



Development of techniques for non-flame spectroscopic determination of trace metals
by Darryl Duane Siemer

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

A mercury analysis system is presented which is adaptable to the determination of mercury in any type of sample. Mercury vapor in air or other gases is captured by filtration through gold plated, porous graphite carbon rod atomizer tubes. Mercury in solid samples is converted to the metal vapor by burning the sample in pure oxygen. Mercury in aqueous samples is reduced to the vapor with stannous chloride. The gold plated porous tubes are placed between the rods of a carbon rod atomizer and the mercury atomized and measured with an atomic absorption spectrometer. Substances which normally interfere in the atomic absorption determination of mercury pass through the walls of the porous graphite tubes and are not a problem. Operating parameters and some applications are discussed. Detecting limits in the ppm to the ppb level with relative standard deviations of 4% to 10% range are achieved.

Porous graphite tubes are used as air filters. Particulate matter filtered from the air is analyzed for a wide range of metallic elements by atomizing the material on the tubes directly into the light path of an atomic absorption spectrometer with a carbon rod atomizer. The filtration characteristic of the tubes, standardization, and the applications are discussed. The detection capabilities of the technique for most elements are better than those of most other methods published to date.

A process for coating graphite objects with an impervious coating of pyrolytic carbon is described. The method consists of passing natural gas over the object to be plated inside a wire-wound tubular quartz furnace. The coating process and the properties of the pyrolytic carbon coating are discussed. The pyrolytic carbon coatings are demonstrated to significantly improve flameless atomic absorption atomizers. The process also allows construction of graphite objects useful for other purposes.

DEVELOPMENT OF TECHNIQUES FOR NON-FLAME SPECTROSCOPIC
DETERMINATION OF TRACE METALS

by

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ABSTRACT

A mercury analysis system is presented which is adaptable to the determination of mercury in any type of sample. Mercury vapor in air or other gases is captured by filtration through gold plated, porous graphite carbon rod atomizer tubes. Mercury in solid samples is converted to the metal vapor by burning the sample in pure oxygen. Mercury in aqueous samples is reduced to the vapor with stannous chloride. The gold plated porous tubes are placed between the rods of a carbon rod atomizer and the mercury atomized and measured with an atomic absorption spectrometer. Substances which normally interfere in the atomic absorption determination of mercury pass through the walls of the porous graphite tubes and are not a problem. Operating parameters and some applications are discussed. Detecting limits in the ppm to the ppb level with relative standard deviations of 4% to 10% range are achieved.

Porous graphite tubes are used as air filters. Particulate matter filtered from the air is analyzed for a wide range of metallic elements by atomizing the material on the tubes directly into the light path of an atomic absorption spectrometer with a carbon rod atomizer. The filtration characteristic of the tubes, standardization, and the applications are discussed. The detection capabilities of the technique for most elements are better than those of most other methods published to date.

A process for coating graphite objects with an impervious coating of pyrolytic carbon is described. The method consists of passing natural gas over the object to be plated inside a wire-wound tubular quartz furnace. The coating process and the properties of the pyrolytic carbon coating are discussed. The pyrolytic carbon coatings are demonstrated to significantly improve flameless atomic absorption atomizers. The process also allows construction of graphite objects useful for other purposes.

GENERAL INTRODUCTION

The use of atomic absorption spectroscopy as a routine analytical tool began in the nineteen forties, when it was applied to the determination of mercury in air (1). In 1954 a paper (2) was published concerning the use of atomic absorption for the analyses of gases. Up to 1955, the use of atomic absorption spectroscopy for analysis work was confined to the applications discussed in these references.

The primary reason for this dearth of progress in the light of the burgeoning application of various atomic emission techniques was that none of the methods in which atomic absorption measurements had been made by experimental physicists satisfied the practical requirements of an analytical tool from the standpoints of the range of elements embraced, sensitivity, and simplicity. Perhaps even more important was the fact that the potential advantages of absorption methods of analyses with respect to emission methods had not been clarified to the extent to promote research in the field.

In 1955 Walsh (3) and, independently, Alkemade and Milatz (4) published papers indicating substantial advantages of absorption methods over emission techniques for quantitative spectrochemical analysis. During the ensuing years several thousand works have been published on atomic absorption. They were concerned both with research on the mechanisms inherent to the absorption measurements and on the extension of the field to an ever increasing range of substances. The method is now widely used in many countries and has become the most pop-

ular technique of elemental analysis for a wide range of sample types.

The need for more sensitive analytical equipment spurred research in nonflame, pulsed atomizers for atomic absorption (5, 6, 7, 8). These atomizers are much more sensitive and, in some cases, allow chemical analysis of samples with no preconcentration or separation steps. Several versions of these atomizers have been made commercially available by major scientific instrumentation companies within the last three years. The purpose of the work described in this thesis is to extend the analytical capability of these atomizers in the area of environmental analysis by improving both the atomizers themselves and the analytical techniques for which they are used. A widely distributed atomizer, the Varian Techtron Model 63, was chosen as the model to be used for this research both because of its availability to analytical chemists and its potential versatility for different atomization chamber modification.

THE DETERMINATION OF MERCURY IN AIR, WATER, AND SOLID SAMPLES WITH THE CARBON ROD ATOMIZER

Introduction

The analysis of samples for fractional part per million levels of mercury is a common problem in analytical laboratories. Several excellent reviews have been published recently which discuss the extent of the contamination problem as well as the analytical methodology presently used. (9, 10, 11) There are three basic approaches used for the analysis. The first and oldest technique involves a controlled pH dithizone extraction of mercury from a solution with subsequent spectrometric analysis. This analysis is neither as specific nor as sensitive as are the other two approaches.

The second approach is neutron activation analysis. The absolute detection limits achievable, on the order of 10^{-8} gram absolute (12), are very good; however, it suffers from poor reproducibility, very high cost, and generally involves sending samples off to central facilities equipped with high neutron flux sources. This feature usually necessitates fairly long waits for analytical results.

Atomic absorption, on the other hand, is relatively inexpensive and can be accomplished with readily available equipment. A. A. analysis for mercury is usually accomplished by adding a reducing agent (usually stannous chloride) to a digestate and sweeping the evolved elemental mercury out of the solution into a cold vapor absorption tube in which the absorption of the Hg 2537 Å resonance line is measured. The analytical sensitivity reported varies but is usually on the order of 1 - 2

ng Hg for 1% absorption.

The flameless technique is feasible because mercury possesses the properties of having an appreciable vapor pressure at room temperature and of not being readily oxidized by air. These properties were first exploited by Woodson (13) who described in 1939 a simple instrument for measuring mercury vapor in air. Ballard et al (14 -16) extended the method to solution analysis. They ran the solutions through asbestos pads soaked in cadmium sulfide. Mercury displaced the cadmium and was effectively filtered from the solutions. It was subsequently driven off into the absorption cell by the application of heat. Pappas and Rosenberg (17, 18) employed a modification of the technique for the analysis of solid foodstuffs. The samples were oxidized in a combustion flask, and the gaseous combustion products were absorbed in 1.2 N HCl. The pH was adjusted to 6 - 7 and the solution passed through CdS impregnated pads as previously described.

Poluektov, Bitkun, and Zelyukova (19) were the first to utilize direct reduction of mercury to the elemental state by stannous chloride for cold vapor A. A. determination of mercury. Hatch and Ott (20) applied the technique to acid digested soil and cobalt and nickel metal samples. The most commonly used technique today for mercury determination in a wide range of organic samples was described by Lindstedt (21) who analyzed urine by combining the potassium permanganate-sulfuric acid digestion method of Jacobs and Singerman (22) followed by stannous

chloride reduction of the mercury. The evolved mercury is swept from the solution with a gas stream which carries the mercury into a quartz-windowed flow-through cell mounted in an A. A. spectrometer. The peak absorption of the 2537 Å mercury resonance line is measured.

The reduction-aeration technique is fairly rapid, adaptable to a wide range of samples, and inexpensive, but it suffers from two major weaknesses. As the analysis is commonly performed, the final measurement is subject to the vagaries of kinetics. The rate of flushing gas flow and the rate of mercury reduction by stannous ion, which in turn is affected by the temperature, volume, and chemical nature of the solution, both affect the peak atomic absorption. The second problem concerns other materials present in the sample which volatilize and subsequently absorb radiation at the mercury 2537 Å line. Among these are cyclic organic compounds, sulfides, acetone, and water vapor.

There are several basic approaches to solving these problems. The most obvious way to solve the problems associated with the kinetics of the reduction process is to integrate the atomic absorption peak and use a peak area instead of peak height as the measure of mercury. However, most atomic absorption instruments are not capable of this.

Several ingenious techniques have been developed to circumvent the problem of non-atomic background absorption by compounds. Ballard (16) took readings of the cell containing the mercury vapor on two separate instruments, the first being a unit containing a mercury lamp and the

second a standard spectrophotometer having a wide bandpass (32 Å) and a continuum source. The difference between the two readings is due only to mercury.

Barringer (23) and Ling (24, 25) compensated for non atomic absorbers by using the wings of the broadened 2537 Å line, the center of which has been completely absorbed by passing through an intermediate absorption cell saturated with mercury vapor. This source is insensitive to mercury but is sensitive to other substances which absorb in that region. By comparing this signal with that obtained using the emission line of the mercury lamp with no intermediate mercury filter, a measure of mercury vapor alone is made.

The background method described by Koirttyohann and Pickett (26) and applied by Kahn (27) in which light from a continuous source and a mercury lamp are alternatively beamed through the absorption cell is also useful. Lech, Siemer, and Woodruff (28) ratioed the absorption of a nearby non-resonance mercury line to the 2537 Å line as a means of background correction.

These expedients, with the exception of peak integration, do not eliminate the kinetics difficulties. In order to solve this problem and to eliminate the bulk of the non-atomic absorption interferences, several means of separating and concentrating the mercury alone in a solution or stream of gas have been used. With these techniques, the mercury is collected over a period of time and released and measured

under carefully controlled conditions in a short period of time.

Moffit and Kupel (29) collected mercury in gas streams with specially impregnated charcoal filters. The graphite was then placed into a sampling boat which was swung over a flame in a standard A. A. spectrometer. The sampling boat A. A. measurement did not fully realize the potential of the system.

Another method for the determination of mercury is deposition from solution onto a silver wire or screen, either by chemical deposition (Hinkle and Learned, 30, 31) or electrolysis (Brandenberger and Bader, 32, 33). The collected mercury was driven off the wire by rapid heating and the mercury introduced into and measured in an absorption cell just as in the aeration method.

Vaughn and McCarthy (34), Ulfvarson (35), Lidduns and Ulfvarson (36), and Anderson et al. (37) concentrated mercury in streams of gas onto finely divided gold by amalgamation. All interfering substances passed through the system and were vented, after which the mercury was driven off the gold by heating to 400 - 500 °C into the absorption cell. Lech, Siemer, and Woodriff (28, 42) used gold plated graphite to collect mercury in air or to retain the mercury from solutions dried in plated cups. The cups were then inserted into a Woodriff furnace atomizer for the mercury determination.

The sensitivity of the furnace technique of Lech, Siemer, and Woodriff was better by a factor of two or three than that of any other A. A.

method reported to date. The only disadvantage of the system as far as the average analytical chemist is concerned is that the Woodriff furnace atomizer is not widely distributed. The purpose of the research to be discussed here was to develop a complete mercury analysis system applicable to a commercially available non-flame atomizer--specifically the carbon rod atomizer.

An outline of the method is as follows. The mercury in the sample is converted to the free metal vapor by stannous chloride reduction or by combustion in oxygen. Then the mercury is carried by a stream of gas into a filter adaptor containing a gold-plated cylindrical tube of porous graphite. The mercury is retained on the gold while potentially interfering gases pass through the tube. The tube is then placed between the rods of a carbon rod atomizer similar to that marketed by Varian Techtron and heated to atomize the mercury. The atomic absorption spike is then recorded.

General Outline of Experimental Technique

The carbon rod atomizer (CRA) was constructed at this laboratory and is depicted in Figure 1. It is designed to fit into a Techtron burner-spray chamber assembly in the same manner that a Varian Techtron Model 63 CRA does. The main functional points of difference between the Techtron CRA and our homemade version is that our model is somewhat larger (to accomodate standard spectrographic $\frac{1}{4}$ " rods and tubes) and features flexible mounting of both rod support posts and a superi-

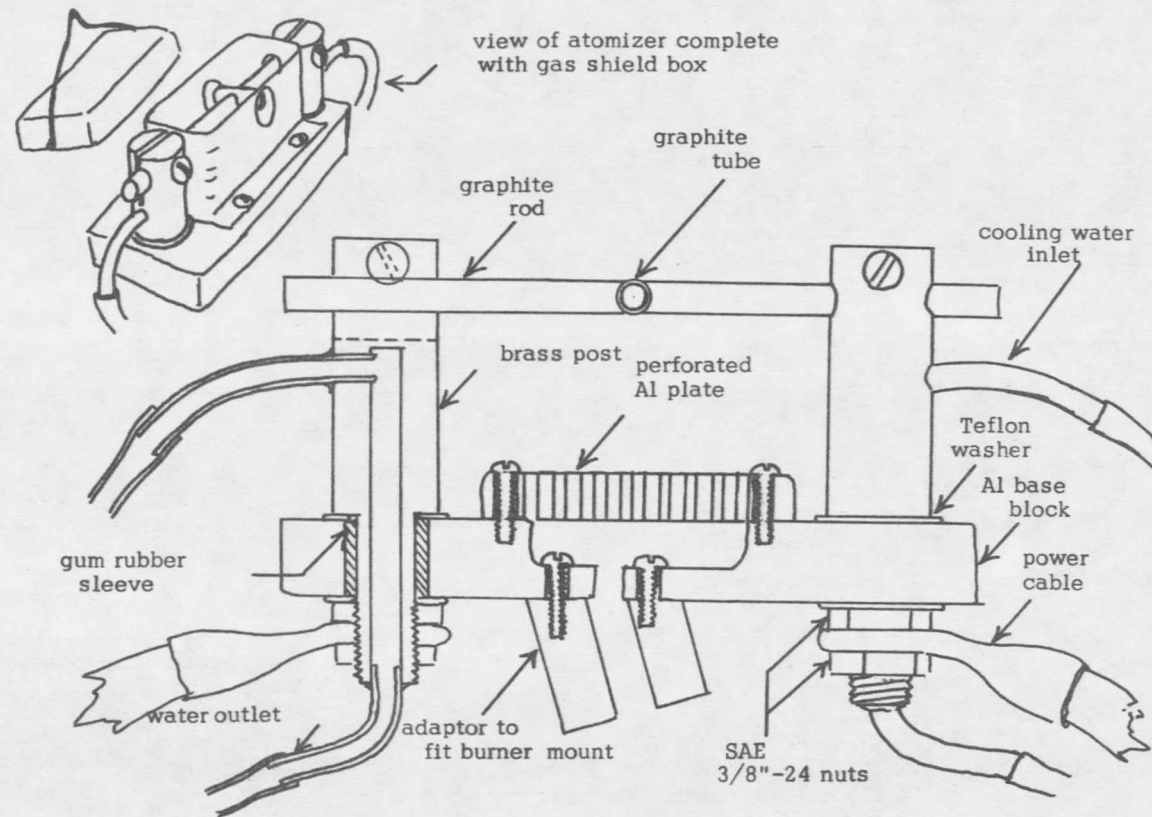


Figure 1. Carbon Rod Atomizer

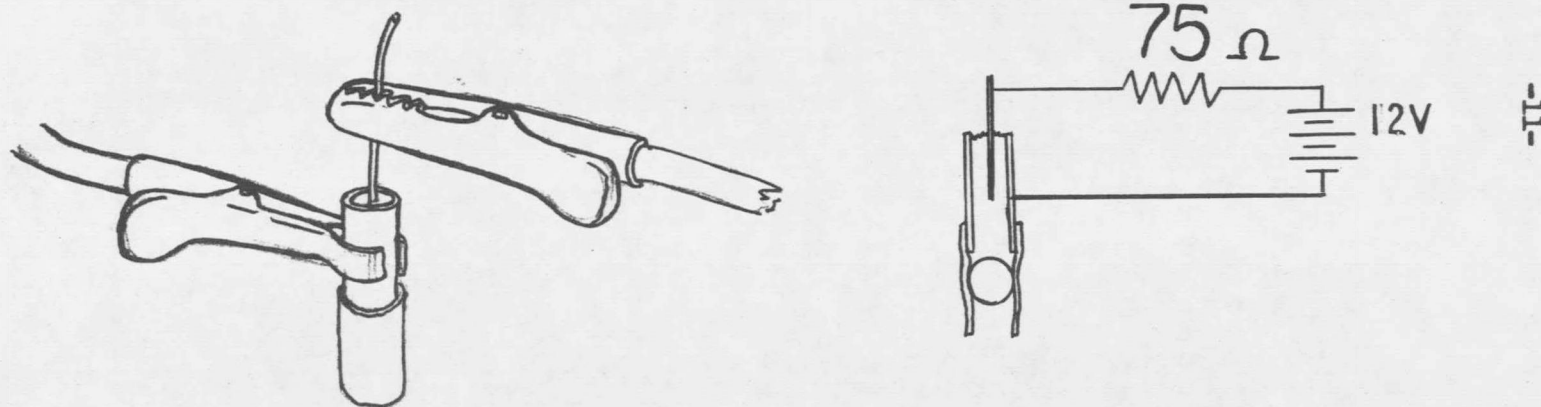
or gas shield system. Nitrogen gas is used to flush the air from around the hot carbon when a sample is atomized.

The CRA is powered with a 5 KVA G. E. transformer (9t21B1037G2) controlled with a type 242, 4.2 KVA Powerstat autotransformer. This power supply provides from 0 to 13 rms volts and can furnish in excess of 400 amps. The temperature of the atomization tube is measured with a Pyro optical pyrometer. Temperatures in excess of 3000 °C are readily obtainable with this system.

The porous graphite tubes are made by drilling a 4.5 mm hole (No. 13 drill) in 15 mm lengths of 6.2 mm diameter National AGKSP or AGKS spectroscopic graphite rods. Each tube is plated on the inside with about 1.5 mg of gold in the following manner: One end is sealed off with a rubber tube sealed with a glass bead; 0.3 ml of an acidified gold chloride solution is placed into the tube; a platinum wire anode is inserted; and the plating current is applied between the tube and the anode for 4 - 5 minutes with a 12 V automobile battery in series with a 75 ohm resistor. The gold solution contains about 5 mg/ml Au. Figure 2 schematically depicts the process.

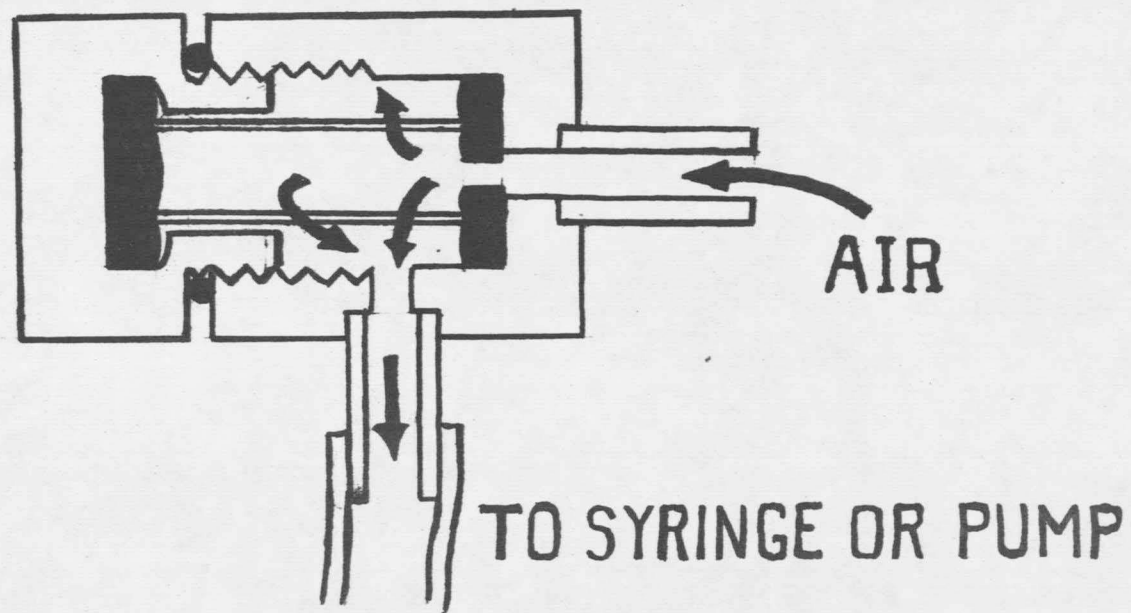
Figure 3 illustrates the filtration adaptor used to support the gold plated tubes. It is essentially similar to the one described by Woodriff and Lech (38) except that the soft elastomer gaskets seal both ends of the tube with the exception of the air inlet. The body of the filter adaptor is machined from acrylic plastic. The gasket material

GOLD PLATING



5 mg Au/ml in dilute aqua regia

Figure 2. Gold plating apparatus



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Figure 3. Filter adapter

was butyl or natural gum rubber in the original models, but it was later discovered that silicone rubber of the type used for gas chromatograph inlet septa provides a surer seal and is cleaner.

The atomic absorption instrumentation used are those described in the paper by Woodriff et al. (39) with the substitution of the CRA for the furnace and the addition of a deuterium lamp background correction system. Figure 4 is a schematic of the A. A. spectrometer with a listing of the individual components used. The CRA power supply and the cooling water lines have been deleted for clarity.

A short (35 mm long), quartz-windowed, cold vapor absorption cell was constructed. Figure 5 depicts how it was used to test the mercury filtration efficiency of the gold plated tubes. Ten cc of air saturated with mercury vapor (at 24 °C) was drawn through the walls of both plated and unplated porous graphite tubes. The filtered air in the syringe is then expressed into the absorption cell and the absorption of the 2537 Å line is measured. A stoppered two liter erhlenmeyer flask containing approximately 5 g of mercury metal served as a source of mercury vapor of known concentration.

A 1000 ppm stock mercury solution was made by dissolving $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in N/10 HNO_3 . This solution was stabilized by adding 0.01 g/100 ml of dry $\text{K}_2\text{Cr}_2\text{O}_7$. Dilutions of this stock were made daily with N/100 HNO_3 .

Eppendorf pipets of 5, 10, 20, 50, and 100 microliter capacity were

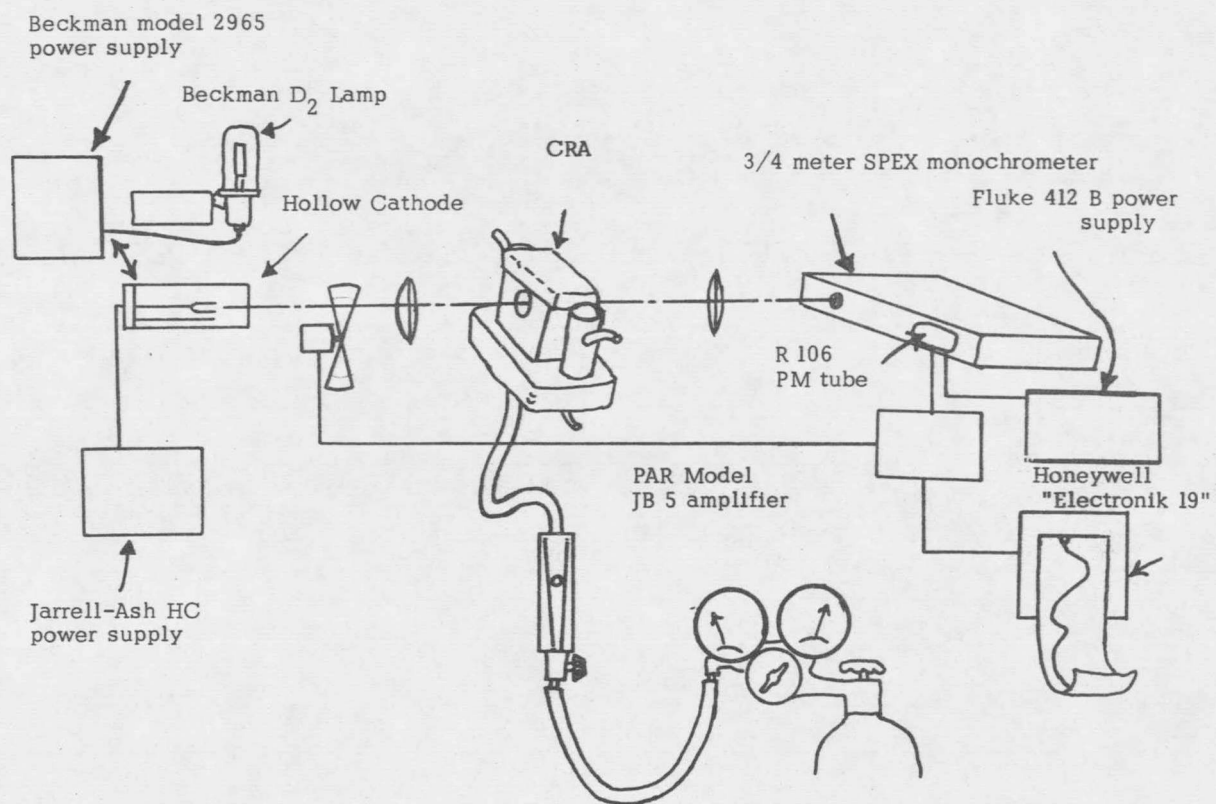


Figure 4. Schematic of AA spectrometer

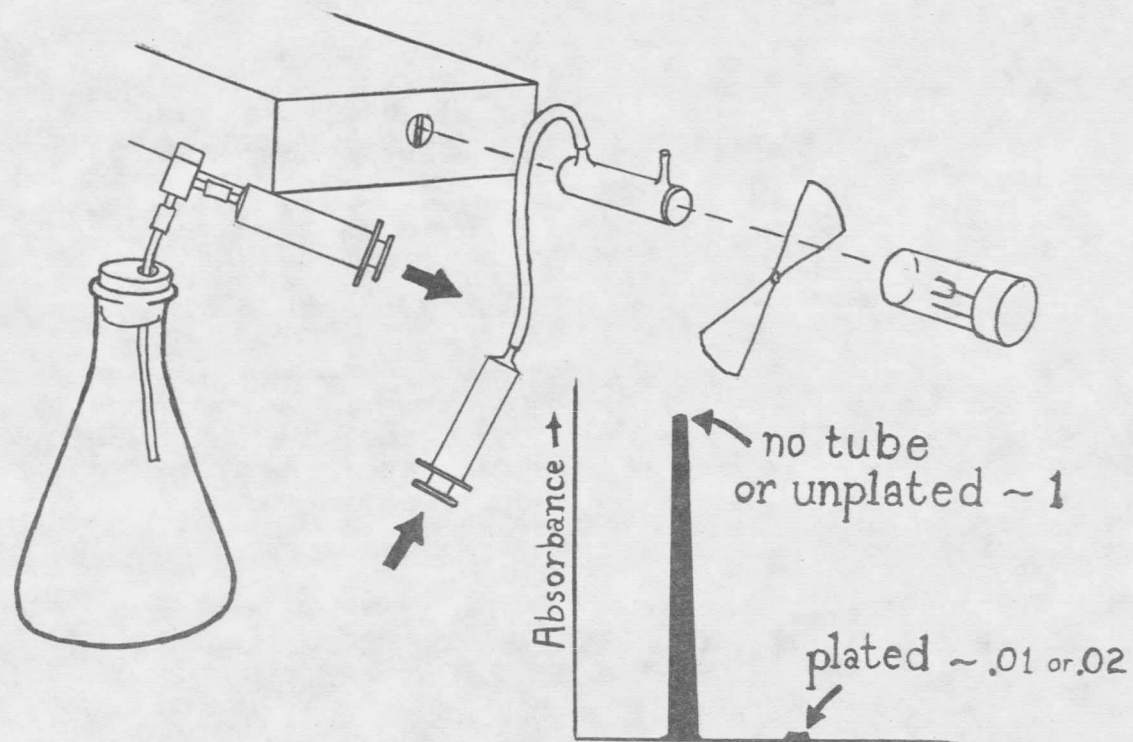


Figure 5. Apparatus for testing filtration efficiency

used to make most of the dilutions and sample additions required.

A homemade nickel-nichrome thermocouple was used to determine temperatures lower than those measureable by the optical pyrometer. The thermocouple output was amplified by a 741 operational amplifier used in a follower-with-gain configuration and the amplified output read with a VTVM.

Results and Discussion of Basic Procedure

The first criterion to be met by a gas sampling system is a good collection efficiency for what is being measured. This was tested (Figure 5) by comparing the results of this experiment performed with eight graphite tubes both before and after they were plated with gold. Table I gives the results of this experiment. The value for "Fraction Hg Collected" in this table is defined as one minus the ratio of the atomic absorbance of the mercury vapor in the air passed through the walls of a tube to the atomic absorbance of the same amount of air drawn through the filtration adaptor with no tube in place. It is clear that essentially all of the mercury is captured by the plated tubes. It is also apparent that AGKSP graphite tubes not plated with gold are ineffective for trapping mercury vapor.

During the actual determination, the gold plated tube is placed between the rods of the CRA and rapidly heated to atomize the mercury. To ascertain whether this repeated heating has any effect upon the tube's ability to trap mercury vapor, the Hg filtration efficiency

TABLE I

MERCURY COLLECTION EFFICIENCY OF POROUS GRAPHITE TUBES

<u>Tube No.</u>	<u>Type of Tube</u>	<u>Fraction Hg Collected*</u>
1	unplated	- 0.032
2	"	- 0.015
3	"	0.025
4	"	-0.015
5	"	0.038
6	"	-0.033
7	"	-0.015
8	"	0.050
		Average: $0.000375 \pm 0.032^{**}$
1	plated	0.972
2	"	0.980
3	"	0.986
4	"	0.986
5	"	0.994
6	"	0.986
7	"	0.986
8	"	0.986

* $1 - \frac{AA(\text{tube})}{AA(\text{no tube})}$

Average: $0.984 \pm 0.0063^{**}$

** one standard deviation

test as described above was repeated ten times upon a single tube (driving off the mercury each time between tests). Table II gives the results of this experiment. There was no diminution of trapping efficiency noticed.

In order to ascertain how much gold is required to effectively trap all of the mercury in air passed through the walls of a plated tube, a series of six AGKSP tubes were plated with differing amounts of gold. The fraction of Hg retention in 10 cc of saturated air (24 °C) was measured (Table III). From literature ⁽⁴⁰⁾ values of the vapor pressure of mercury and the use of the ideal gas law, it can be calculated that 10 cc of air saturated at 24 °C contains 2.0×10^{-7} g of mercury. Because this amount of mercury is beyond the upper range of the analytical curve resulting from determination of mercury in the CRA, it is apparent from the table that 10^{-4} g or more gold is sufficient for the plate. Approximately 1.0 - 1.5 mg gold was finally decided on for normal use, both to ensure a healthy excess and to make visual inspection of the gold plate easier.

A study of the ability of tubes plated with differing amounts of gold to capture successively greater amounts of mercury vapor was undertaken. Repeated aliquots of 10 cc each of air saturated at 24 °C with mercury vapor were drawn through plated tubes and the Hg retention efficiency measured after each time. The mercury was not driven off between each test as before. Figure 6 depicts the results.

TABLE II

EFFECT OF REPEATED HEATING ON A GOLD PLATED TUBE'S
ABILITY TO COLLECT MERCURY

<u>Trial No.*</u>	<u>Fraction Hg Collected</u>
1	0.980
2	0.983
3	0.986
4	0.994
5	0.994
6	0.986
7	0.994
8	0.994
9	0.994
10	0.994
Average:	$0.990 \pm 0.00554^{**}$

*tube heated to 900 °C between trials

** one standard deviation

TABLE III

MERCURY COLLECTION AS A FUNCTION OF THE AMOUNT OF GOLD
PLATED ONTO TUBES

<u>Number</u>	<u>Amount of Gold on Tube (g)</u>	<u>Fraction Hg Collected</u>
1	2.5×10^{-7}	0.561
2	2.5×10^{-6}	0.808
3	1.0×10^{-5}	0.901
4	5.0×10^{-5}	0.970
5	5.0×10^{-4}	0.987
6	1.5×10^{-3}	0.994

Collections from 10 ml air (saturated with Hg vapor)

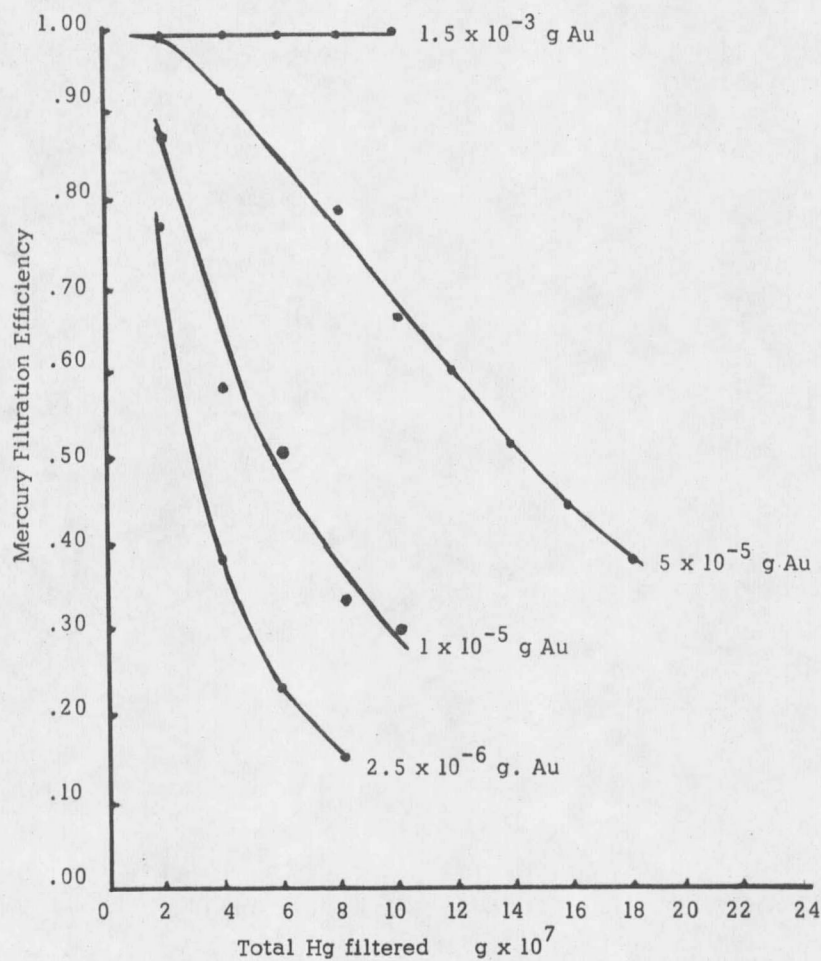


Figure 6. Filtration Efficiency as a Function of the Amount of Mercury and Gold

After the effectiveness of the tubes as filters was established, it remained to determine suitable conditions for the CRA atomizer and subsequent determination of mercury. Figure 7 shows the results of experiments to determine an analytical curve for mercury. Various volumes of air saturated with mercury in a large flask immersed in an ice-water bath at 0 °C were drawn through a series of plated tubes. The mercury was atomized at a CRA power setting resulting in a final temperature of 850 °C and measured by the A. A. spectrometer. The figure shows data from two methods of standardization. The points denoted with a triangle are based on filtration of the air saturated with mercury at 0 °C with calculation of the amount of mercury based on a literature value of the vapor pressure (32). Those denoted with a circle are based on the drying of 5, 10, or 15 microliter aliquots of a freshly prepared 2 ppm mercury solution onto the tubes.

The relative standard deviation for the filtration technique was found to be 6.0% for a series of five tubes each with 10 cc of saturated air (3.2×10^{-8} g Hg) filtered through them. The R. S. D. for solutions pipeted directly into the tubes, dried and atomized was considerably poorer (9.6% for 7 replicates of 2.0×10^{-8} g Hg). Because there is no demonstrable difference in the slopes of analytical curves drawn based on either method of standardization and that based on filtration of vapor is more reproducible, it is probably better to use it for standardization for routine air analyses.

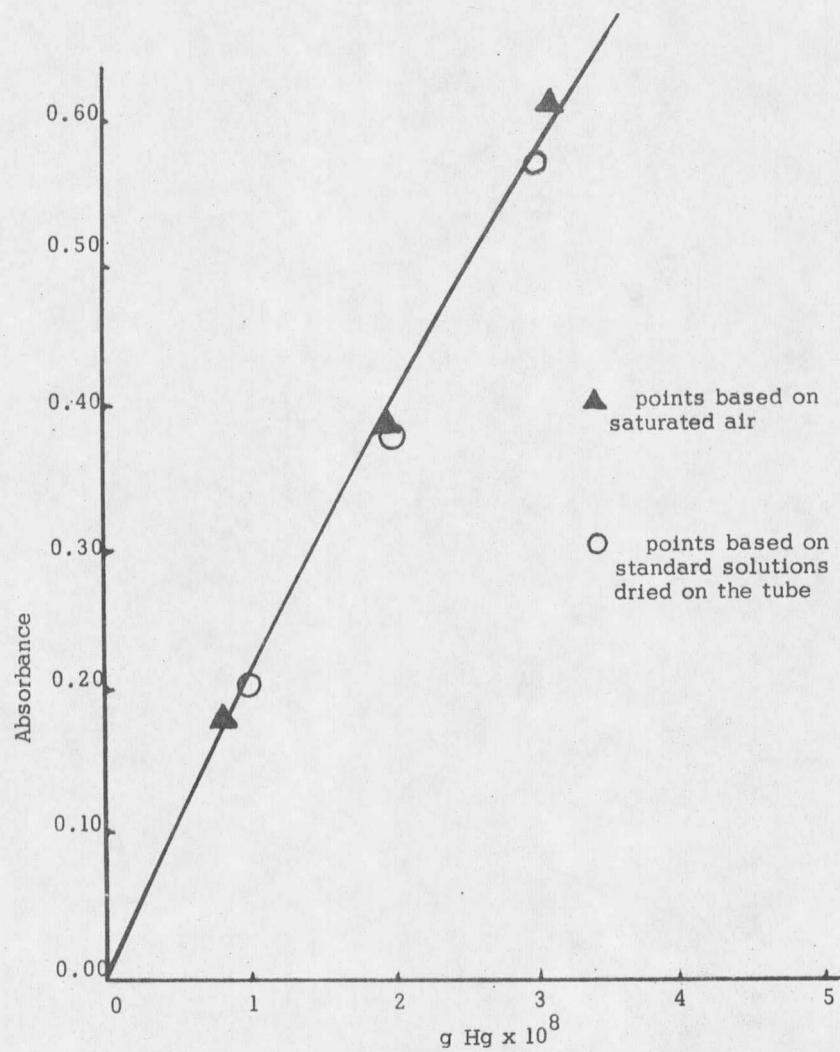


Figure 7. Standard Curve for Mercury Based on Two Different Methods of Standardization

The choice of CRA power supply atomization settings is largely arbitrary and the final analytical results depend more upon the particular setting than do the results when similarly prepared cups are used in the Woodruff furnace (28, 41, 42) at different temperatures. This is because the absorbance peak height is what is measured--not the area. When low atomizer power settings are used, the first volatilized mercury atoms have an opportunity to diffuse out of the light path before the last of the mercury is driven off of the tube. In the Woodruff furnace, the atoms are confined to the optical axis for a longer time and have less chance to escape before complete volatilization occurs. See Appendix I for clarification.

A study was made of the temperature to which a plated tube could be heated before appreciable mercury was lost. This was done by filtering 2 cc of saturated air (27 °C) through a tube and then placing it into the CRA. The power supply was first turned on to a low setting for one minute, after which the temperature of the tube was measured with the thermocouple. Then the N₂ flushing gas was turned on, the CRA power supply turned to a higher setting (450 watts), and the remaining Hg atomized and the peak height measured. Up to a final temperature of 150°C no mercury was lost from the plated tubes. At 230 °C all of the mercury was vaporized.

Figure 8 depicts results of a study to ascertain the best CRA power setting for atomization. Two and one half cc samples of mercury

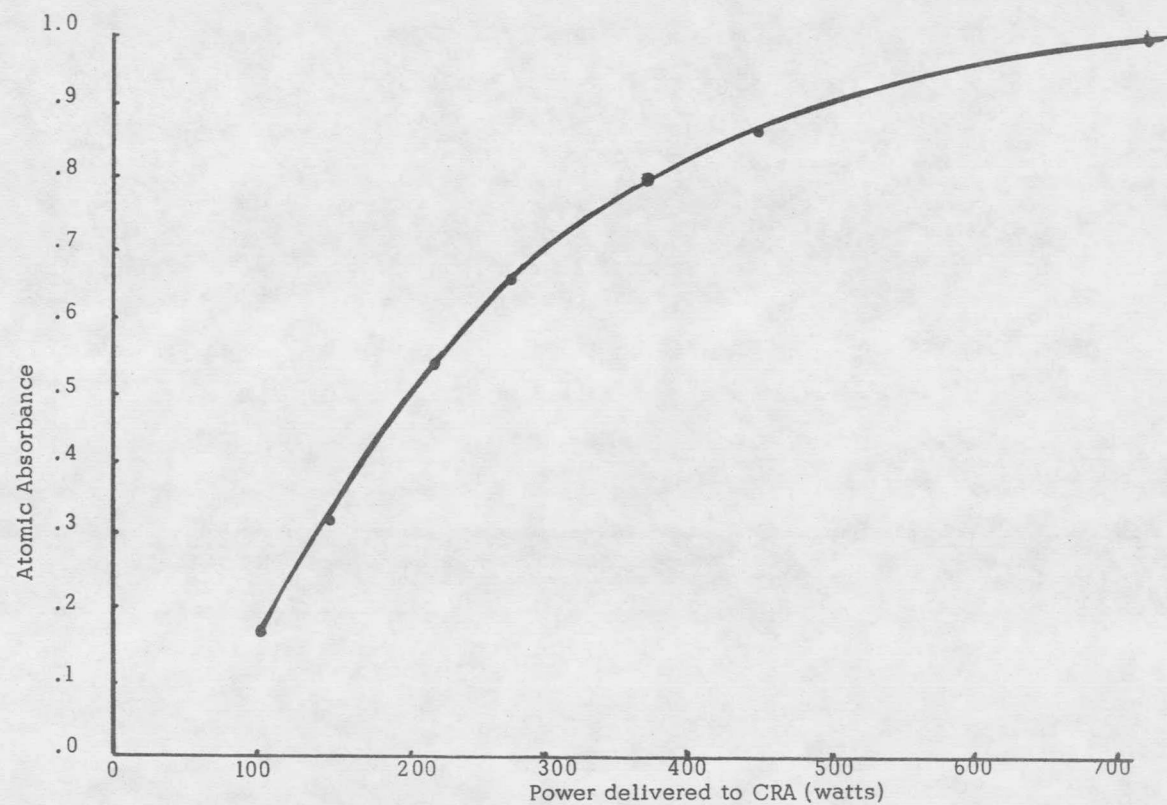


Figure 8. Power Input Versus Observed Atomic Absorbance

saturated (27 °C) air was drawn through a porous tube and the mercury atomized at different power settings. As can be seen by the figure, it is important to heat the tube as rapidly as possible. It is also very important that the tube not exceed 1100 °C at any time during the atomization. If this is done the gold plating melts (m. p. 1060), runs together, and the tube is ruined for mercury analysis. The actual cycle decided upon for most routine analyses with the homemade CRA was a short pulse of about 450 watts (50% of autotransformer setting) followed by a quick cooldown to avoid overheating.

Experiments done with the Varian Model 63 atomizer at the Chemistry Station at MSU revealed that a satisfactory power setting for general analysis is "3.5" for 2.5 seconds with the commercial CRA. This setting results in a sensitivity of 1.3×10^{-10} g. The automated power supply should give better reproducibility than the manual one used with the homemade CRA.

To be really useful a filter used for sampling gases must allow a fairly large sample to be taken in a reasonable time. The filtration rate of air with respect to the pressure differential across a tube was studied with a manometer and a Gilmont flow meter. Figure 9 gives the results. No measurable difference was noticed with respect to whether or not a porous graphite tube was plated with gold. Apparently, gold, when plated under the high current, high acid, conditions used comes out in a form which does not plate over the pores in the graphite.

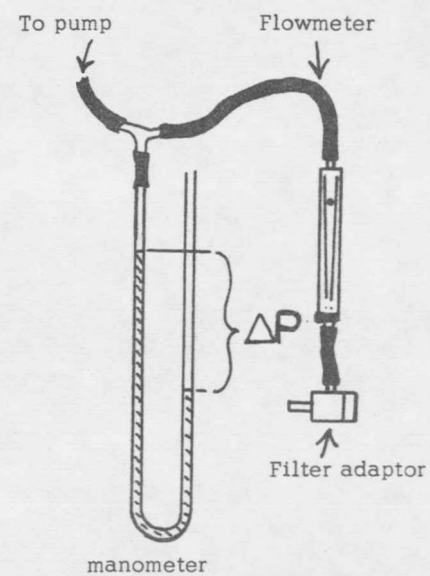
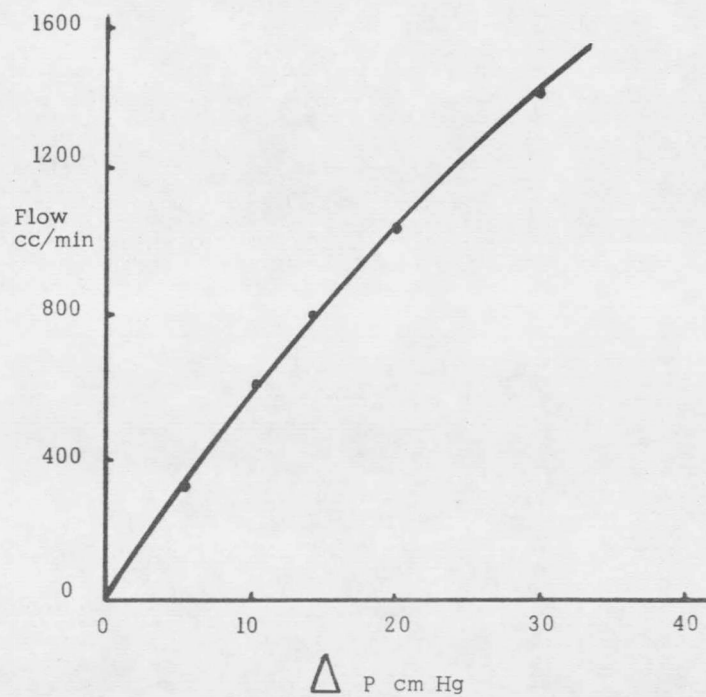


Figure 9. Air flow with Respect to Pressure Differential

Application of the Technique to Air Sampling

The sensitivity (1% absorption) of this technique is about 2×10^{-10} g (depending on atomization rate). To translate this figure to a "detection limit" it is necessary to define what we mean by the term. It is commonly (but not always) defined as that quantity of analyte which gives an analytical signal equivalent to twice the standard deviation of the blank. Blank values for this technique are made by placing a clean plated tube into the filter adaptor, letting it sit for a few seconds, removing it and checking it for any mercury that it may have picked up. On different occasions, with different filter adaptors, different tube-tweezer etc., mean blank absorbances corresponding to 0 to 4×10^{-10} g Hg with standard deviations of 0 to 2×10^{-10} g Hg have been measured. A typical value of 2 s (detection limit) would be about 1×10^{-10} g. (An A. A. spectroscopist is happier speaking of "sensitivities" because they are rigorously defined and not subject to the vagaries of interpretation and outright fudging as are "detection limits".)

The American Conference of Governmental Industrial Hygienists has adopted a threshold limit value for mercury vapor and inorganic compounds of mercury in air of $100 \mu\text{g}/\text{m}^3$ (10, p. 236). To detect such a level of mercury in the air with a dithizone method would require collection of a ten liter sample (45, p. 3) and considerable chemical manipulation before analysis. The method based on the CRA would require

a 2 cc sample and no chemical preparation before analysis.

All that is needed to sample mercury levels in air are a few clean plated tubes, an airtight container to carry them in, the filter adaptor, and a syringe or simple pump to draw air through the tubes. A syringe is adequate for levels of mercury down to about $1 \mu\text{g}/\text{m}^3$; at lower levels it is handier to use a pump. We have used Nalgene sink aspirators in the laboratory to sample for low, background levels and a mechanical pump elsewhere.

An interesting series of samples was run on June 10, 1973 in room 328 around Sherry Farwell's polarographic apparatus. Table IV gives the results. Sixty cc samples of air at various points around the room were taken except that 120 cc were taken near the open window. It is easy to see that a very small quantity of spilled mercury can result in appreciable levels in the air.

To ascertain the degree of reproducibility possible when sampling low ambient levels of mercury, relatively large (6.5 - 7.5 liter) samples of air were taken in a well-ventilated room (room 233) by drawing air through a series of four tubes for five minutes each using a faucet aspirator as a pump. A Gilmont flowmeter was used to measure the rate of sampling. A mean value of $0.24 \mu\text{g}/\text{m}^3$ and a RSD of 7.8% were the results achieved.

On Saturday, December 1, 1973, a mercury spill occurred in the hood in room 221. When it was cleaned up, a test of the air in the hood

TABLE IV

RESULTS OF MERCURY DETERMINATIONS IN THE AIR OF A ROOM WITH
VISIBLE SPILLED MERCURY

<u>Tube Number</u>	<u>Location</u>	<u>Hg $\mu\text{g}/\text{m}^3$</u>
1	top of equipment bench	38
2	under polarograph	43
3	floor by eastern wall	18
4	floor by western wall	32
5	near open window	5

ACGIH limit 100 $\mu\text{g}/\text{m}^3$

revealed $147 \mu\text{g}/\text{m}^3$ of mercury. This was not surprising in view of the situation but subsequent tests revealed that air samples taken on all four floors of Gaines Hall contained from 17 to $30 \mu\text{g}/\text{m}^3$ of mercury. Figure 10 depicts the results of determinations run in room 233 at various times during that day. The windows were opened at about 10:30 A. M. upon the discovery of these high levels. A series of 360 cc samples taken over a five minute period in room 234 gave a mean concentration of $23 \mu\text{g}/\text{m}^3$ and a relative standard deviation of 10%. A syringe was used for all of the sampling done on that day.

Follow up determinations were made from 9:30 to 10:00 A. M. on the following Monday. Samples taken in the halls on all four floors of the building contained from 4 to $7 \mu\text{g}/\text{m}^3$ mercury. In view of the fact that several authorities (37, pp. 236 - 237) have recommended maximum environmental mercury levels as low as $0.3 \mu\text{g}/\text{m}^3$, the levels encountered in the building are of some concern to the author. These levels were probably the results of both a large number of mercury spills over the years and the fact that, due to the weather, the building had been sealed up with relatively little ventilation.

As compared to commercially available mercury detectors (most of which utilize a crude form of atomic absorption measurement) this technique has several advantages. First of all, it captures and measures both particulate and gaseous mercury. The graphite tubes are effective filters for particulate matter down to $0.016 \mu\text{m}$ in dia-

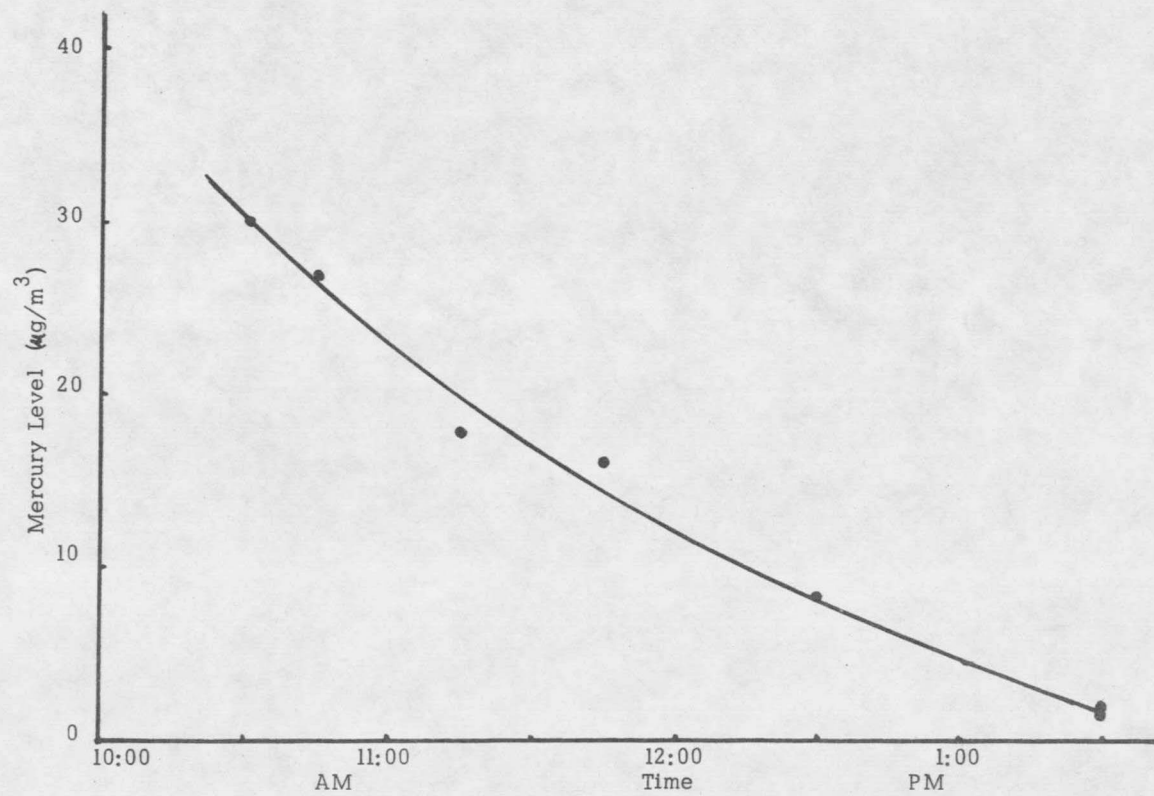


Figure 10. Mercury Levels in Room 233 on December 1, 1973

meter (41). This size is considerably smaller than that of the bulk of airbourne particulate matter (46), so particulate mercury is effectively trapped.

Another advantage of the gold plated graphite filters is that they do not collect and subsequently measure SO_2 , benzene, acetone, etc. as do most of the common mercury monitoring equipment (Beckman Instruments Inc.; General Electric; Sunshine Scientific Instruments, Inc.; etc.). Experiments were performed by drawing air saturated with benzene or acetone through these tubes and seeing if a noticeable "blank" resulted. None did. Later experiments with gases resulting from combustion of high sulfur coals also revealed no interferences from CO_2 , SO_2 , or NO_2 .

Non-atomic absorption as measured by use of a deuterium lamp has never been observed in air samples taken in the Bozeman area. However, it is conceivable that an interference would be noted in a sample of air containing very high concentrations of tarry smoke resulting from incomplete burning of organic materials. If this should occur, some modification of the mercury-in-solids combustion apparatus to be discussed later in this thesis should eliminate the problem.

Portions of this section of the thesis have been published. (47)

Application of the Technique to Water Samples

The most commonly utilized method for the analysis of mercury in aqueous solutions is the straightforward addition of stannous chloride to the sample, whereupon the mercury is reduced to the metal and is

carried as a vapor into a cold vapor absorption tube by a carrier gas bubbled through the solution. Mercury in organic forms is first converted to the ionic form by pretreatment of the sample with H_2SO_4 and KMnO_4 . The main problems associated with the technique are those related to the kinetics of the reduction-aeration process as enumerated before. Water vapor along with volatile organic compounds interfere with the final measurement and must be either removed from the gas stream or their effects corrected for.

Figure 11 is a diagram of the final version of several apparatus made to allow application of the plated-graphite CRA technique to water analysis. The bubbling flask was made of a 125 cc erlenmeyer flask to which was added a longer neck, an entrance port sealed with a rubber septum, a side tube, and a drain tube in the bottom. A thistle tube with a glass frit gas diffuser is mounted in a rubber stopper of a size to fit the neck of the flask. A gold plated porous graphite air filter mounted on a stopper to fit the thistle tube was used (when necessary) to reduce "blank" levels resulting from measurement of the mercury in the air used to carry the reduced mercury from the solution. The bottom of the flask was drawn to a slightly conical shape and the drain was sealed off with rubber tubing and a glass bead. By squeezing the tubing over the bead, it is possible to drain the flask in a few seconds.

The filter adaptor is mounted on the side tube and air is drawn

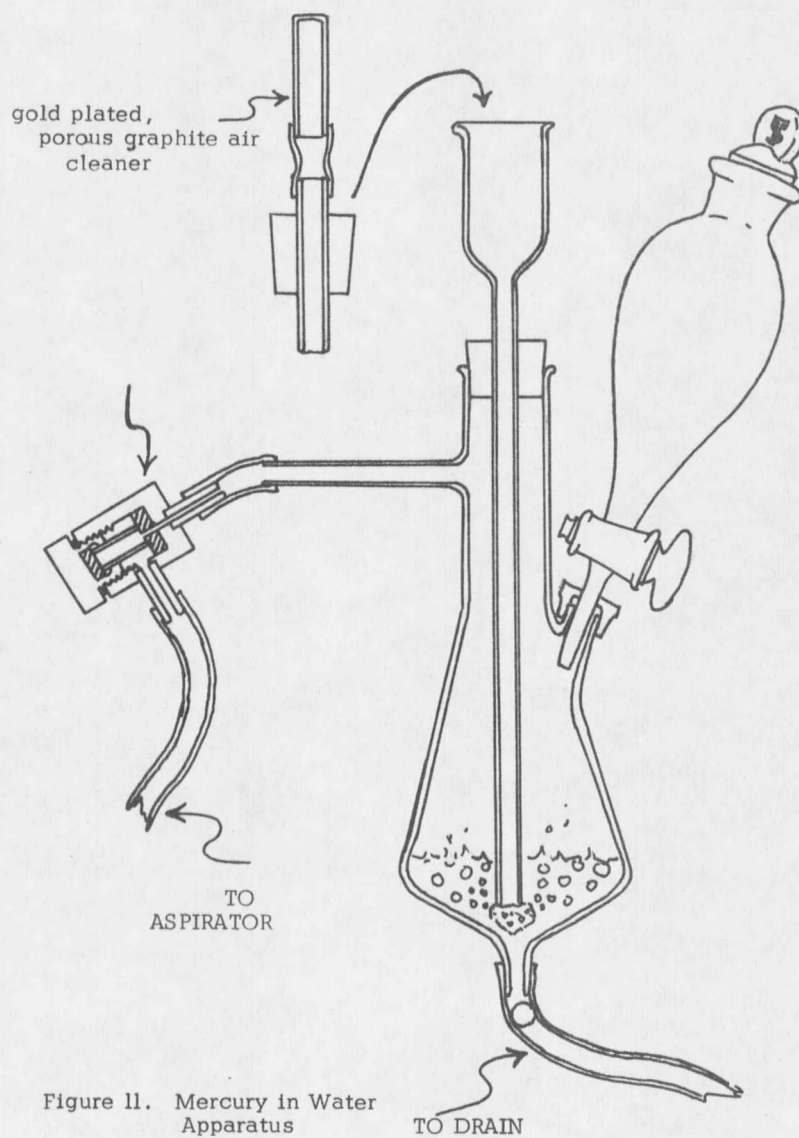


Figure 11. Mercury in Water
Apparatus

through both it and the rest of the system with a sink aspirator at a flow rate of 400 to 500 cc/minute. The only reagent used was 20% SnCl_2 (B-A reagent grade) in 6 F HCl.

The procedure used to analyze a sample is as follows. The aspirator is turned on and air drawn through the system. Initially, no gold plated tube is placed in the filter adaptor. One or two ml of stannous chloride reagent is added to the flask. This is usually done by pipetting it into the thistle tube and washing it down with a few ml of water. The system is allowed to bubble for a minute or so to flush out any mercury present in the stannous chloride or distilled water. Then a gold plated filter tube is put into the adaptor and the water sample added. If the sample is turbid, it is added through the funnel; if clear, it is placed into the thistle tube. The purpose of adding turbid samples through the funnel is to prevent clogging the gas diffuser frit on the end of the thistle tube. The system is allowed to bubble three or four minutes before the gold plated tube is removed and the evolved mercury determined.

To determine the bubbling time required to ensure complete reduction and subsequent mercury collection, a series of tests was run with 1.5×10^{-8} g mercury as Hg^{++} in 10 ml of water. The plated tubes were removed and analyzed following different intervals after the sample was added and the observed atomic absorbances were plotted against the bubbling time (Figure 12). The shape of the resulting curve was calculated

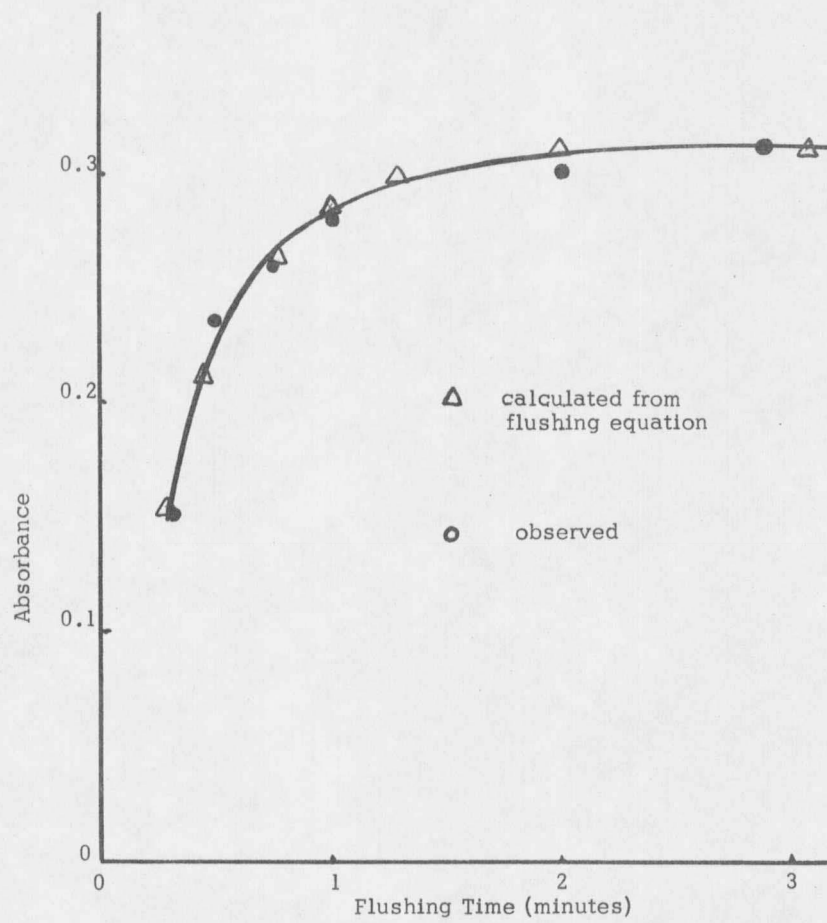


Figure 12. Flushing Time Versus Recovery

utilizing the "flushing equation" (36, p. 199). The bubbling rate was 470 cc/min.

$$\ln \frac{C_0}{C_T} = \frac{V}{V_0}$$

V_0 = volume of system (200 cc)
 V = volume of flushing gas (vol/min x t)
 C_0 = initial level of Hg in flask
 C_T = level of Hg in flask at time "t"

Because the observed flushing rate is so well accounted for by the equation, the actual reduction time for mercury in the simple solution used must be very small. A typical analytical curve for this system is given in Figure 13.

A standard addition experiment was performed on a sample received from the U. S. Forest Service of drainage water from a lead mine in Langhor Canyon. Differing amounts of 1 ppm Hg solution were added to 5 milliliter samples of the water and the total mercury results compared to those of similar aliquots of the standard alone. A rather substantial blank ($\bar{x} = 0.063$, $n = 5$) has not been subtracted from any of the points plotted in Figure 14.

Five more samples were run of tap water taken at various points in the city of Bozeman. There was little variation in the mercury levels measured. The concentrations ran from 0.018 to 0.025 ppb-- all far below the USPHS limit of 5 ppb.

There has been only a limited amount of application work done to date with this technique. The technique is very fast (4 - 5 minutes), sensitive (4×10^{-3} ppb in a 50 ml sample) and should be useful in geochemical prospecting as well as in routine trace level water analysis.

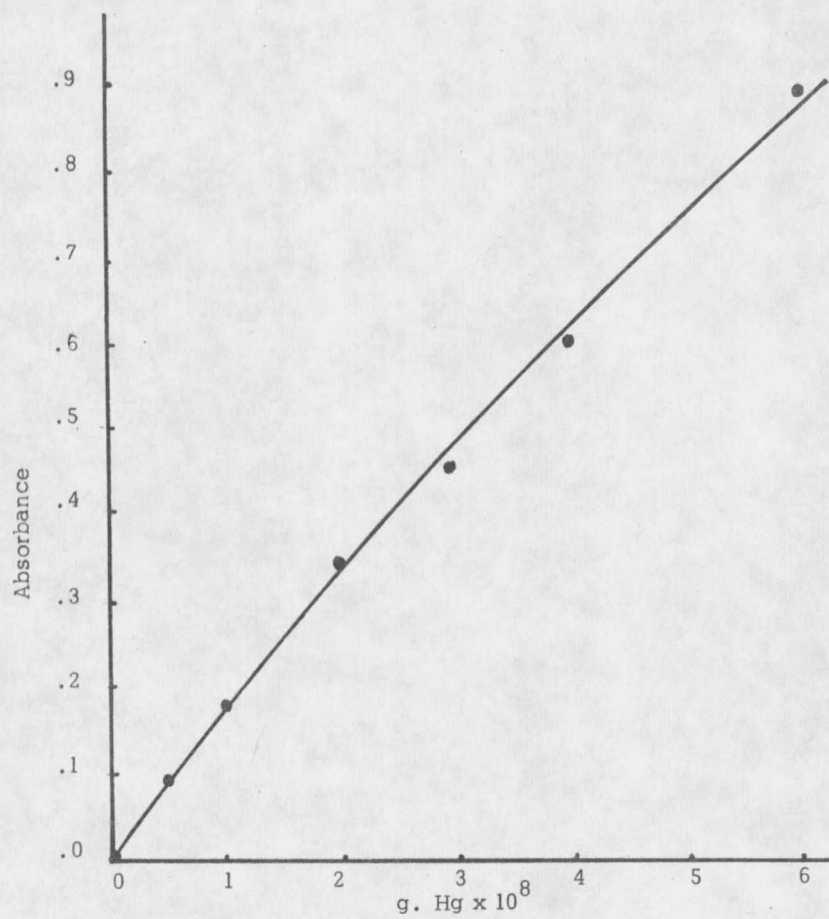


Figure 13. Typical Analytical Curve for Water Analysis System

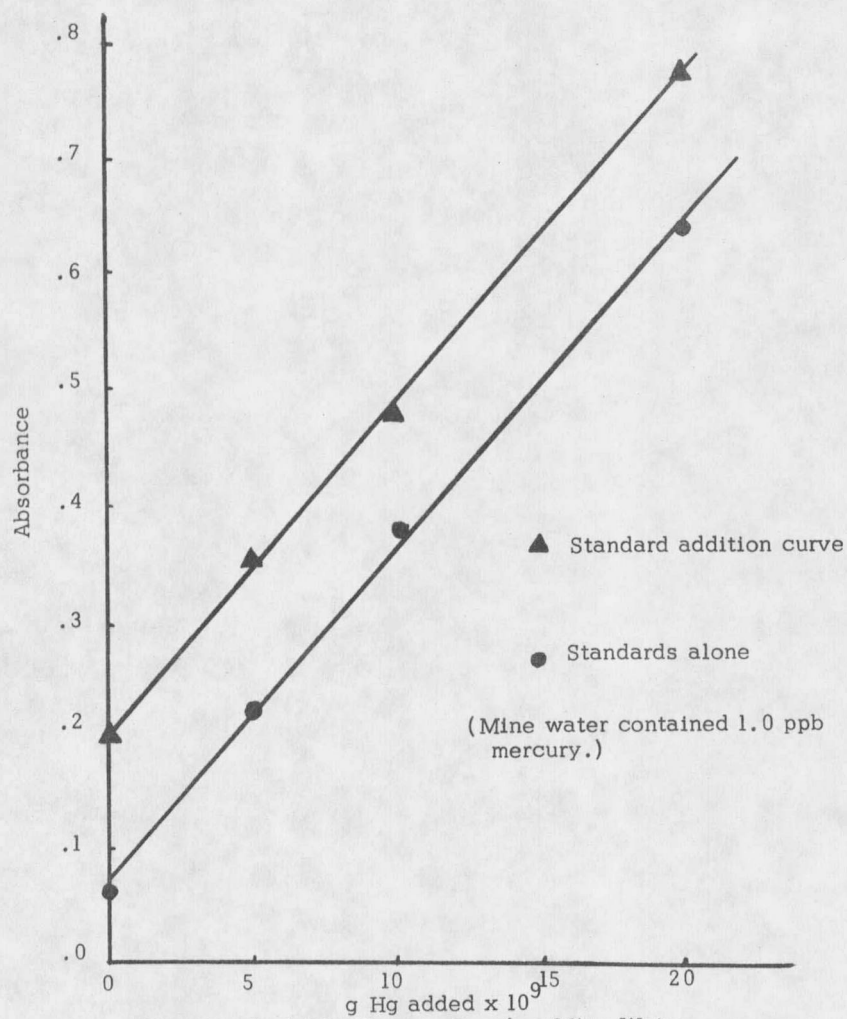


Figure 14. Standard Additions to Langhor Mine Water

Application of the Technique to Solid Samples

Direct combustion of solids as a means of releasing the mercury into a gas stream for subsequent analysis has been utilized in some form or another for several years (36 - 37, 48 - 49). Gold or silver was used by most of these workers to concentrate the mercury and to eliminate interferences.

The apparatus that was used to adapt gold plated CRA tubes to the direct determination of mercury in solids is shown in Figure 15. This is the latest of several versions that have been tried. Basically, it is simply a nichrome wire-wrapped Vycor combustion tube with two oxygen inlets and an entrance port. The tube has two main sections: the combustion chamber proper and a following "afterburner" section loosely filled with a granulated fusion mass of 4 parts CaO to 1 part Na_2CO_3 . Oxygen flow is controlled and measured by a pair of Gilmont flow gauges and needle valves. The combustion boat is made from a short section of 10 mm diameter quartz tubing which has been split in half and sealed to a length of 4 mm quartz rod. An earlier version (50) incorporated a cold finger in the train to remove water vapor; however, it is not generally necessary to do so. A balloon on the first oxygen inlet tube serves as a pressure indicator. As in the bubbling apparatus discussed in the last section, a faucet aspirator is utilized to draw the evolved gases through the walls of the graphite tubes.

Sample analysis is performed as follows. The power is applied to

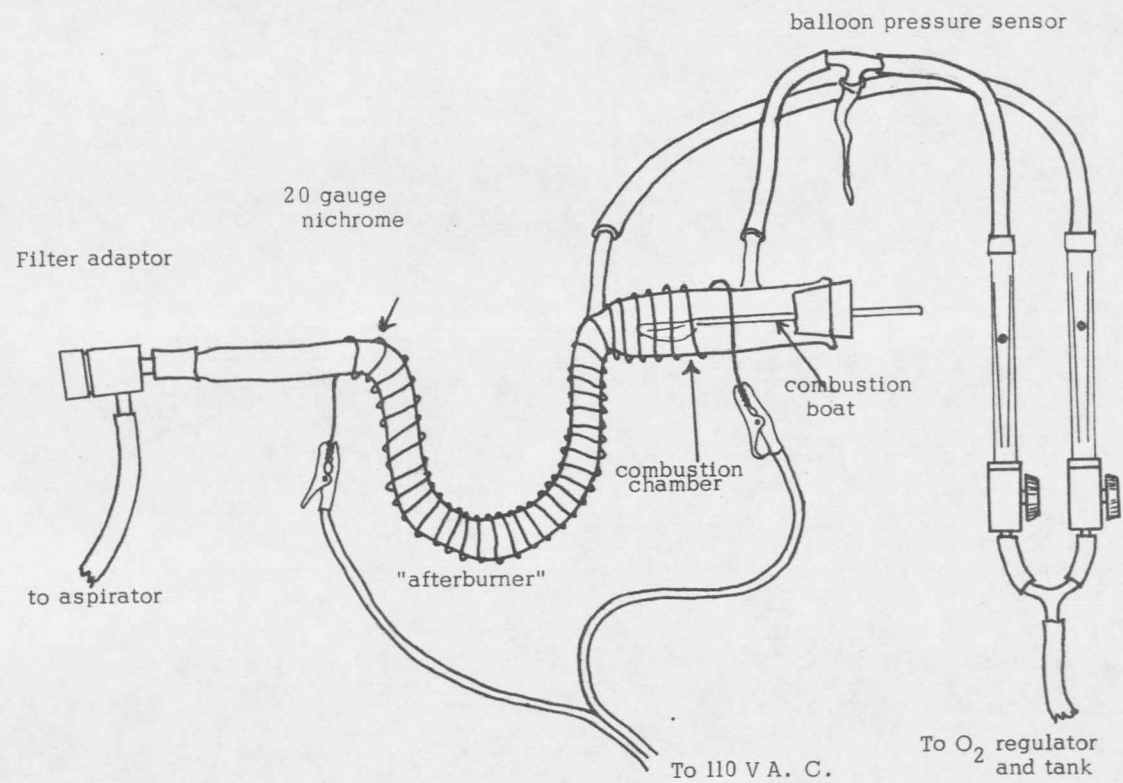


Figure 15. Mercury In Solids Combustion Apparatus

heat the tube and the aspirator turned on. (It is left running for as long as any samples or standards are being run.) Then a clean, gold plated tube is placed into the filter adaptor. The sample (1 - 100 mg) is weighed in the combustion boat and then the boat is inserted into the combustion chamber. The oxygen flow is adjusted to the maximum which permits a net total pressure in the combustion tube of less than one atmosphere (usually about 200 cc/min. for each of the two inlets). The purpose of this is to assure that a leak in the system results in no loss of mercury vapor. Complete combustion takes from 10 seconds to about a minute. The system is allowed to flush for two or three minutes more and then the CRA tube is removed and the captured mercury determined as previously described.

The method is calibrated by placing various volumes of mercury standard solutions into the combustion boats and treating them exactly like solid samples. A comparison was made of this method of standardization with respect to that of adding the same amount of standard mercury solution directly to the plated CRA tube, drying it, and finally atomizing it. Five microliters of a four ppm Hg solution (20 ng Hg) were alternatively placed into either the combustion boat (and "burned") or directly into a CRA tube. The results are given in Table V. The data support those given on Figure 7 and the conclusion is the same; i. e., mercury vapor standardization is more reproducible than solution standardization, but there is no otherwise significant difference in re-

TABLE V

COMPARISON OF DIRECT ATOMIZATION TO COMBUSTION
FOR STANDARDIZATION

	<u>Combustion Boat</u>	<u>CRA Tube</u>
Number of determinations (n)	8	8
Mean Absorbance (X)	0.418	0.406
Standard Deviation (s)	0.0126	0.0295
Relative Standard Deviation (RSD)	3.0%	7.4%

$$t = 1.05$$

$$t_{95\%} (14 \text{ degrees of freedom}) = 2.10$$

no significant difference between means at 95%
confidence level

$$F = 4.85$$

$$F_{(0.05)} (7 \text{ \& } 7 \text{ degrees of freedom}) = 3.79$$

There is a significant improvement in reproducibility
when standards are "burned".

sults with respect to method.

Because mercury is usually found in the presence of sulfur in organic as well as mineral matrices a test was run to see if net recovery of mercury was affected by an excess of sulphide. The addition of a thousand-fold excess of $(\text{NH}_4)_2\text{S}$ to 2×10^{-8} g of mercury in a standard solution placed into the combustion boat had no effect on either the recovery of mercury or on the background.

Several different types of organic samples were analyzed. It was necessary to grind the sample to less than 100 mesh to get reproducible results in some cases. In all cases studied, standard additions of mercury solution to the samples gave analytical curves parallel to curves prepared with solutions alone. The amount of sample was chosen to give on the order of ten to fifty nanograms of mercury collected on the tube. Molecular absorption due to incomplete oxidation of tars was a problem in preliminary work. However, changing the position of the combustion boat in the combustion chamber, or the O_2 flows, or, if necessary, reducing the size of sample burned has eliminated this problem in every type of sample studied. A simultaneous background correction system would eliminate some problems along this line if one were available.

Ground orchard leaves (NBS no. 1571) were the only samples analyzed with a known mercury content. The results obtained with seven replicates of about 50 mg leaves each time were a mean value of 0.16 ppm and

a relative standard deviation of 7.8%. The accepted value for these leaves is 0.16 ppm.

A large number of coal samples were the primary reason for beginning research on a quick, reliable method for determining mercury. Recent development of low sulfur coal deposits in eastern Montana has sparked considerable interest in possible trace metal contamination of the environment resulting from use of the coal. Values for a series of forty-three such coals ranged from 0.06 to a high of 0.6 ppm with relative standard deviations of about 7% for replicates on individual samples. Very finely ground samples were required for good reproducibility with coal.

Hair and toenail samples from a number of individuals were analyzed. Approximately 3 - 5 milligrams of sample is required for these tests. Values ranged from 0.8 ppm to 3.0 ppm for hair and somewhat less than this for the nail samples. Relative standard deviations for chopped hair samples were 8%.

At this writing three of these mercury determination systems have been built for use in analytical laboratories. The Chemistry Station uses one on a routine basis for a wide variety of samples. Mr. Laszlo Torma has requested permission to present the results of his findings concerning the technique at a national A. O. A. C. meeting. Dr. Frank Munshower purchased one for his laboratory for feed and forage analysis. The Department of Health and Environmental Sciences in

Helena is presently getting one set up for comparative tests. All of these laboratories have Varian model 63 carbon rod atomizers.

Conclusions

The basic approach studied has proven to be applicable to the determination of mercury in the entire range of sample types normally submitted to analytical laboratories. The degree of freedom from interferences and sensitivity is unusual for so simple an analytical approach. The main problems associated with it have been with imperfect sealing of the tubes in the filter adaptors allowing the gases sampled to go around and thereby causing a loss of signal. This is primarily due to roughness on the ends of the filter tubes caused by normal wear as well as by dropping, etc. The silicone rubber gaskets have been helpful in this respect because that material "upsets" to fill (and seal) surface imperfections better than did the earlier materials used. An improved model of the filter adaptor utilizing a freely-turning rear gasket has shown promise of reducing wear on both the gaskets and the tubes.

Another problem seen only with the commercial (Varian Model 63) CRA is with breakage of the porous tubes. The porous tubes are fragile as compared to the thick-walled, impervious graphite tubes that the CRA is designed to use, and the spring tension on the carbon rods must be adjusted within narrow limits. A weaker (although entirely strong enough for either type of tube) spring would alleviate this problem.

The work to date has been with the carbon rod type of atomizer and Woodruff furnace; however, the basic technique should be applicable to any of the several carbon tube atomizers presently on the market.

DIRECT A. A. DETERMINATION OF METALLIC POLLUTANTS IN AIR
WITH A CARBON ROD ATOMIZER

Introduction

The effective control of airbourne particulate matter requires the capability of analyzing airbourne particulates. For this purpose optical emission spectroscopy has been extensively used to obtain most of the data. A relatively large number of elements can be determined simultaneously by this technique. However, the technique is neither as sensitive nor as accurate as atomic absorption and it also requires both more expensive equipment and more highly trained personnel than does A. A. Internal standardization ⁽⁵¹⁾ improves the precision and accuracy but does nothing to alleviate the other problems. X ray fluorescence spectrometry is sometimes used but it suffers to an even greater degree from most of the same problems as does atomic emission analysis. It is even more expensive, prone to interelement interferences, and the preparation of proper standards is very difficult ⁽⁵²⁾.

In recent years atomic absorption analysis has been widely used for the analysis of trace metals in atmospheric particulates ^(53 - 59). The chief reasons for this trend include good selectivity, sensitivity, simple operating techniques, and low initial equipment costs. The conventional flame A. A. system suffers from two major disadvantages. It has a large consumption (1 - 2 ml/minute) of sample solution, and it lacks the sensitivity to perform ultratrace analyses unless very large

air samples are taken. This volume requirement can be drastically reduced by using non-flame atomic absorption because of its inherently greater sensitivity.

Collection of lead particulates on a filter from air volumes as small as ten liters followed by chemical digestion and non-flame atomic absorption had been reported by Omang (60). The continuous determination of atmospheric lead by an induction heated carbon tube furnace has been reported by Loftin et al. (61).

Much of the difficulty in achieving good detection limits is as much due to the sample collection and chemical pretreatment steps as to the actual sensitivity of the analytical tool used for the final analyses. A typical example would be the analysis of beryllium particulates. A commonly accepted approach would be to draw air through a millipore filter, digest the filter in acid, and bring the solution volume up to 50 or 100 ml prior to analysis. If beryllium particulates at the maximum level accepted by law in Montana (0.01 ug/m^3) were to be detected in this manner, even with a very sensitive non-flame atomic absorption technique (62), a total of sixty cubic meters of air would need to be sampled. A sample this size would require about a day to collect on a millipore filter. The factor limiting the sensitivity in this case is the sample pretreatment step with its attendant dilution, not the actual analysis step.

To minimize sample pretreatment and dilution, Matousek and Brodie

(63)

used Varian Techtron carbon cup atomizer for direct air sampling of lead. An essentially standard cup is perforated through the bottom with many small holes. A small disk of millipore acetate filter is placed in the cup (a la Buchner funnel) and the air to be sampled is drawn through. The filter material is burned off slowly first; then the lead is atomized in normal fashion. Because there is a large amount of lead in the millipore disks (62), they were pre-cleaned by soaking in nitric acid to minimize blanks.

Lech and Woodriff (30) were the first to report on the filtration of lead particulates by graphite furnace atomizer cups. Air was drawn through the walls of porous graphite cups which were inserted into a Woodriff furnace with no pretreatment whatsoever. The sensitivities reported are the best in terms of amount of lead detectable per unit volume of air of any technique cited to date. Seeley and Skogerboe (64) followed up on Lech's work by using an emission spectrographic technique to determine metals captured in porous graphite electrode filters. The sensitivity of the emission method is generally considerably inferior to that of the atomic absorption method of Lech but it does have the advantage of the simultaneous determination of several elements on the same filter.

The Woodriff furnace is not yet widely used in analytical laboratories while the Varian Techtron type of carbon rod atomizer (CRA) is. The CRA has absolute sensitivities generally comparable to the

Woodruff furnace and possesses the easily removable atomizer tubes necessary for successful adaptation to filters. A flexible power supply allows sample pre-ashing directly in the atomizer tubes so no reagents are needed. For these reasons the author decided to investigate the use of this type of atomizer for the direct analysis of a wide range of particulate matter in air.

Experimental

The spectroscopic apparatus, the carbon rod atomizer, and the filtration adaptor used have already been described in this thesis. The porous graphite tubes are identical to those used for the work on mercury except they are not plated with gold for particulate analysis. National AGKS or AGKSP proved to be equally satisfactory for graphite filters with the nod going to the first because of its lower price.

Contrary to Lech's findings (41) it was found by this author that filtration adaptors machined from Lucite were fully as desirable as those made from Teflon. The Lucite is much cheaper and easier to machine than Teflon and seems to be as easy to clean. The contamination problems that Lech experienced were likely due to the nature of the gasket material he used rather than to the material of the body of the filter adaptor. Silicone rubber has proven to be a satisfactory gasket material in Lucite filter adaptors with no contamination problems for the determination of Pb, Ag, Cd, Be, Se, As or Hg.

Particulates were generated in the laboratory in a variety of

ways. An approach used in several instances involved aspirating solutions into spectroscopic premix or total consumption burners. The droplets of solution containing a salt of the element of interest were carried into the flame where they were decomposed. The gases above the flame contain particulates resulting from recombination of the elements entering the flame. These systems feature a reproducible concentration of particulates per unit volume of gas but give an unknown particle size distribution and composition. A Beckman double slot CH_4/air A. A. burner fitted with a premix desolvation chamber is pictured in Figure 16. A Beckman $\text{C}_2\text{H}_2/\text{O}_2$ total consumption burner was used for generating Cd containing particles.

An ultrasonic nebulizer (Tomorrow Enterprises, Portsmouth, Ohio) fitted with a desolvation system and a dilution/mixing chamber was used to produce reproducible concentrations of particles of roughly known dimension for collection efficiency studies. Figure 17 depicts the apparatus. Solution droplets of mean diameter $2.5 \mu\text{m}$ are generated by the ultrasonic nebulizer and are carried by a flow of 90 cc/minute of air into a nichrome wire heated desolvation tube in which the solvent (methanol) is driven off. The excess methanol is condensed and removed with a cold finger. The desolvated particles are then mixed with a large volume of air and blown down the length of a mixing tube before they are sampled.

A motorcycle burning regular gas was used to generate lead-contain-

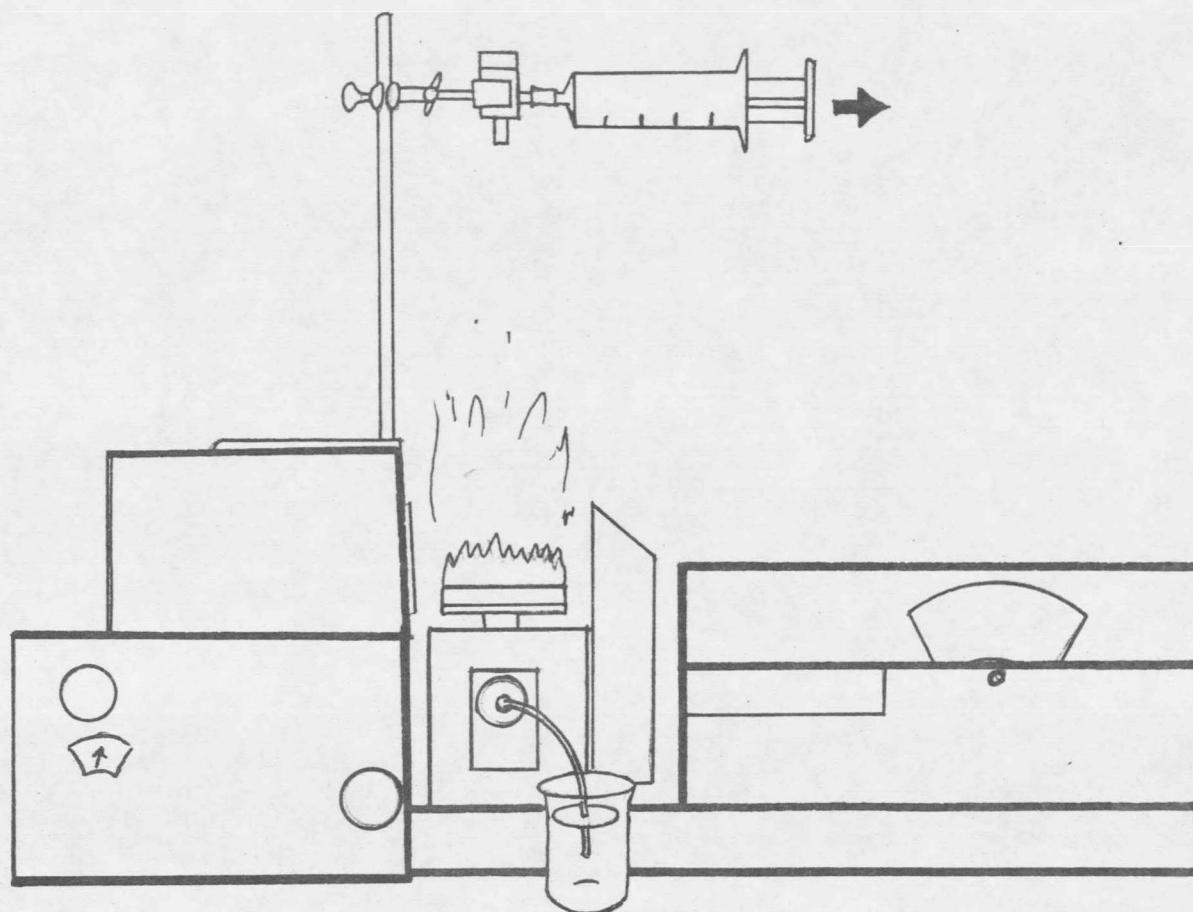


Figure 16. Beckman DB flame particulate generator

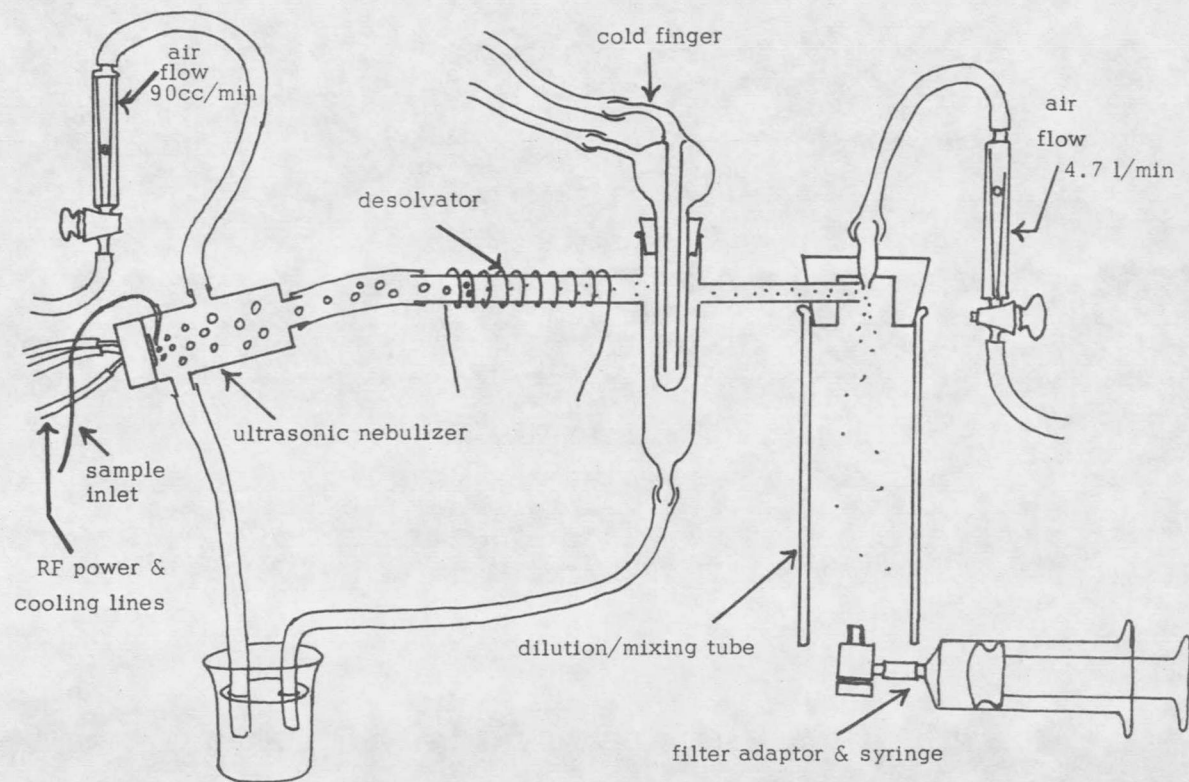


Figure 17. Ultrasonic nebulizer particulate generator

ing particulates for a comparison study of millipore versus graphite filtration. Figure 18 shows the entire apparatus. A fraction of the exhaust gases are diluted and mixed with compressed air prior to sampling in a mixing chamber similar to that used with the ultrasonic nebulizer described above.

Several other systems which generated particles containing metals hazardous to human health were investigated. Included in this category are cigarettes, certain types of candles, and gasoline lamp mantles. A more complete discussion of these will be given in the following sections.

For most of this work, a 60 cc disposable syringe was used to draw air samples through the walls of the filter tubes. A much larger (1.35 liter) homemade syringe was used in some cases. A Nalgene faucet aspirator was used in the laboratory for higher volume sampling. A small battery-powered air compressor (Auto Flator, W. R. Brown Corp., Chicago Ill.) was modified for use for high volume sampling outside the building.

The analytical technique is similar to that already described for the determination of mercury in air. A pre-heated CRA tube is placed into the filter adaptor and a measured volume of air is drawn through the walls of the tube. Then the tube is removed, placed between the rods of the carbon rod atomizer, pre-heated to 400 - 500 °C for a few seconds to destroy tars, smoke, etc., and finally heated to a pre-deter-

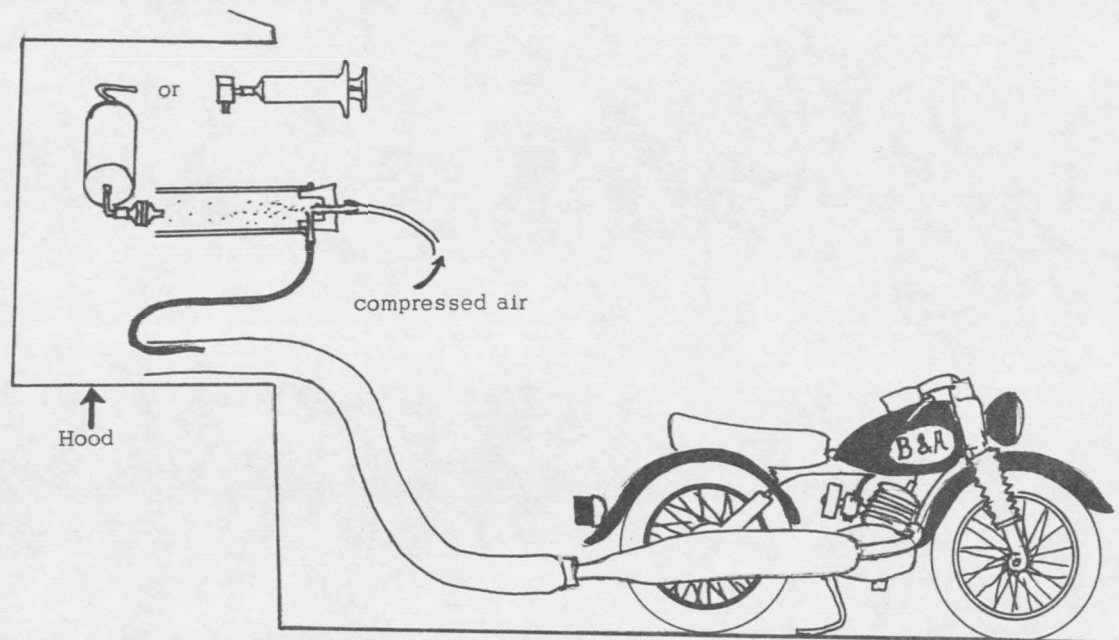


Figure 18. Lead Particulate Generation Apparatus

mined temperature high enough to atomize the analyte. In most cases, the pre-ash step is not necessary for ambient air samples.

The atomic absorbance values of the elements in the material filtered from air are compared to those of an aliquot of a standard solution of the element of interest pipeted into and atomized in the same tube in order to calculate the amount of material captured.

Results and Discussion

The efficiency of porous graphite filters for tiny particles has been established by Lech (41). Lech generated particles of a known size in a stream of gas and measured the total metal concentration of the gas both before and after filtration by injecting measured quantities into a Woodruff furnace fitted with a side tube (65). The atomic absorption signals resulting from the injection of filtered and unfiltered gas were compared to assess the efficiency. Table VI gives the retention efficiencies of filters made of National AGKSP graphite for particles of different sizes.

Some preliminary work was done with beryllium containing particles generated by aspirating beryllium solutions into a Beckman A. A. burner and sampling the gases above the flame (66). A current sufficient to raise the temperature of the tube to 2800 °C was applied and the peak atomic absorbance measured. When the burner was aspirating a 10 ppm Be solution, a series of seven samples of the beryllium particulates gave a mean atomic absorbance of 0.158 and a coefficient of variation

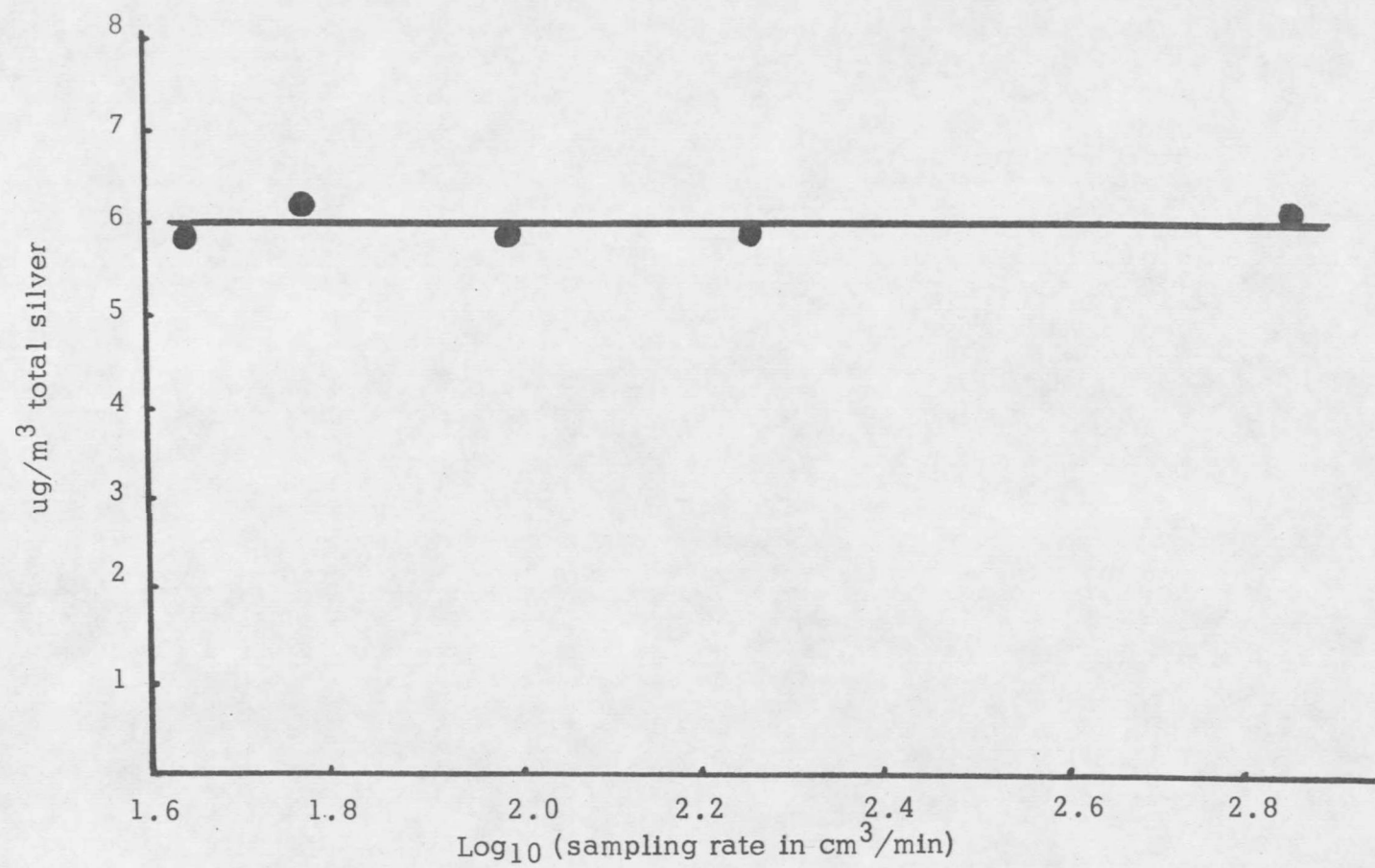
TABLE VI

FILTRATION EFFICIENCY OF POROUS GRAPHITE FILTERS

<u>Particle</u>	<u>Mean Diameter (μm)</u>	<u>Efficiency (%)</u>
$\text{Pb}(\text{NO}_3)_2$	0.15	99.2
$\text{Pb}(\text{NO}_3)_2$	0.09	98.6
AgNO_3	0.076	99.4
$\text{Pb}(\text{NO}_3)_2$	0.077	97.9
AgNO_3	0.037	97.7

of 14.5%. The same filter tubes, when 5 ul of a 0.1 ppm Be solution (5×10^{-10} g Be) was dried and atomized in them, gave an absorbance of 0.443 with a coefficient of variation of 4.9%. The sensitivity of the method is such that a sample of only two liters of air containing Be (at the maximum allowed level, $0.01 \mu\text{g}/\text{m}^3$ in Montana) would be required for detection. A sample of this size would require one and one half minutes to collect.

In order to ascertain the efficiency of AGKSP porous tubes with respect to the rate of filtration the apparatus depicted in Figure 17 was used. Desolvated particles of silver nitrate are mixed with a large volume of air and blown down the length of a mixing tube prior to sampling. The high total flow in the system (4.8 liter/min.) allows a much higher sampling rate to be used than is possible with Lech's system. A solution of silver nitrate in methanol (2×10^{-7} g Ag/ml) was pumped into the ultrasonic nebulizer resulting in a calculated particle size of $0.014 \mu\text{m}$. A series of 60 cc samples of the mixed/diluted particle bearing gas stream was drawn through the walls of porous graphite tubes at widely differing sampling rates. The concentration of silver in the 60 cc of gases sampled by the tubes is plotted against the sampling rate in Figure 19. There is no loss in filtration efficiency as the rate of sampling is changed. This is important because in some situations it is desirable to get an analysis in as short a time as possible; e. g., after an industrial accident. In other cases, it is



-19-

Figure 19. Measured Particulate Concentration as a Function of Sampling Rate

more desirable to ascertain a mean ambient level averaged over a relatively long sampling time.

There was some question as to whether a standard solution dried and atomized in a carbon tube would be a valid way to quantitate particulate matter filtered by such a tube. There are two reasons it might not be. First, the geometry is different. Particles filtered by the apparatus described are fairly uniformly distributed over the inner surface of the tubes. Therefore, when the tube is heated, sample atoms enter the optical path from all sides and not from a single spot on one side as is the case when a droplet of solution is dried in the tube.

Second, the material filtered is of unknown composition. Different salts of the same element should volatilize at different times during the atomization cycle and dissociate to a greater or lesser degree. This would result in different free atom populations and a consequently different analytical signal.

L'vov (35, pp. 236 - 245) indicates that the fact that an element is present in different forms actually makes little difference in carbon furnace atomic absorption. Indeed, this has proven to be the case in the Woodruff furnace. A test of this proposition was made with the carbon rod atomizer in the following manner. Five microliter aliquots of a 2.0×10^{-7} g/ml (10^{-6} M) lead solution (lead as nitrate salt in distilled water) were dried in an atomizer tube. Then, five microliters of 0.1 M HCl, HNO_3 , or H_2SO_4 were pipeted into the tube and dried

over the lead. The approximately 10^5 fold excess of acid should convert the metal to the respective lead salt. When the lead was atomized there was no difference in the analytical signal from lead treated with the different acids. Table VII gives the results.

The geometrical aspect of the standardization question was studied by analyzing cadmium particulates captured on porous graphite tubes by an independent method and comparing the results with those achieved with direct atomization and solution standardization.

Forty cc of the gases above a Beckman O_2 , C_2H_2 , burner aspirating 1000 ppm cadmium solution were drawn through each of twelve porous CRA tubes. Six of these tubes were placed into small test tubes which had calibration marks at two milliliters. Ten microliters of a solution containing 4×10^{-8} g of cadmium were placed into each of three more porous CRA tubes and dried. These "standard" CRA tubes were also placed into calibrated test tubes. One microliter of 1:10 nitric acid was added to each of the nine test tubes and the cadmium salts dissolved by placing the tubes in a hot water bath overnight. The test tubes were each filled to 2.0 ml with distilled water and the contents mixed.

Ten microliter aliquots of each solution were analyzed in an impervious CRA tube using the 228.8 nm resonance line. The atomic absorbances from analysis of the solutions from the six CRA tubes used as filters were compared to those of the solutions from the three standard tubes to calculate the amount of Cd in the particulate matter filtered.

TABLE VII

SALT EFFECT ON LEAD DETERMINATION

CONDITIONS: 5 ul of 2×10^{-7} g/ml Pb, 283.3 nm line, 3400 Watts,
5 ul of 0.1 M HCl, H₂SO₄, or HNO₃, pre-ash to 500 °C
after drying

	With HCl	With HNO ₃	With H ₂ SO ₄
MEAN ABSORBANCE	0.247	0.240	0.246
COEFFICIENT OF VARIATION	4.3%	7.3%	3.6%
NUMBER OF RUNS	4	4	4

There is no significant difference in
the mean values at the 95% confidence
level.

The mean value calculated for this indirect analytical approach was 2.80×10^{-8} g per tube.

The other six tubes containing filtered Cd particles were analyzed directly on the carbon rod using the far less sensitive 326.1 nm resonance line. The atomic absorbances observed were compared with those measured when aqueous standard solutions of cadmium were pipeted into and atomized in the same tubes. Two standard solutions were used; the first contained 3.0×10^{-8} g Cd in 10 microliters and the second 3.0×10^{-8} g Cd in 1 microliter. The mean values by this direct approach for the total cadmium filtered by the six porous tubes were 2.81×10^{-8} g and 2.79×10^{-8} g based on the atomic absorbances of the 10 microliter and 1 microliter standards respectively.

Table VIII summarized the results. Basing a measurement of the metal contained in particulate matter filtered from air upon the atomic absorbance of 1 μ l standard solutions dried in the same tubes appears to be valid with a possible 16% error ($t_{crit} \times RSD$ (Δ method) at the 95% confidence level). Actually the experience gotten with mercury standardization in which the geometrical considerations are the same indicates that the probable error due to this effect is likely less than 5%.

A comparison of the results of lead analysis using conventional millipore filtration with subsequent dissolution of the membrane filter and analysis of a fraction of the resulting solution and the direct

TABLE VIII

COMPARISON OF DIRECT TO INDIRECT MEASUREMENT OF CAPTURED PARTICULATES

	Calculated Mean Value (g)	RSD %	Degrees of Freedom
Direct (1 ul standard)	2.79×10^{-8}	18	11
Direct (10 ul standard)	2.81×10^{-8}	23	9
Indirect	2.80×10^{-8}	13	7

RSD (Δ method) RSD of the statistic ($\bar{X}_{\text{direct}} - \bar{X}_{\text{indir.}}$)

$$\text{equals } \sqrt{\frac{(18)^2}{11} + \frac{(13)^2}{7}} = 7.3\%$$

Critical value of $t_{95\%}$ (11+7-2) degrees of freedom

equals 2.13

porous tube approach was made using a motorcycle burning regular gasoline as a particulate source (Figure 18). A fraction of the exhaust from the motorcycle was diluted with compressed air to bring the lead level down to manageable levels with a system similar to that depicted in Figure 17. A series of five 20 cc samples was taken through porous graphite tubes and two 1350 cc samples were drawn through 13 mm diameter disks of 0.45 μ m millipore membranes. The membranes were dissolved by heating with 100 μ l of HNO_3 and the solution diluted to 1.0 ml before analysis on the CRA. Five microliters of 5×10^{-7} g/ml Pb solution was pipetted into porous tubes to standardize the direct analysis.

The results are given in Table IX. It would have been desirable to collect a greater number of samples but the motorcycle couldn't run for more than ten minutes in a stationary state without overheating. It took approximately four minutes to draw each sample through the millipore filters compared to about five seconds each for the porous tubes.

Filtration of the gases above burners aspirating solutions containing metal ions with subsequent atomization and atomic absorption determination of the collected metals was undertaken with selenium, beryllium, lead, and cadmium. In all case, plots of the recorded atomic absorption versus either the volume of gas sampled or the concentration of the solutions aspirated were linear. The relative standard deviation

TABLE IX

COMPARISON OF MILLIPORE FILTER TO POROUS GRAPHITE FOR
LEAD PARTICULATES

CONDITIONS: Pb 283.3 nm line, 2800 watts power

FILTER	MILLIPORE	GRAPHITE
VOLUME SAMPLED	1350 cc	20 cc
NUMBER OF DETERMINATIONS	2	5
MEAN VALUE ($\mu\text{g}/\text{m}^3$)	205	173
STANDARD DEVIATION ($\mu\text{g}/\text{m}^3$)	30	9.3

More samples would have been run, especially with the millipore filters, if the motorcycle had not overheated and threatened to stall.

of such experiments ranged from 10 - 15%.

Table X lists some of the important features of the method. The penultimate column gives the volume of air to be sampled to get an absorbance signal equal to ten times the sensitivity of the method provided that the air sampled contains levels at the recognized limits. It is clear that for situations involving possibly dangerous levels of air contaminants (e. g. a mercury spill) a determination can be made with only a very small sample taken in a few seconds.

The last column gives the sensitivity of the technique in terms of the concentration ($\mu\text{g}/\text{m}^3$) of these metals based on a ten liter air sample requiring about eight minutes to collect. These sensitivities compare favorably with those given by Thompson et al. (67), who reported their detection limits on the basis of a 2000 cubic meter sample collected on a fiberglass filter over a period of twenty-four hours!

The ambient level of lead in a laboratory in the chemistry building at MSU was measured to assess the degree of reproducibility possible at fairly low levels. Air was drawn through a series of porous tubes for five minutes at flow rates ranging from 220 - 1400 cc/minute using a faucet aspirator for a pump. A mean value of $0.144 \mu\text{g}/\text{m}^3$ with a relative standard deviation of 13% was achieved for nine lead determinations. High volume samples (14 - 29 liters) taken from the roof of the same building on a holiday gave a mean value of $0.052 \mu\text{g}/\text{m}^3$ with an RSD of 7% for three lead determinations. Samples taken on the same oc-

TABLE X: TYPICAL ANALYTICAL PARAMETERS FOR THE DIRECT ANALYSIS

Element	Line nm	Atomization Temp. ¹ degrees C	Safety Limits ² μg/m ³	Volume ³ cc	Sensitivity ⁴ μg/m ³
Co	240.7	3000	---	---	0.01
Mn	279.5	3000	5000	0.009	0.0004
Hg	253.7	900	100	22	0.02
Se	196.0	3000	---	---	0.02
Be	234.9	3000	2	22	0.0004
Cd	228.8	2000	200	0.04	0.0001
Pb	217.0	2200	200	0.7	0.001
Cu	324.7	3000	---	---	0.004
Ag	328.1	2200	---	---	0.0004
Cr	357.8	3000	100	2	0.002

1. Temperature of atomization is only approximate. Values given were measured with an optical pyrometer approximately five seconds after the power was turned on.
2. ACGIH limits taken from Jae Hwang, Anal. Chem., 44, No. 14, 20A(1972).
3. Volume of air sample at the ACGIH limit necessary to give an absorbance signal ten times the sensitivity (atomic absorbance of 0.044).
4. Sensitivity of the method (1% absorption) in terms of μg/m³ based on 10 liter air sample

casion for beryllium and chromium indicated that these elements were at levels below 0.0003 and 0.0007 $\mu\text{g}/\text{m}^3$ respectively.

A common cause of cadmium inhalation is the use of silver brazing alloys in poorly ventilated areas. In order to simulate such a condition, approximately two milligrams of silver solder were brazed to incandescence in the glassblowing laboratory. Fifty cc samples of the air in the room were taken periodically and the cadmium concentration determined. Figure 20 illustrates the results. In an industrial situation Cd levels could run much higher.

Additional experiments were performed in a little used laboratory room. An uncolored candle of a common decorative variety having a tiny lead wire in the wick to stiffen it was lighted and the air sampled for lead. A single candle succeeded in raising ambient levels of lead from 0.14 to 1.5 $\mu\text{g}/\text{m}^3$ in an hour. In another test in the same room, a propane gas mantle lamp raised the beryllium level from nil to 0.8 $\mu\text{g}/\text{m}^3$ in seven minutes. Most of the beryllium was given off in the first few minutes after a fresh mantle was first lit. Immediately above the lamp, levels exceeding 30 $\mu\text{g}/\text{m}^3$ (15 and 3000 times the ACGIH and Montana state limits respectively) were observed. This indicates that lighting such a lamp equipped with a new mantle in an enclosed space such as a tent would be inadvisable.

The only samples checked which gave an appreciable non-atomic interference peak were of undiluted cigarette smoke. A pyrex cigarette

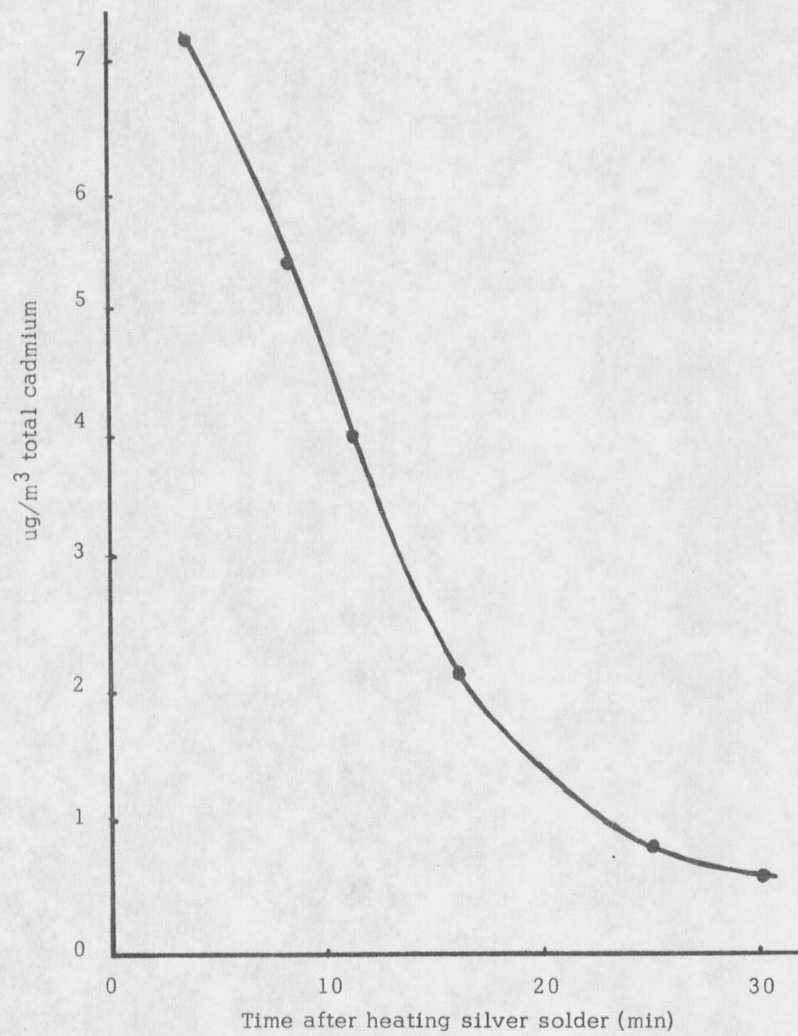


Figure 20. Silver solder experiment

holder was made and the filter adaptor was connected to it with a short piece of rubber tubing. Twenty-five cc samples of the smoke from two unfiltered Camel cigarettes were drawn through porous tubes. The tars were ashed by heating the tubes to a very dull red in the carbon rod atomizer. With lead there was no problem in removing the tars without losing lead; however, with cadmium, because of its greater volatility, it was necessary to adhere to a careful ashing sequence of thirty seconds at 450 - 475 °C to effectively remove tars without loss of the metal. The cadmium level averaged about 5 $\mu\text{g}/\text{m}^3$ and the lead about 50 $\mu\text{g}/\text{m}^3$ with the final samples (taken from the cigarette butt) being higher than the first.

Conclusions

This technique features very low detection levels for a wide range of elements in air samples. The chief reason for this is that all of the collected material is atomized and measured in one instant. Another contributor to its sensitivity is the low "blanks" associated with it. High reagent or filter blanks unavoidable in many analytical techniques drastically limit the detection capabilities possible. For example, a single square centimeter of common organic membrane filter contains an average of 8 ng of lead (62). This blank amount of lead is 800 times that associated with metal picked up in handling the porous tubes, contact with the filter adaptor, storage, etc., is usually less than the sensitivity of the final analysis; i. e., for lead

this blank is on the order of 10^{-11} g or less.

The direct technique is best used where speed of analysis or extreme sensitivity is required. Examples are studies of the diffusion of particles from a source or for rapid determination of possibly dangerous levels of contaminants in a working space. It should also prove useful for the determination of background levels for some elements which are at levels too low for detection by the more common analytical approaches (62).

Applications to which it is not ideally suited are those in which the small sample size and single element capability are limitations. An example of this would be the determination of the average amount of lead over a twenty-four hour period in the air in a car parking lot. Another example would be the determination of the average level of iron, manganese, chromium, and nickel in the air over Gary, Indiana.

The method is cheap, simple, sensitive, and readily adaptable to commercially available instrumentation. The basic approach has proven to work well with the Woodriff furnace and the carbon rod and should be applicable to any carbon furnace with easily changed atomization tubes.

Much of the material in this section has been accepted for publication in *Spectrochimica Acta* (68).

A SIMPLE TECHNIQUE FOR COATING GRAPHITE WITH PYROLYTIC CARBON

Introduction

Recent literature is replete with evidence that carbon non-flame atomizers used for atomic absorption or atomic fluorescence are improved by the use of non-porous pyrolytically coated graphite or vitreous carbon in lieu of the more common and cheaper forms of carbon (44, 69, 70, 71). The reasons lie in the permeability of the usual grades of spectroscopic graphites and "carbons" to gases and solutions. This permeability allows actual loss of sample atoms through the walls of the atomization chamber and shortens the effective residence time of atoms within the optical path. Analyte material from solution partially absorbed into the graphite substrate before drying enters the optical path more slowly upon heating than does material dried on the surface of the graphite. This causes a broadening and lowering of the peak atomic absorption signal that is measured.

This laboratory has been concerned with research on flameless atomic absorption atomizers such as homemade varieties of the Massman furnace (72), carbon rod and, of course, the Woodruff furnace for several years. Over a year ago we became interested in using either pyrolytic graphite or vitreous carbon because of the low porosity of these materials. However, it quickly became apparent that making the required atomizer parts of commercially available varieties of those materials would be prohibitively expensive. Also, the difficulty experienced in machining a sample of vitreous carbon made it apparent that, even if that

material were available in bulk at reasonable cost, construction of atomization furnace parts would be a major undertaking. With these practical constraints in mind we decided to devise a system to coat readily available (and machinable) forms of graphite with an impervious coating.

The Super Temp Company of Santa Fe Springs, California, graciously provided us with the material that got us started (73 - 76). At elevated temperatures, methane will decompose in several steps, eventually forming hydrogen gas and carbon. If a suitable surface is present, the carbon will be deposited upon it. The physical characteristics of the resulting coating are dependent both upon the temperature of deposition and the pressure of the methane. At low (1000 °C) and high (>2100 °C) temperatures, dense carbon coatings are formed regardless of pressure (73). At intermediate temperatures from 1300 °C to 2100°C reduced pressures on the order of a torr of methane are necessary to avoid isotropic, sooty deposits. Commercially, the coating of graphite is done at around 2100 °C at reduced pressures with induction heating of the graphite substrate. We set out to develop a process with which useful pyrolytic carbon coatings could be produced cheaply with equipment available in a general spectroscopic laboratory.

Experimental

To simplify the commercial process, we used a simple tube furnace instead of an RF induction heating apparatus and no vacuum system. The reason that these substitutions are possible is that we utilized rela-

tively low temperatures in the range of 950 to 1150 °C for the deposition. Preliminary experiments were performed by passing methane gas through a quartz tube heated to about 1000 °C in the flame of a torch used for working glass. A hard, shiny coating of carbon was deposited in the heated portion of the tube. By wrapping the quartz tube with a coil of nichrome wire, much more uniform heating and, consequently, better coatings, resulted. From that point the development of the apparatus that we are presently using followed naturally (Figure 21). This apparatus is simply a 17 mm Vycor tube wrapped with about fifty turns of 18 gauge nichrome wire and insulated with a loosely wrapped layer of quartz wool. A large (4.2 KVA) Powerstat variable autotransformer supplies the heating current. A three-way valve allows either nitrogen or natural gas to pass through the tube. The exit tube is placed in a pan of water (or turpentine) to prevent oxygen diffusion into the system. This pan should be in a hood to sweep away the possibly toxic, highly unsaturated hydrocarbon fumes exhausted.

The coating process is simple. The valve is adjusted to pass N₂ through the system and the power is turned on. Then the object to be plated is placed into the right end of the tube furnace and pushed into the center of the heated zone with a quartz rod. The rod is removed and the entrance port restoppered. Then the valve is turned to pass methane through the tube. When the plating time has elapsed, nitrogen is again admitted, and the object is moved with the quartz rod to one

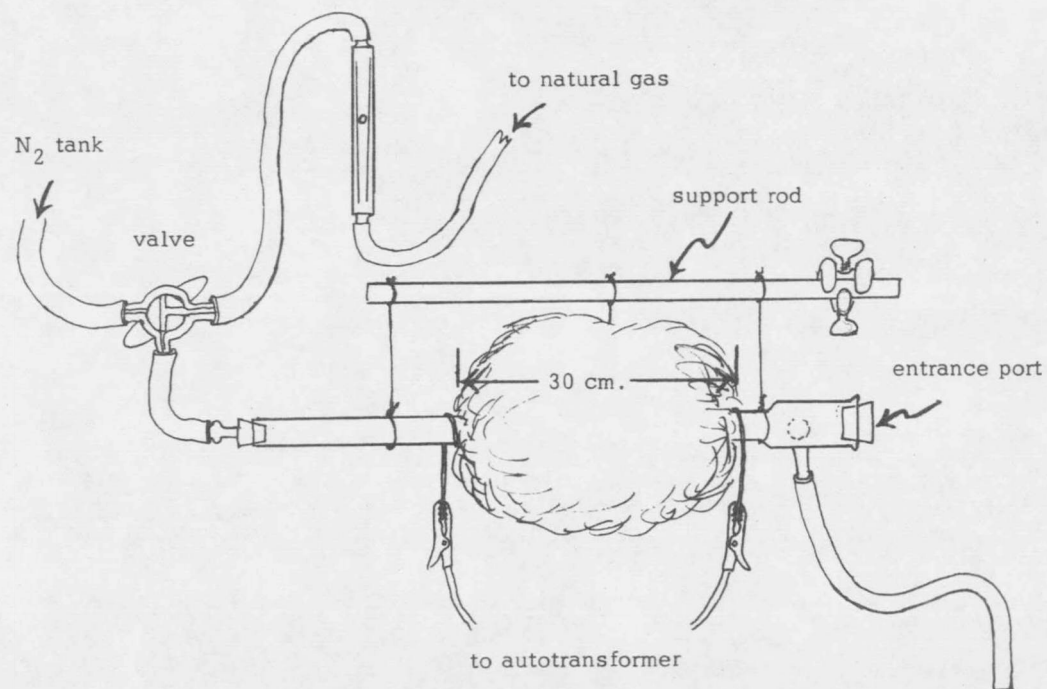


Figure 21. Pyrolytic Carbon Deposition Apparatus

of the cool ends of the tube. When the plated object has cooled it is pushed out of the end of the tube.

The temperature of deposition is measured with an optical pyrometer focussed on the object being plated. The flow rate of the natural gas is from 50 to 200 cc/minute as measured by a Gilmont flowmeter. There must be sufficient flow to assure a fairly uniform bathing of parts to be plated with the natural gas. Too high flows cool the system excessively. Power input to the tube is on the order of 1400 watts.

The carbon rod atomizer described previously in this thesis and a Woodruff furnace were used to compare graphite atomizer components both before and after deposition of pyrolytic carbon coatings.

Results and Discussion

The pyrolytic carbon coatings are metallic grey in appearance, hydrophobic, and very hard. Depending on the size and shape of the object and the temperature, the rates of deposition vary, but are usually in the range of 0.01 to 0.3 mm/hour. Even the lower figure is two orders of magnitude greater than the rate quoted by Kotlensky ⁽⁷³⁾ for depositions at similar temperatures. The only explanation that I can offer for this is that the commercial process utilizes reduced pressures of methane while ours does not.

The rate of deposition as a function of the temperature of deposition was determined by coating a Woodruff furnace heater tube at

different temperatures. These tubes are made of Ringsdorff graphite type R W 105 and are 14.9 cm long with an outside diameter of 1.0 cm and an inside diameter of 80 mm.

The methane flow rate was approximately 120 cc/minute. Figure 22 is a plot of the logarithm of the gain in mass of these tubes in milligrams per minute versus $1/T$. The fact that the data definitely indicate a curved line probably indicates that more than one intermediate species is important in determining the overall deposition rate.

A check of deposition rate with respect to the flow rate of methane gas was made. A Woodriff furnace heater tube similar to the ones used for the temperature effect experiments served as the substrate. At a temperature of 1040 °C, flow rates from 50 to 200 cc/min gave similar results (about 5 mg deposited/minute). At lower flow rates the carbon deposit was not uniform, while at flow rates in excess of 200 cc/minute the deposition was slower. This was probably due to the cooling effect of the excess gas.

The density of the deposited carbon was measured by measuring the mass and volume of low porosity graphite objects both before and after plating. The density of crystalline graphite is 2.26* (76). This figure is commonly approached in commercially deposited pyrolytic graphite. The measured density of the carbon deposited by our apparatus ranges

*Commercial grades of graphite contain a considerable number of voids, resulting in actual densities from 0.9 to 1.9.

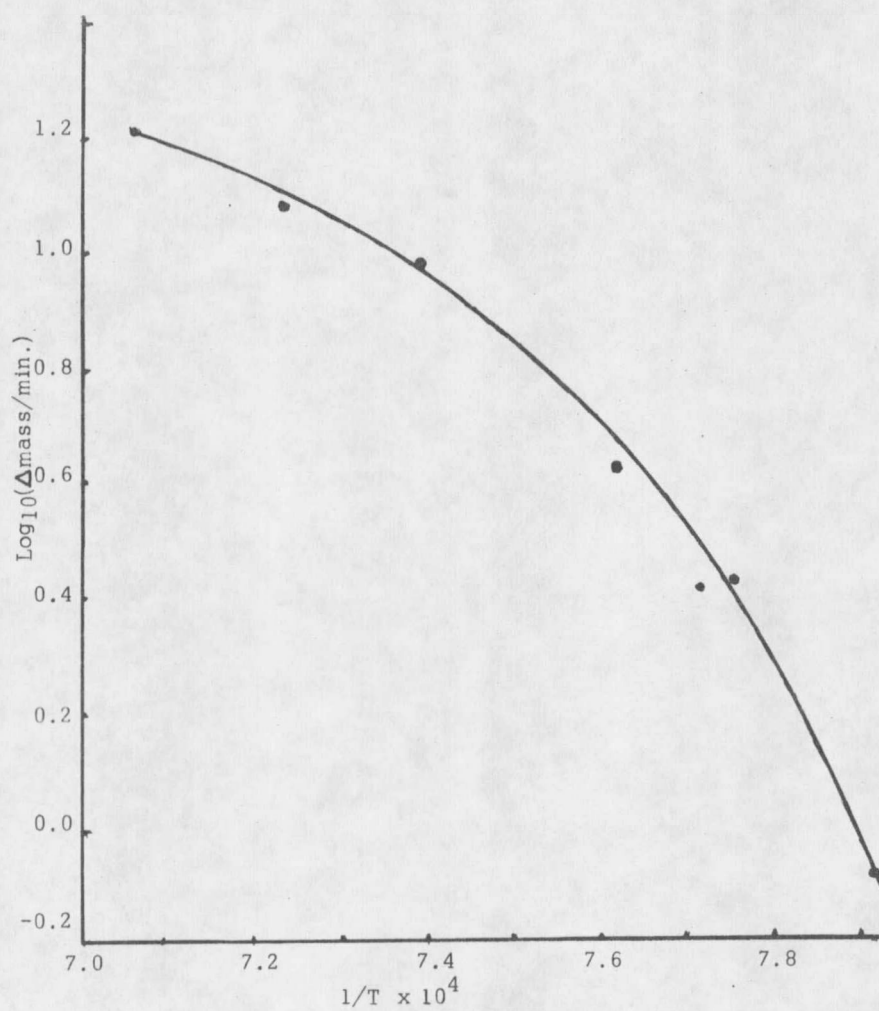


Figure 22. Deposition Rate as a Function of Temperature

from 2.28 to 2.43 g/cc indicating that some infiltration of the substrate graphite's surface takes place during deposition of the pyrolytic coating.

Air was drawn through the walls of porous graphite tubes using the apparatus shown in Figure 9. An uncoated National AGKSP tube, 14 mm long, 6.2 mm o. d. and 4.7 mm i. d. will pass about 1400 cc/minute of air with a pressure differential of 30 cm of mercury across it. The air flow (i. e., the porosity of the graphite) of such a tube is reduced to essentially zero after a forty minute plating period.

A comparison of carbon rod atomizer tubes of these dimensions under conditions of accelerated oxidation gave evidence of the superiority of tubes plated with pyrolytic carbon to those that are not. The data are given in Table XI. Two tubes were made; the first was drilled with a #13 drill and the second with a #12 drill (This results in a 0.13 mm larger diameter hole than the first does.). When the second tube was plated for one half hour, its mass and internal diameter matched the uncoated tube's quite closely.* The tubes were alternatively placed between the rods of the CRA and heated to approximately 3000 °C for four seconds each time for several trials. The amount of N₂ flushing gas was reduced in steps from 20 to 0 foot³/hour as the test proceeded.

*It is important to match the size and mass of carbon rod atomizer tubes quite closely to achieve similar results with different tubes. This is because the analytical signal depends strongly on the rate of atomization, hence, upon the electrical resistance and heat capacity of the tube.

TABLE XI

COMPARISON OF COATED AND UNCOATED CRA TUBES

<u>Tube</u>	<u>no. of cycles</u> ¹	<u>N₂ flow (cfh)</u> ²	<u>mass loss (mg)</u> ³	<u>flow (cc/min)</u> ⁴	<u>A. A.⁵ copper</u>
coated	initial	—	0	50	0.059
coated	2	5	1.2	50	0.065
uncoated	initial	—	0	1300	0.050
uncoated	2	5	3.2	1400	0.048
coated	5	3	3.6	75	0.061
uncoated	5	3	7.8	1500	0.031
coated	3	0	16.2	250	0.054
uncoated	3	0	30.0	1900	0.029

1. All heating cycles were to approximately 3000 °C for 4 seconds (4100 watts atomization power).
2. The usual flushing gas flow is 20 cfh.
3. Cumulative mass loss from initial weighing.
4. A measure of tube porosity; the larger the flow, the more porous the tube.
5. 324.7 nm line, 5×10^{-10} g Cu in 5 ul aqueous solution, 4100 watts atomization power, 20 cfh flushing rate.

After several heating cycles, the porosity (as measured by the air flows through the walls of the tubes with a pressure differential of 25 cm Hg), the loss in mass due to oxidation, and the atomic absorption of 5×10^{-10} g of copper were measured. The plated tube oxidized only one half as fast and gave higher and more reproducible atomic absorbance values throughout the test.

Similar tests were performed comparing coated and uncoated CRA tubes for the determinations of Be, Co, Mn, and Pb with the carbon rod atomizer. In all cases the coated tubes gave both more sensitive and more reproducible analytical results. Coating the heater tubes of a Woodruff furnace atomizer improved the sensitivity for copper almost two-fold. These heater tubes were drilled from Ringsdorff type R W 105 spectrographic graphite and were tested before and after coating for an hour in the plating apparatus.

Another application of the technique is in joining pieces of graphite together. If the items to be bonded are placed in intimate contact, they will be quite securely welded after about an hour's treatment in the tube furnace. The threads of graphite screws and other components of the high temperature atomizers used in this laboratory are strengthened and their useful life extended by coating them.

Some fritted carbon filter crucibles were made using this process. Graphite powder from 80 to 150 mesh was wetted with a two percent solution of Duco cement in benzene and packed into a 2 - 3 millimeter

thick layer at one end of a short graphite tube (Figure 23). The resulting assembly was dried for a few minutes and then inserted into the tube furnace for fifteen minutes. Deposition of pyrolytic carbon in the closely packed frit sealed the particles together and to the graphite cylinder. The resulting filter crucibles are both physically strong and highly resistant to chemical attack. They filter at a high rate (60 ml/minute/cm² filter area) and will quantitatively filter fine BaSO₄ precipitates. They should prove useful in the filtration of solutions which are highly corrosive to the usual fritted glass or porcelain crucibles. The fineness of the frit can be easily controlled by using carbon powders of different sizes.

Some preliminary experiments were performed using a fritted bottom carbon rod atomizer cup (in lieu of the CRA tube used for air particulate analysis) for the direct analysis of suspended matter in natural waters. The filtration apparatus is depicted in Figure 24. Tygon tubing supports the CRA cup and seals the sides from vacuum or water leaks. A measured quantity of pond water is poured into the funnel on top and drawn through the fritted cup. Then the cup is placed between the rods on the CRA and the contents first dried, then ashed, and finally atomized. A portion or all of the filtrate can be caught in a test tube suspended in the suction flask.

A few experiments were performed attempting to relate the ratio of dissolved to suspended lead in the water in the fish pond adjacent

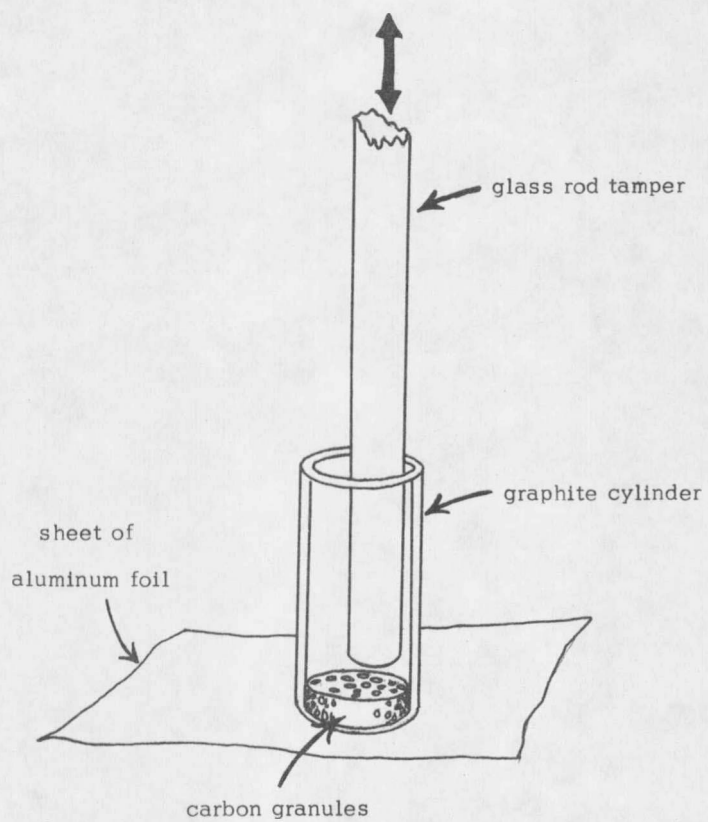


Figure 23. Filter Crucible Construction

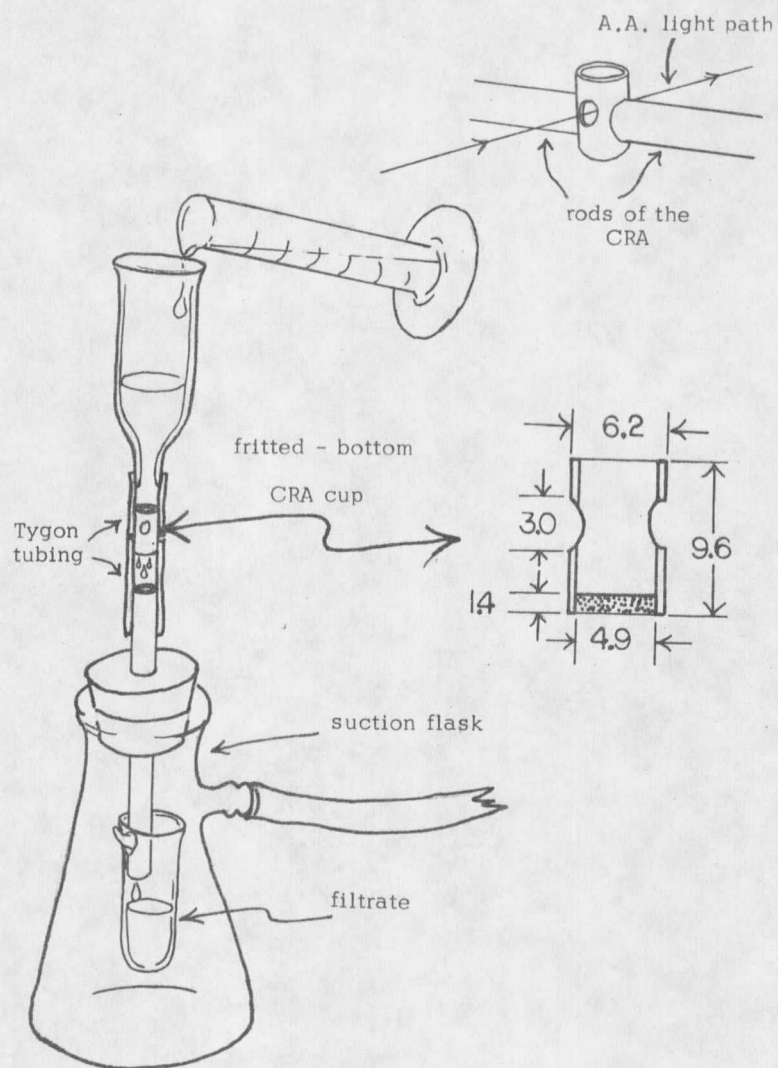


Figure 24. Direct solution particulate analysis

to the music building at MSU. A plot of volume filtered versus total lead retained by the cup is roughly a straight line. However, it was soon apparent that the fritted carbon captures ions from solution as well as those in particulate matter. The cup absorbed approximately two percent of the lead in two milliliters of 2.0×10^{-7} g/ml Pb solution which was filtered. In another experiment with a more dilute lead solution (10 ml of 8×10^{-9} g/ml Pb) the cup absorbed approximately 5% of the lead. This was not entirely unexpected, as some experiments in another study testing different absorbers including graphite for soil solution analysis indicated that almost everything acts as a concentrator of ions from extremely dilute solutions. Attempts were made to pre-saturate sorption sites in the fritted cup with ions such as Ba^{+2} and La^{+3} before passing lead solutions through the cup. These ions were ineffective for this purpose.

For these reasons I feel that a similar application proposed by Wang (77) will be unsuccessful for solution/suspended matter differentiation. However, this approach should prove to be useful on a semi-micro level in which the quantities of materials analyzed are at the microgram rather than the nano and pico gram levels usually measured with flameless atomic absorption. At these relatively high concentration levels the amount of lead absorbed by graphite is insignificant compared to the quantity analyzed. These direct filtration techniques should also prove useful for the determination of ions which can be

quantitatively coprecipitated with a suitable carrier from relatively large amounts of solution.

Conclusions

The pyrolytic carbon deposition process described is certainly not at its peak of potential development; however, it serves the purpose for which it was intended admirably. It allows an experimenter to significantly improve his spectroscopic apparatus quickly and at low cost. What is more important, it allows a degree of freedom in fabricating new equipment (such as the fritted-bottom carbon crucibles) which is not commercially available. The potential used in fields of chemistry other than spectroscopy are manifold. Electrochemists often use non-porous graphite electrodes. Pyrolytic graphite reaction vessels may prove useful for synthesis or analysis.

Much of this work has been accepted for publication in Applied Spectroscopy.

APPENDIX

APPENDIX

A good estimate of the theoretical sensitivity of the CRA for mercury if all of the mercury atoms could be atomized into the light path before any loss through diffusion occurs can be made with standard calculations. The experimental evidence (p.24, this thesis) indicates that the mercury is volatilized from the plated graphite in the temperature range of 200 - 300 °C. At these temperatures and at atmospheric pressure of nitrogen the width of the absorption line is determined primarily by Lorentz broadening. The following equation is from Mitchell and Zemansky (43, p. 10):

$$(eq. 1) \quad \nu_L = \frac{2\sigma_L^2}{K} N^2 RT \left[\frac{1}{M_1} + \frac{1}{M_2} \right]$$

σ_L^2 = Lorentz broadening collision cross section of N₂ gas molecules with Hg atoms

N = Number of N₂ molecules/cc in the absorption cell

M₁ + M₂ = molecular wts of Hg and N₂ respectively

putting in Mitchell & Zemansky's value of σ_L^2 for nitrogen - Hg and 573 °K for T:

$$\nu_L = 2(64.8 \times 10^{-16}) \frac{(9.740 \times 10^3)}{(5.73 \times 10^2)} (6.40 \times 10^2) (10^{15}) \cdot$$

$$2 (8.31 \times 10^7) 573 \left[\frac{1}{201} + \frac{1}{28} \right]$$

$$\nu_L = 4.64 \times 10^9 \text{ sec}^{-1}$$

Atomic absorption follows an exponential law for the intensity I of transmitted light against absorbing length l:

$$(eq. 2) \quad I = I_0 e^{-Kv l}$$

When the absorption line profile of the Hg atoms in the CRA tube is

much wider than that of the emission profile of the hollow cathode lamp (as is the case in our technique) it is permissible to use the absorption coefficient at the center of the absorption line K_0^L instead of K_v in equation 2.

L'vov (44) gives an equation for K_0^L on page 12:

$$(eq. 3) \quad K_0^L = \frac{2e^2}{mc} + \frac{Nf}{v_L}$$

Substituting into this equation the number of atoms/cm³ (N) resulting when 2×10^{-8} g of mercury is atomized in a CRA tube (inner diameter 4.6 mm and length 15 mm) and literature values for e (charge of an electron), c (speed of light), m (mass of an electron), f (the oscillator strength of the 2537 Å Hg line), and our calculated value of v_L , we obtain a K_0^L as follows:

$$K_0^L = \frac{2(4.8 \times 10^{-10})^2}{(9.1 \times 10^{-28})(3 \times 10^{10})} + \frac{(2.4 \times 10^{14})(3.0 \times 10^{-2})}{4.64 \times 10^9}$$

$$K_0^L = 2.6 \times 10^1$$

Substituting this value of K_0^L into equation 2 using a 1.5 cm path length, we expect to see:

$$I = I_0 e^{-26(1.5)}$$

$$I = I_0 10^{-(.434)(26)(1.5)}$$

$$Abs = (.434)(26)(1.5) = 17$$

The absorbance actually observed when 2×10^{-8} g of mercury is atomized in the rod is about 0.4. This indicated that at no time is more

than a small fraction $\left(\frac{0.4}{17}\right)$ of the total mercury atoms in the optical beam. The results of similar calculations based on the dimensions and instrumental conditions in the Woodruff furnace agree with the actually observed absorbances measured to within a factor of two or three. This indicates the greater atomization efficiency of the furnace as compared to the carbon rod atomizer.

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