introduction using an asbestos disc to carry particles to the flame. For solids which are good electrical conductors, a spark source in which the electrodes are made of the sample will yield an aerosol which may be introduced into the flame. Winge et al. (47) described a method in which the sample serves as the cathode of a low-current dc arc discharge. Jones and his coworkers described a quite similar system (48). The system of Winge was used with atomic absorption while that of Jones was used to supply particles to a capillary arc plasma (CAP) emission source. Willis (49) described a method which relied on forming a suspension of sample particles and aspirating this suspension into the flame. Geological samples ground to a fine powder were determined as a water suspension. A method for similar samples described by Govindaraju et al (50) relies on inserting an iron screw rod impregnated with sample into an air-acetylene flame. Both of these methods gave good results with analyte concentrations in the 10 ppm range. The Delves Sampling Cup technique has also been applied to solids. This technique

uses a nickel absorption tube mounted above the burner head. Nickel crucibles are inserted under the tube and the sample allowed to vaporize into the tube. This method shows marked sensitivity dependence from crucible to crucible. It also is limited in applicability due to its low maximum operating temperature (51).

Belyaev et al. present an interesting scheme for the atomic absorption analysis of trace elements in rocks (52,53). Their method involved the use of an electrocontact heater (similar to the Varian carbon cup) to selectively evaporate and atomize analyte elements from powdered solid samples. They experienced considerable difficulty due to differences in evaporation rate of the analyte element from different matrices and due to background scatter. In order to standardize the matrix small amounts of sample or standard were mixed with graphite powder. While this procedure assures a more predictable sample peak, it also dilutes the sample and results in a loss of sensitivity and accuracy. In an attempt to avoid this problem, the authors increased the current applied to the electrocontact atomizer. At a current of 200 A, a temperature of 2300°C was attained and the evaporation rates from the various matrices was found to be similar

enough to partially eliminate peak shape variation. At this temperature a considerable background was noted. Fortunately the background was not of sufficient magnitude to make correction (using a continuum source à la Koirttyohann and Pickett) impossible.

Experimenters who have tried atomizers similar to that of Belyaev for other types of matrix have not been so lucky. Much attention has been directed to the problem of analyzing for inorganics in glasses. This interest is due to the importance of trace element characterization in glass to the forensic scientist (54,55,56) to those working in archeological chemistry (57) and to analysts in the fiber optics industry (58). The last application is of particular commercial importance since it has been shown that concentrations of copper or iron in the part per million range in fiber optic material are sufficient to greatly attenuate light transmission. Direct methods similar to that described by Belyaev have been unsuccessful. Woolley (58) reported using a carbon rod atomizer in an attempt to determine copper and iron in high purity glass. It was his conclusion that it was impossible to effect the determination directly due to the extreme background caused by SiO_2 . Thus, it is still common to find

articles in the literature detailing new and better ways to dissolve glasses prior to trace metal determination (59).

Several methods of analysis for inorganics in glass deserve mention in order to gain an understanding of the current status of the field. Adams (60) described a method for the determination of alkalis in glasses and silicates. The procedure for sample preparation, which he claimed required 30 minutes, calls first for the sample to be ground, sieved and carefully weighed. To this weighed sample, in a polyethylene vessel, is added a mixture of HF and HCl with stirring. When dissolution is complete the vessel and its contents are transferred to a polyethylene bottle containing deionized water. Insoluble material is removed by centrifugation after mixing. A reagent blank is necessary. Jones (61) described a very similar method which also requires the use of HF. In this case the sample solution was analyzed by atomic absorption spectrophotometry.

Activation analysis has been a popular choice for glass analysis. Workers at the National Bureau of Standards have made extensive use of neutron activation analysis (NAA). Detection limits for NAA are generally excellent, precision is good, and sample pre-handling is not excessive. Unfortunately, cost is high, analysis time may be

lengthy and necessary instrumentation and reactor facilities are not commonly available. In addition, handling of the sample after irradiation may be quite involved. In some cases the determination may be absolute but it is more likely to be done comparatively. The one great advantage of NAA is its low detection limits and it is for this reason that much of the certification work on glass standards has been done by this method (62,63,64). The other activation analysis work that has been attempted involved the use of charged particles. Swindle, Novak and Schweikert (65) have examined the usefulness of various charged particle activation methods for the determination of iron in glass. Many of the same objections which apply to neutron activation analysis also apply to charged particle activation analysis. It should be noted that in all the methods reported dissolution of the glass samples with HF was required.

The other method of choice for recent glass analysis work is isotope dilution mass spectrometry. Barnes et al. reported using this method for the determination of Lead, Uranium, Thorium and Thallium (66). Moore et al. used the same technique for the determination of Rubidium and

Strontium in standard glasses (67). Both reported using HF for the dissolution of the glass matrix.

In summary, the analysis of inorganics in glasses, as well as in most other solid matrices, is commonly considered to require the elimination of the matrix. The range of time for this procedure is from 5 minutes to 16 hours depending on the sample and the method chosen. For glasses, HF is the reagent most commonly used for sample dissolution. Total analysis times range from 30 minutes to several weeks.

It would seem that the ideal analysis of solids can be described rather clearly. No sample preparation, other than cleaning and grinding, if necessary, should be required. Sample particle size should not be critical. There should be little or no difference in results when changing from one matrix to the next. Total analysis time should be in the order of minutes, not hours. In order to assure a quick analysis, background signals should not be so complex or so large as to cause difficulty. In addition, instrumentation used should be relatively inexpensive and available. The study undertaken had as its goal the attainment of this ideal.

Experimental

A modified Woodruff furnace was used for sample atomization (68,69). Figure 7 shows a diagram of this unit. Several minor, but important, modifications were made to the basic design. Ports for cooling water were added so that the unit could be installed in an upright position with the sample introduction port facing down. Samples were introduced using the injection system shown in Figure 8. A vycor tube with a ground glass joint at one end is normally used as an entrance side tube on the Woodruff furnace. In this configuration the normal side tube is incorporated with a steel guide tube through which a graphite rod with a graphite pedestal at the top rides on a spring loaded clamp. The sample cup is placed on the pedestal and raised into the furnace. The pedestal seals against the furnace guard tube so that the whole cup is enclosed in the heated chamber. In earlier designs the lip of the cup formed the seal. This method allows the use of a simple sample cup which need not be attached to the rod used to insert it. With no need for threads in the base or for a uniform lip, difficult to machine materials such as vitreous carbon and molybdenum were used. This design

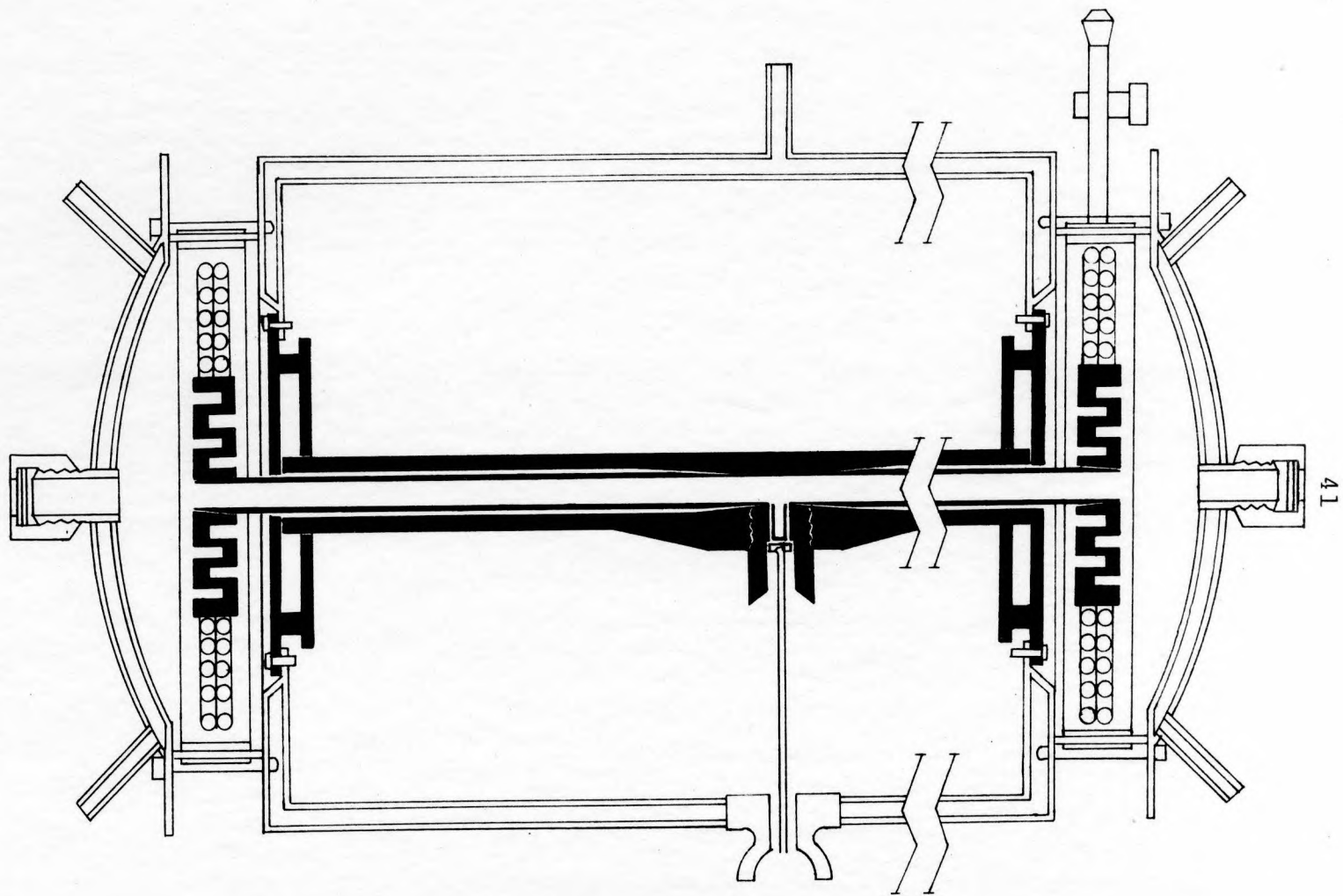


Figure 7. Woodriff furnace with pedestal sample injection system

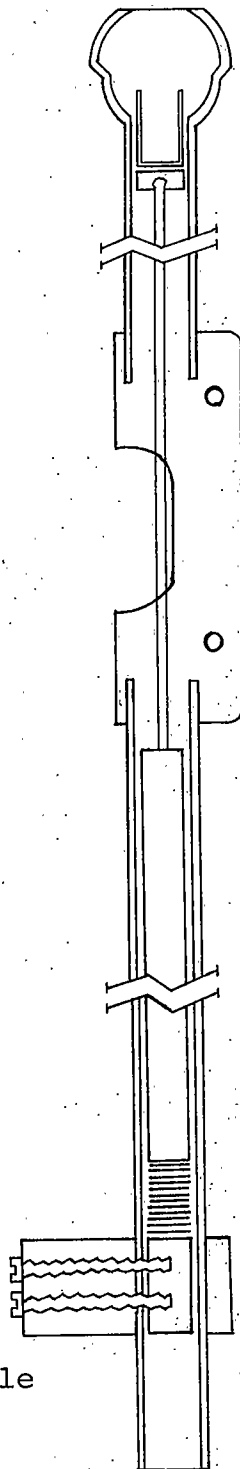


Figure 8.
Exterior portion
of pedestal sample
injection system

also lends itself to schemes for automated sample introduction more readily than prior systems.

The background correction system described in the previous section was used for all measurements where background problems were anticipated. Other instrumentation was also as previously described.

For work requiring a pulse type atomizer, the unit described by Siemer (70) was used. This unit is very similar to the commercial Varian carbon rod-carbon cup atomizer (71,72,73) and may be expected to give similar results.

Glass samples used were N.B.S. standards numbers 614 and 616. The composition of the glass support matrix is 72% SiO_2 , 12% CaO , 14% Na_2O and 2% Al_2O_3 . The nominal trace concentration for each of the 61 elements in these standards is 1 ppm for S.R.M. 614 and 0.02 ppm for S.R.M. 616. These standards are available as 3 mm. thick wafers. The material was prepared in rod form and cut with a copper-bonded diamond wheel. The wafers as received required cleaning with alcohol followed by a mild surface cleaning with 1:10 nitric acid. The cleaned wafers were broken and ground in an agate mortar and stored in glass sample bottles. All implements and glassware used were

cleaned with nitric acid prior to use. No attempt was made to grind to a uniform size. Sample sizes were in the range of tenths of a milligram to a few milligrams. All samples were weighed to the nearest hundredth of a milligram on a Mettler type H16 balance. Weights were determined by weighing a sample cup with and without sample present and taking the difference. Sample cups were then inserted into the Woodriff furnace without any sample pretreatment.

Standards for all determinations were aqueous solutions of the analyte ion prepared in the respective standard way for each element. Silver and copper were present as the nitrates. Gold, after treatment with aqua regia, would have been in solution as the chloride. The required amount of solution was placed on a sample cup using a micro pipet and the water was evaporated under a heat lamp. The cups were then inserted into the furnace.

Peak area measurements were used almost exclusively with the areas being determined by the "clip and weigh" method. Electronic peak integration would be preferable but an integrator was not available at the time of this study.

Results and Discussion

Based on conclusions drawn by L'vov (17) and on experience gained in prior studies, it was deemed advisable to attempt to totally contain the sample cup within the heated chamber. Thus, when the bottom loading system previously described was installed, provision was made to have the pedestal form the seal with the heated chamber rather than having the cup make the seal. This was prompted in part by the observation that liquid samples were able to wet worn cups more easily than new ones. This leads to slower volatilization and thus to lower peak heights and poor reproducibility when the peak height mode of analysis is used. It was hoped that the pedestal system would provide quicker, more uniform heating of the cup base which would minimize volatilization rate differences. In addition, when the cup makes the seal with the analysis chamber, there is a problem with uniformity of the cup lip and thus, with the gas tightness of the seal. It was not certain whether the sample would diffuse back through an imperfect seal in the face of the pressure provided by the inert gas but this possibility certainly can not be ignored. Another possible reason for loss would be diffusion through the hot graphite cup itself. Most of these

problems should be ameliorated by the new system if indeed they do exist. Table III shows the results of work done with the new system. The peak height variation was similar to that noted by Stone (74) and seems to confirm the opinion that the older a cup gets the lower the peak signal obtained is going to be. As previously noted, the reason for this is the quite noticeable increase in surface porosity as the cup wears and the subsequent absorption of sample solutions. While this study did not demonstrate the superiority of the pedestal seal configuration, it did show the superiority of the peak area mode of analysis. As can be seen from the table the relative standard deviations for this mode are considerably better than for peak height mode. Subsequent use of the new sample injection system confirmed the initial findings that peak configuration was not changed significantly. No increase in peak size was noted which would indicate elimination of the modes of sample loss previously mentioned. Either sample loss by these mechanisms does not occur or occurs equally with both the new pedestal system and the system described in prior work.

The greatest advantage of the new sample injection system appears to be purely mechanical. Ease of use is

Table III. Silver Analysis with Pedestal Forming Seal

Cup	Condition	Abs (peak height)*	Peak area*
1	new	0.65	.0249
2	old	0.59	.0248
3	new	0.64	.0241
4	old	0.56	.0245
		Avg. 0.61	Avg. 0.0246
		r.s.d. 7%	r.s.d. 1%

* 2.5×10^{-8} g silver (aqueous solution)

improved over prior systems. Fabrication of sample cups is much easier. It is this last advantage that has proved to be the most useful. The ability to use substances other than graphite, particularly substances such as molybdenum, tantalum and vitreous carbon, for cups has proved to be invaluable.

Initial studies on glass samples involved analysis for silver. Silver was considered to be a logical choice since a good value was available for N.B.S. standard reference material 614 and since considerable prior work had been done on the determination of this element in other matrices. Since it was intended to run the samples directly and use aqueous standards, it was important to study the effect of sample size and consistency on the absorbance recorded. Figures 9 and 10 show the curves obtained when peak height and peak area were plotted versus weight of standard glass. Assuming that the glass standard reference materials (S.R.M.) are homogeneous in composition, the amount of silver present should be proportional to sample weight and absorbance versus weight should plot as a straight line if the silver is volatilized from the matrix reproducibly. Table IV shows the characteristics of the samples represented by each of the points in the two figures and the analysis parameters. The important points to be noted are that the sample is reasonably homogeneous as assumed and the form of the sample (powder or chunk) is of no apparent importance. This last is of particular interest in light of the work of Belyaev et al. mentioned earlier (52,53). Considering the results

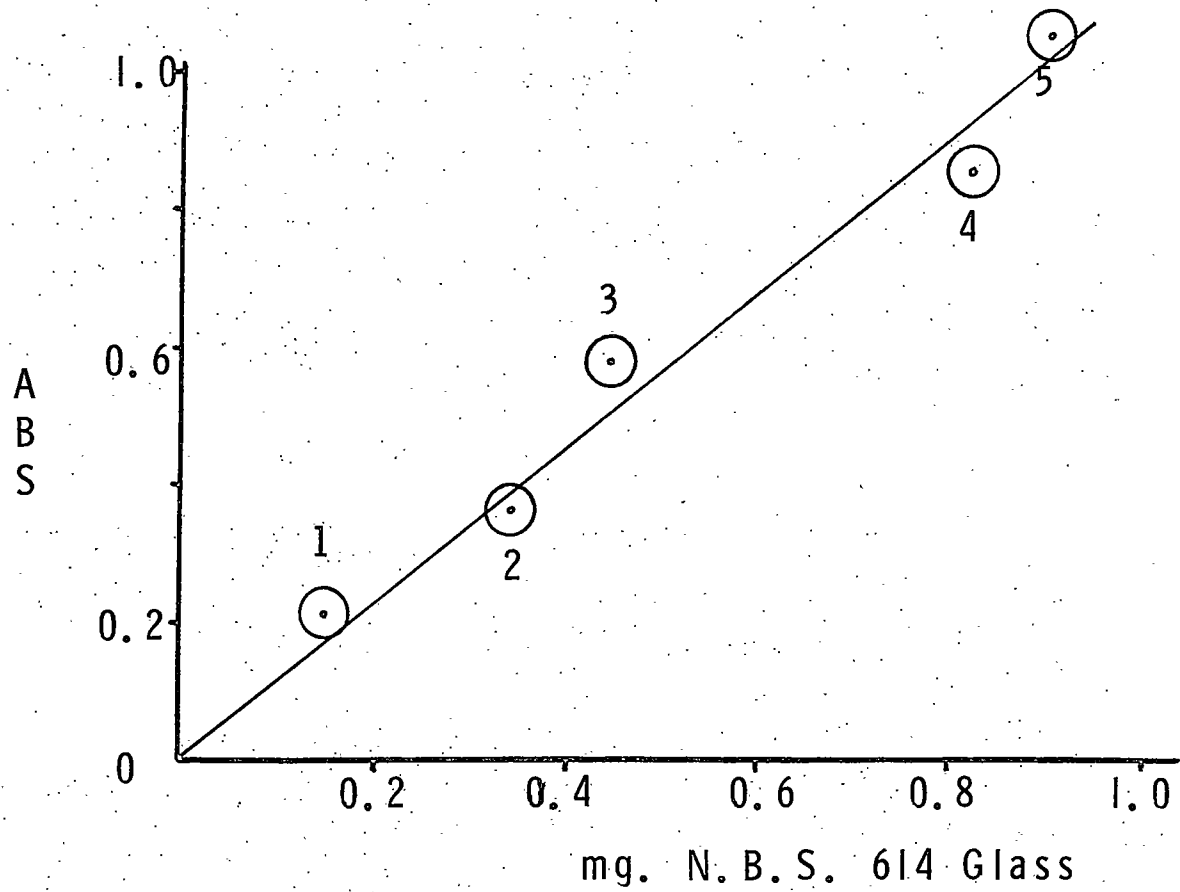


Figure 9. Sample size for N.B.S. glass versus peak height absorbance for silver

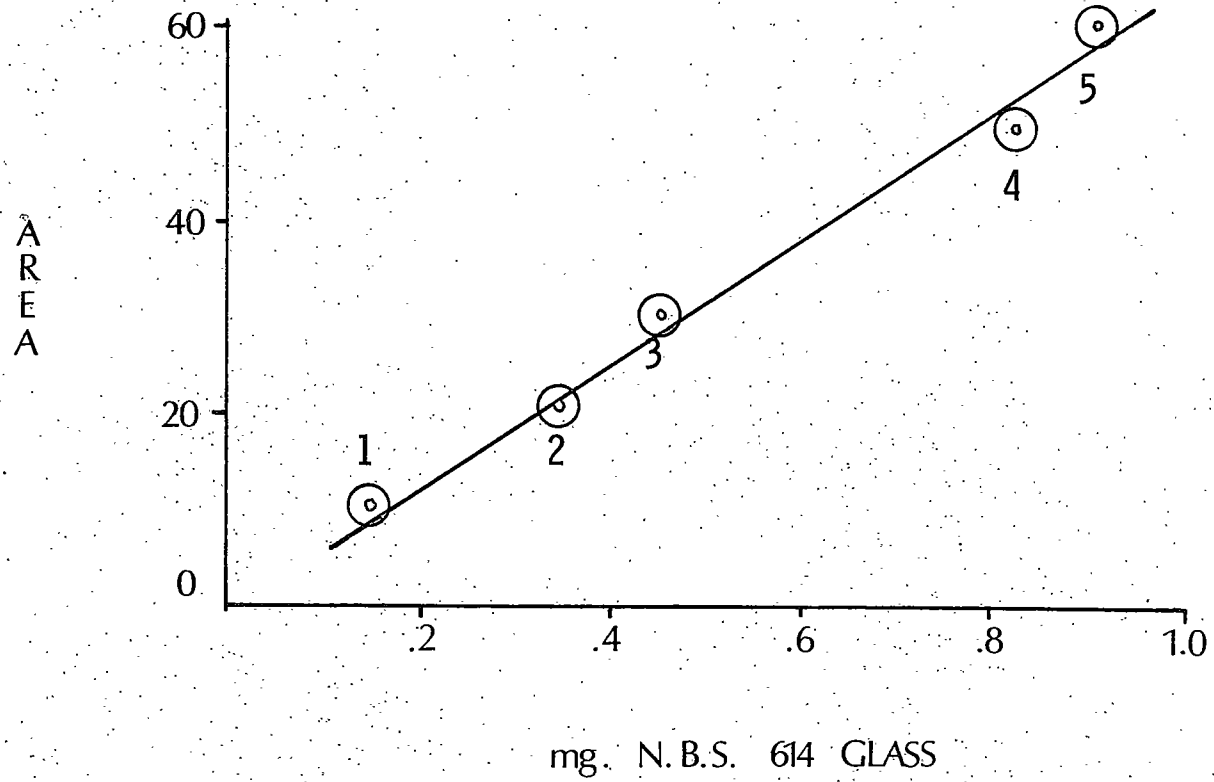


Figure 10. Sample size for N.B.S. glass versus peak area absorbance for silver

Table IV. Sample Characteristics

Sample No.	Description	Mg SRM 614	Abs (peak height) *	<u>Abs wt.</u>	Peak* area	<u>Area wt.</u>
1	2 pieces	0.15	0.24	1.60	9.6	64.0
2	1 piece	0.35	0.37	1.06	20.7	59.1
3	powder + piece	0.45	0.57	1.27	30.8	68.4
4	fine powder	0.83	0.84	1.01	50.4	60.7
5	1 piece	0.90	1.12	<u>1.24</u>	60.4	<u>67.1</u>
				rsd 0.185		rsd 0.062
	<u>Element</u>	Ag	<u>Line</u> 328.1	Temperature	1850°C	

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*Analysis done without simultaneous background correction

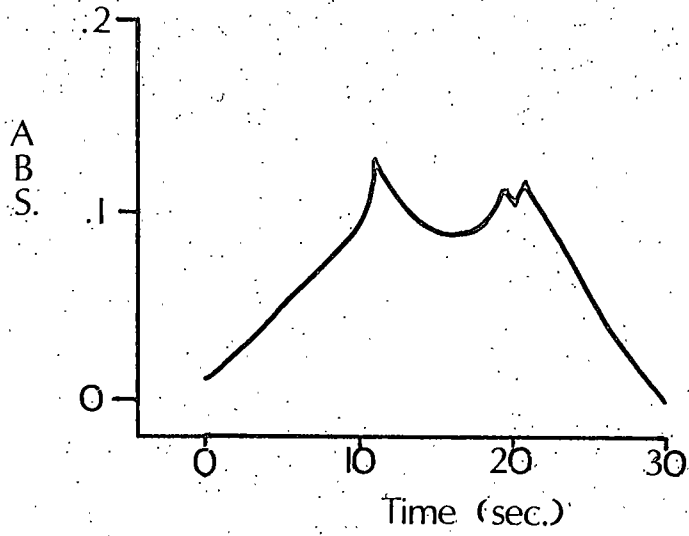
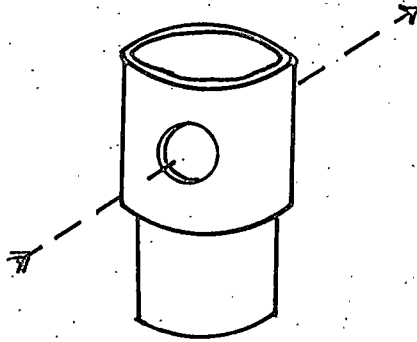
presented and later work on copper, it seems apparent that at 1850°C silver is vaporized quickly enough so that no significant difference in peak height appears.

Vaporization times for the radically different water matrix were also obviously comparable. It is important to note that in speaking of "water matrix" there is no true matrix since the analyte element is present as a relatively pure salt after the water is evaporated. In cases where the water solution wets the cup to a significant extent the salt may be in the pores of the graphite. In such cases the graphite does exert an influence on the rate of vaporization. In practice, then, it is true that in nonflame atomic absorption "liquid samples" are solids when analyzed. An important observation made during the silver determinations was that most of the glass matrix remained in the cup. When the cup was withdrawn from the furnace small spherical beads were present in the cup or, more rarely, the cup would be coated with glass. An attempt was made to determine the weight of the residue. This proved to be impossible due to random changes in the weights of the graphite cups themselves. Small amounts of material are lost from the cup on each use due to oxidation,

flaking of the graphite, and a variety of other causes. All determinations for silver were made without simultaneous background correction.

The decision not to correct for background was made after careful checking over a period of time to determine that no background absorption was present. Work by Woolley (58) strongly indicated that background absorption or scatter by SiO_2 would be excessive. Since Woolley had used the Varian type carbon cup atomizer in his work, an attempt was made to determine if this unit was more susceptible to such interference than the furnace. The result was that, for several reasons, the carbon cup did show a greater susceptibility to SiO_2 interferences. Normal operating parameters for the commercial carbon rod-carbon cup system allow for a drying cycle of up to 60 seconds, an ash cycle of up to 60 seconds and an atomization cycle of up to 10 seconds (18). Maximum temperature attained is around 3000°C . A temperature of this magnitude is necessary to volatilize the sample in a short period of time. It is possible to atomize for longer periods of time but this is not commonly done, in part because of extreme wear on the atomizer. Figure 11 shows a representation of the carbon cup used and a typical signal for a

55



Carbon Cup System

Figure 11. Results for determinations using carbon cup system

very small sample of S.R.M. 614. The first peak represents maximum silver evolution from the glass matrix while the double peak that follows was found to be totally caused by background from the glass. Maximum temperature was approximately 2800°C. The unit was held at this temperature for 30 seconds in order to follow the development and decay of the background signal. Determinations using a hydrogen lamp continuum established that a large percentage of the area under the total curve was due to background absorption. The apparent difference between Woolley's results and those obtained using the Woodriff furnace stems from his use of the carbon cup at its peak temperature. At temperatures of 2800-3000°C background is indeed excessive.

Values for S.R.M. 614 and S.R.M. 616 are shown in Table V. National Bureau of Standards values were determined using neutron activation analysis and isotope dilution mass spectrometry. N.B.S. has not attempted to determine a value for S.R.M. 616 as yet. It should be noted that N.B.S. reports either range or 95% Confidence limit (95% C.L.), whichever is larger. For this data and for the work reported later in this paper, the definition

Table V. Silver Determination*

<u>N.B.S. S.R.M. 614</u>	Value	Range	95% C.L.
Peak Height Value	0.47	0.06	0.07
Peak Area Value	0.47	0.04	0.01
N.B.S. Value (63)	0.42		0.04 [†]
<u>N.B.S. S.R.M. 616</u>			
Peak Height Value	0.027	0.006	0.005
Peak Area Value	0.031	0.003	0.002
N.B.S. Value (64)	None		

*Average of 5 or more determinations
Aqueous standards

[†]Range or 95% C.L., whichever larger

$$95\% \text{ C.L.} = \frac{ts}{\sqrt{n}}$$

t = constant from table (75)

s = standard deviation

n = number of data points

is used. For sake of comparison, both the range and the 95% C.L. are used for the atomic absorption data.

Since a sharp peak was obtained for silver at this atomization temperature (1850°C), peak height values were determined in addition to peak area values. Means were quite comparable for both modes. Ranges and confidence limits were better when peak area was used.

Gold content of the N.B.S. standards was also determined. Table VI shows the results of this study. Gold determinations were made using an atomization temperature of 2000°C. At this temperature vaporization is not quick enough to give a good spike peak. However, since work with silver had shown that peak area values were not only acceptable but possibly superior all determinations were made using this mode. Again, aqueous standards were used. Background correction was not found to be necessary. All National Bureau of Standards values are from neutron activation analysis determinations. In the case of S.R.M. 614 the value listed by N.B.S. is the average of work done by two separate groups. This value is not certified and no statistical data is given due to the extreme irreproducibility of the results. A similar problem was noted in the atomic absorption data. No cause has been determined for this problem but it would seem possible that it is a function of the material rather than the technique since it was noted by three independent groups. S.R.M. 616 presents a most interesting study. The N.B.S. value given is the result of determinations made by one neutron activation analysis group within the bureau. A separate group assigned to determine background levels in the base glass

Table VI. Gold Determination*

N.B.S. S.R.M. 614	Value	Range	95% C.L.
Peak Area Value	0.28	0.14	0.15
N.B.S. Value** (63)	0.5	none given	
N.B.S. S.R.M. 616			
Peak Area Value	0.20	0.01	0.01
N.B.S. Value** (64)	0.18	0.01 [†]	
Glass Background Value (Ref. 62)	0.217 ± 0.013		

*Average of 5 or more determinations
Aqueous standards

**Uncertified

[†]Range or 95% C.L., whichever larger

arrived at a different and slightly higher value. The two values appear to be mutually exclusive. Results of the atomic absorption determinations yield a value intermediate between the two N.B.S. values. Precision for all three values is quite good. Since S.R.M. 616 is supposed to have a nominal 0.02 ppm gold concentration, it seems clear that what is being determined in all these cases is the base level in the glass. It is impossible to say which value is correct. The important point to note is that the atomic absorption value is at least as valid as those determined by neutron activation analysis.

The next element studied was copper, the last of the coinage metals and one of the most important to those working the glass analysis field. Initial attempts at determining copper in the N.B.S. standards gave values greatly in excess of accepted values. Subsequent attempts yielded an array of irreproducible results. Checks for background absorption indicated that the problem was not background. Since the determination of other elements had gone well, the assumption was made that the problem was peculiar to copper and not a flaw in the basic method. This proved to be true only in part. Prior experience with copper in aqueous solutions had shown that this element did not give the precision normally expected with other elements. Conditions of the cups appeared to have a marked effect with older cups giving values considerably lower than new cup values. Possibly some property of this "graphite matrix" was retarding volatilization. The possible formation of a non-stoichiometric copper carbide was also considered. Carbide formation is an inherent problem in the Woodriff furnace and in all other graphite systems. If some reaction were taking place between the aqueous standards and the sample cup such that part of the copper standard was not being properly atomized, this would lead to low standard curves.

In the case of the glass, the copper was evolving from the glass and would not come in contact with the cup. In order to study this possibility, a series of determinations were made using cups of other materials. Molybdenum and vitreous carbon cups were used in the Woodriff furnace. In a cross study, tantalum lined graphite cups were compared to graphite cups on the carbon rod atomizer. In all cases the findings were similar to those shown in Table III. The impervious materials behaved in the same way that new cups did. Peaks were higher but peak areas were the same. Reaction with the cup was not occurring to any measurable degree. Again a check for background was made since this was the obvious problem. Again none was found.

The lack of precision in the data indicated that the problem was one of lack of consistency in some basic analysis parameter. An attempt was made to standardize the matrix in the manner of Belyaev et al. (52,53). Glass samples were ground to a fine powder and mixed with graphite powder. This mixture was put into a sample cup and graphite powder was added on top. Results for these determinations were in the 5 ppm range for S.R.M. 616. Precision was improved. Assuming that the National Bureau of Standards values were correct, the value obtained was over

six times higher than the anticipated value. Since the aqueous standards used had been carefully cross checked and found correct, it seemed unlikely that the problem lay with them. Another background check using the hydrogen lamp gave evidence of a low but substantial background absorbance. At this point a complete profile of temperature versus absorption using the hydrogen lamp was made for the glass samples. Figure 12 shows the results of this determination. No absorption is noted up to and slightly above 2000°C. Between 2150 and 2300°C broad-band absorption or scattering increases to an extremely high level. By 2400°C the level is high enough to make accurate determinations with or without background correction difficult. It is worth noting that the boiling point for SiO_2 is approximately 2200°C (76). It is, thus, probable that SiO_2 is the background producing substance.

In retrospect it seems probable that the failure to note background absorption at an earlier time was due to the close proximity of the temperature chosen for atomization to the inflection point in the glass vaporization curve. The furnace temperature will vary by $\pm 50^\circ\text{C}$ from one day to the next when run at the same apparent power settings. In prior work this has not been a problem but

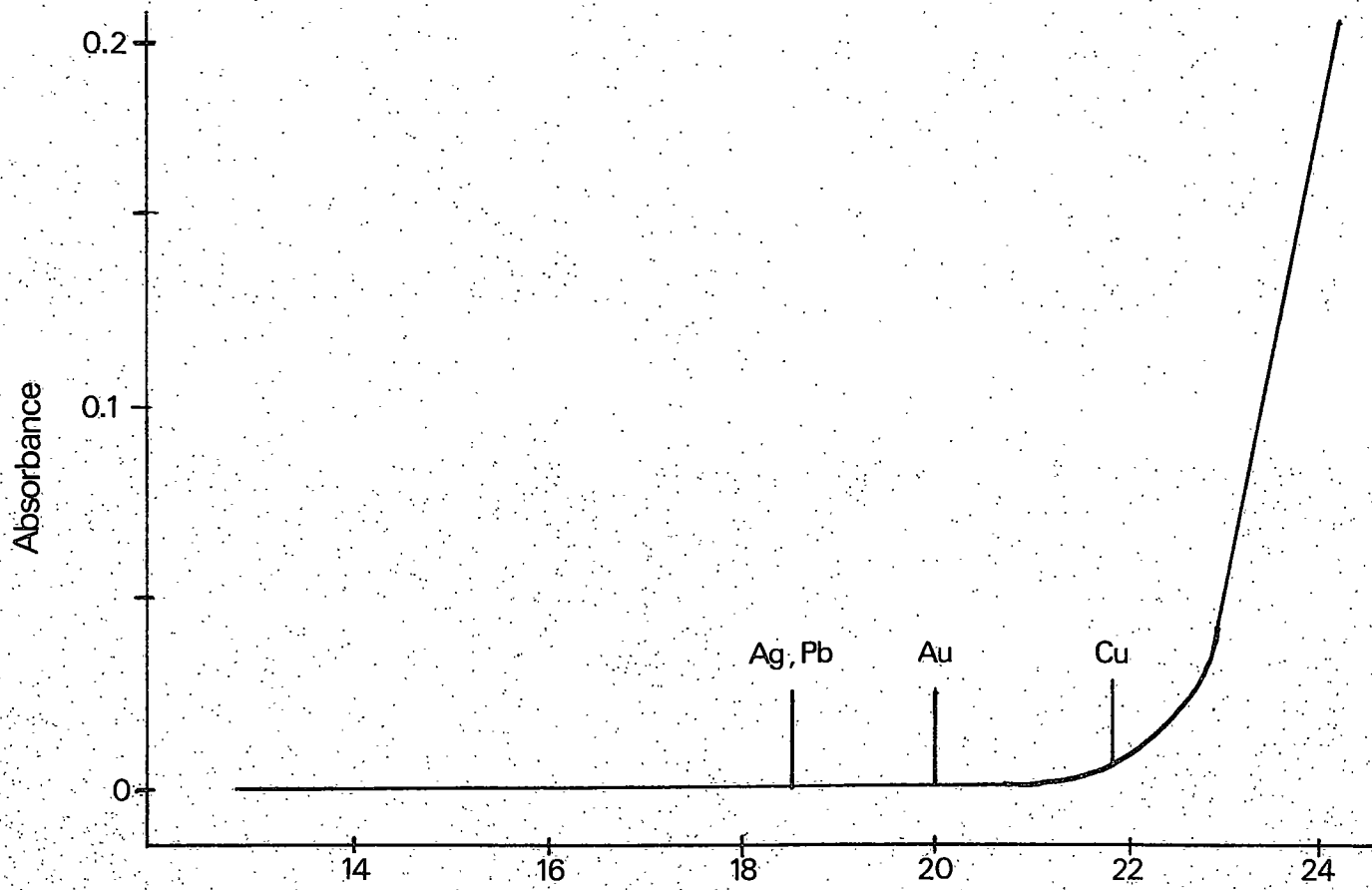


Figure 12. Background absorbance versus temperature for N.B.S. S.R.M. 616

examination of the glass vaporization curve shows that at the temperature at which copper was determined, such a variation would be critical.

One interesting observation was that the disappearance or retention of the glass in the cup did not correlate with background in all cases. With extremely small samples the glass may be plating out totally without entering the light path. Examination of the furnace after numerous determinations showed that the glass was plated near the ends of the heater tubes but no evidence was found of glass residue in other parts of the furnace. The fate of these small amounts of glass is thus unclear. It is tempting to say that the slight elevation in values versus N.B.S. values for silver and gold is caused by a low background component added to the sample signal but no evidence of this was found after exhaustive study. It does seem that whether the element of interest distills from the glass or is vaporized with a small part of the glass one can obtain the same result. It is also clear that simultaneous background correction is needed when operating above 2000°C.

Results of copper determinations without background correction were presented in Table II. Table VII shows the results obtained for the two S.R.M.'s using proper

Table VII. Copper Determination*

N.B.S. S.R.M. 614	Value	Range	95% C.L.
Peak Area Value	1.61	0.32	0.24
N.B.S. Value (63)	1.37		0.07 [†]
N.B.S. S.R.M. 616			
Peak Area Value	0.82	0.16	0.04
N.B.S. Value** (64)	0.80		0.09

*Average of 5 or more determinations
Aqueous standards

**Uncertified

[†]Range or 95% C.L., whichever larger

background correction of the type described earlier. N.B.S. values for S.R.M. 614 are from isotope dilution mass spectrometry work. Values for S.R.M. 616 are from neutron activation analysis determinations using S.R.M. 614 as a standard.

In the case of copper, in particular, the choice of correct operating temperature coupled with background correction made possible an otherwise difficult analysis. The ability to use varying temperatures stems from the fact that studies show that peak areas are the same for identical analyte element concentrations over a wide range of temperatures and matrices. Figure 13 shows examples of the effect of varying the matrix. In the water matrix case it may be supposed that the time from first appearance of the signal to the attainment of maximum peak height is proportional to the time required for vaporization of the sample while the slow decay represents the time for diffusion of the sample from the light path (74,77). For the other matrices, this assumption is incorrect. In these cases the maximum peak height represents the point at which the vaporization rate to sample loss ratio is at a maximum. Figure 14 shows a striking example of this. The peak multiplicity is due to the evolution of analyte element from

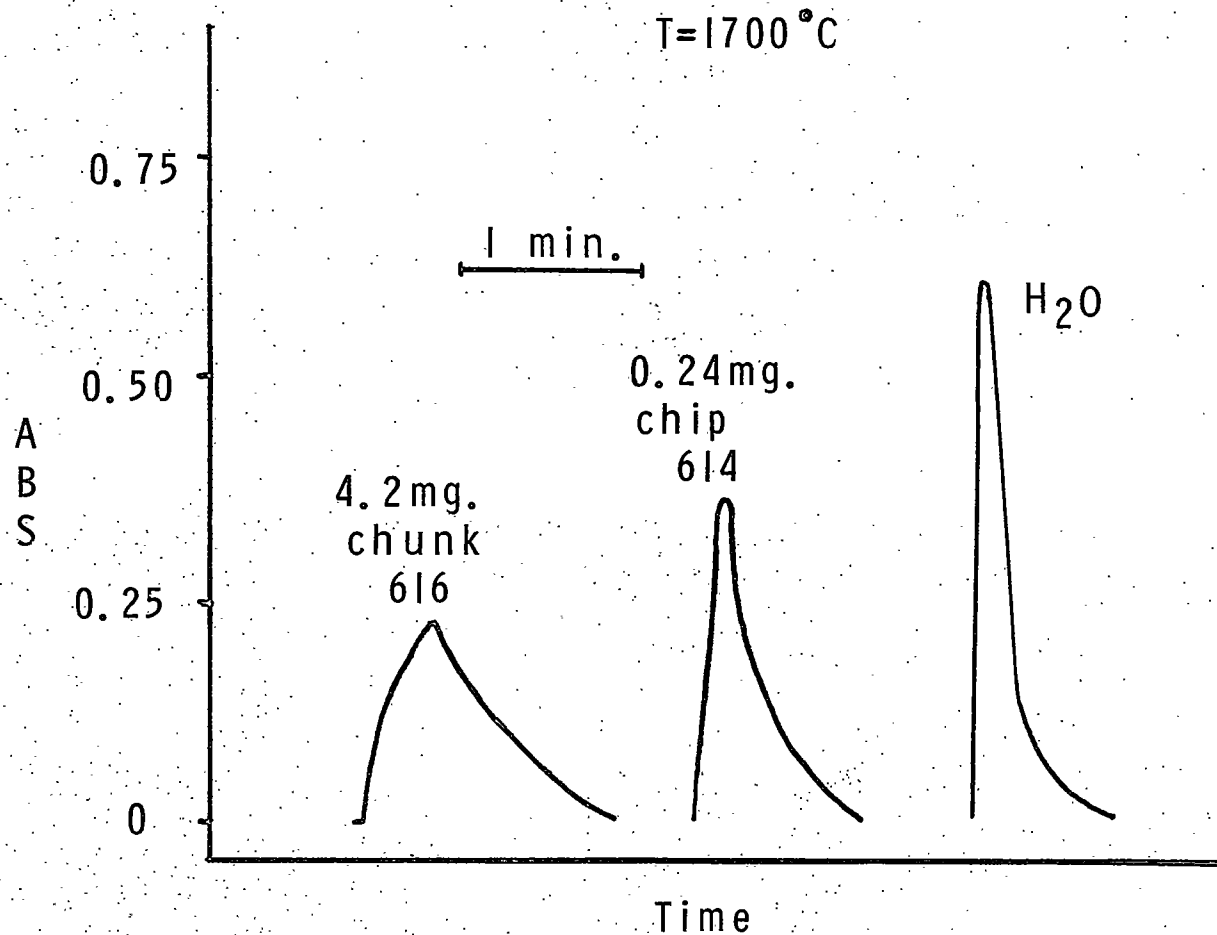


Figure 13. Peak shapes for 10^{-10} g silver for different sample matrices

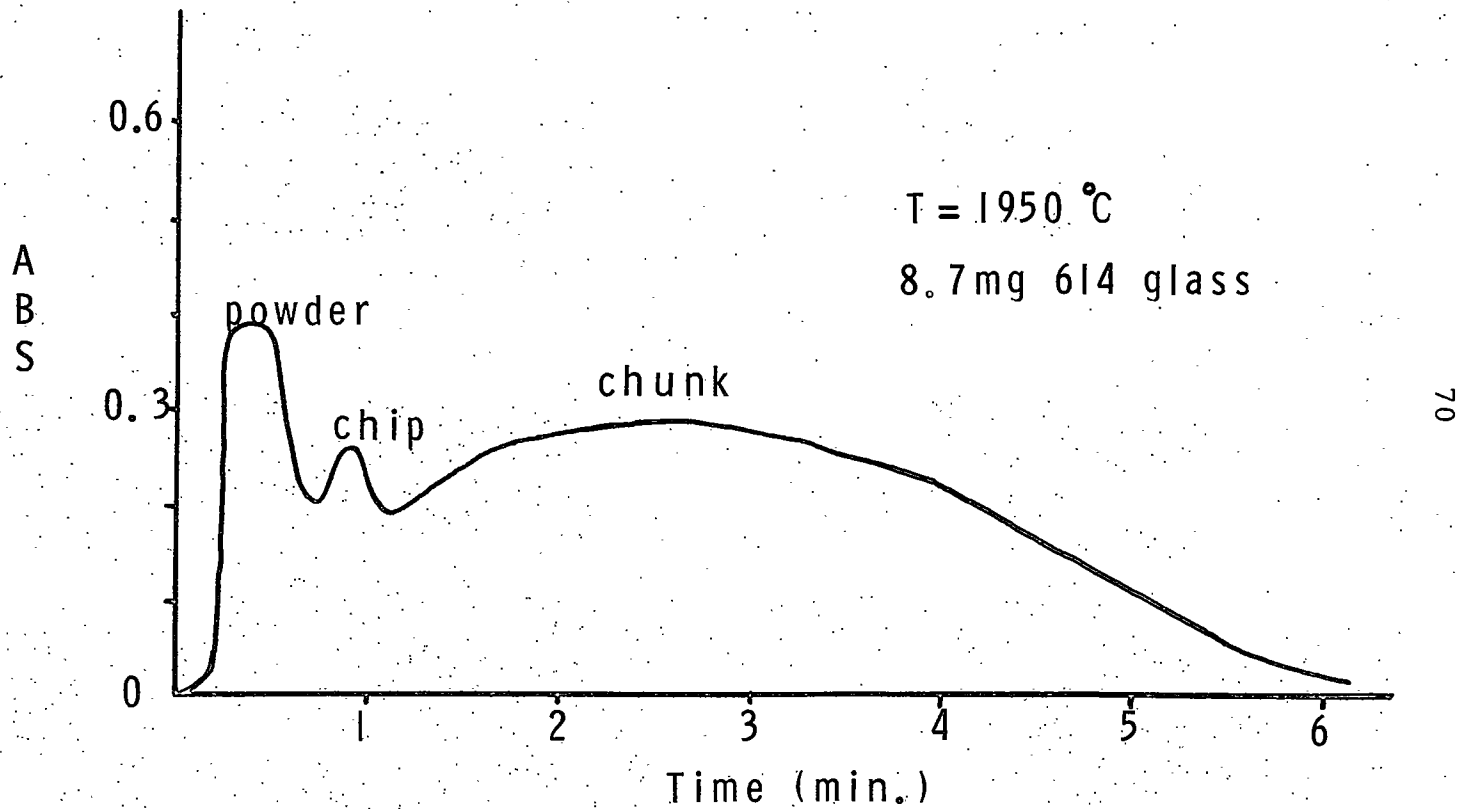


Figure 14. Typical copper peak

various parts of the overall sample. Since residence time for most atoms in the furnace is less than 10 seconds, it is obvious that a great amount of the analyte element is gone before the last part enters the light path. Theoretical studies attempted (17,77) have made the assumption that the area from which the sample is vaporized is a known constant. For the glass samples studied and for similar samples, this is not true. Avni and Harel (78) noted that when silicate rock samples were analyzed in the d.c. arc, a rapid fusion took place which resulted in the formation of glass beads. This resulted in loss of sample surface area and change in vaporization rate. Similar beads are formed irreproducibly in the furnace.

Since control of vaporization rate is difficult, it is important for experimental conditions such as flow rate to be as constant as possible. It is also important that all avenues of sample loss be reproducible from sample to sample. The extent to which this is true for the Woodriff furnace is indicated by the results for copper. It should be noted that the peak shown in Figure 14 supplied one of the data points for Table VII.

CONCLUSIONS

This work was undertaken to develop instrumentation and methods which would allow the analyst to determine trace inorganics in solids without significant pretreatment. It was demonstrated that with proper choice of temperature, it is possible to selectively distill analyte elements from the solid matrix. Using peak area mode of data acquisition, it is possible to determine trace element concentrations for these solids using aqueous solutions as standards. Precisions for atomic absorption spectroscopic determinations made in this way were comparable to those reported for determinations made by isotope dilution mass spectrometry and neutron activation analysis. Sample preparation is not critical and analysis time is cut to a few minutes per sample. In addition, instrumentation for atomic absorption is cheap and readily available.

For determinations where background correction is advisable, the sequential hollow cathode system provides an inexpensive, accurate method which is comparable to commercial units in performance. The hollow cathode lamp designed for this system eliminates the need for complex optics. In addition, the lamp has the advantages offered by a demountable configuration.

Use of the techniques and instrumentation presented with a Woodruff furnace atomization system provides a direct and reasonable alternative for the analysis of solids.

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