



A background correction technique for double beam spectrophotometers and the analysis of microtrace concentrations of silver using furnace atomic absorption spectroscopy
by Bruce Robert Culver

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
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Abstract:

Two aspects of furnace atomic absorption spectroscopy were studied.

The first involved the development of a background correction technique using plane polarized light. Two perpendicularly polarized light beams were compared to one another — a continuous background source and the hollow cathode radiation. Solid and liquid samples were run. The solid samples were inserted into the furnace using a graphite cup and the liquid samples were ultrasonically nebulized into the furnace. Calibration curves for Co, Cr, and Ag were run. Blank cups were inserted using: Al, Co, Cr, Cu, Dy, Mg, and Mn hollow cathodes.

No blank reading was observed. An optical system employing a Glan-Taylor calcite polarizer was used. A Beckman D. B. was used to compare the two polarized beams. Sensitivities ranged from about 10-11 g for solid samples and 10-10 g/ml for liquid samples.

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The second feature covered was the development of an analytical method for analyzing for microtrace concentrations of Ag in snow, hail or water. The method involved preconcentration of the Ag by solvent extraction and its subsequent analysis by furnace atomic absorption (FAA). The extractant was a ditbizon-CCl₄ solution. Two hundred twenty five snow and four hail samples were analyzed by this method. A comparison between flame boat AA, neutron activation analysis and furnace AA was presented. The results obtained by the boat technique were quite different than those obtained by the other two methods. Where neutron activation analysis is +30% reproducible, FAA's reproducibility is +5%. The concentration ranges involved were on the order of 5x10⁻¹¹ gm/ml. The sensitivity for the FAA method was 5x10⁻¹³gm/ml.

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Bruce R. Culver

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Sept. 21, 1971

A BACKGROUND CORRECTION TECHNIQUE FOR
DOUBLE BEAM SPECTROPHOTOMETERS
and
THE ANALYSIS OF MICROTRACE CONCENTRATIONS OF
SILVER USING FURNACE ATOMIC ABSORPTION SPECTROSCOPY

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BRUCE ROBERT CULVER

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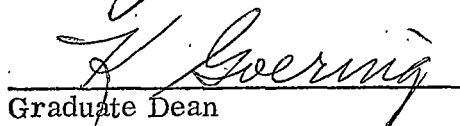
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ABSTRACT

Two aspects of furnace atomic absorption spectroscopy were studied. The first involved the development of a background correction technique using plane polarized light. Two perpendicularly polarized light beams were compared to one another — a continuous background source and the hollow cathode radiation. Solid and liquid samples were run. The solid samples were inserted into the furnace using a graphite cup and the liquid samples were ultrasonically nebulized into the furnace. Calibration curves for Co, Cr, and Ag were run. Blank cups were inserted using: Al, Co, Cr, Cu, Dy, Mg, and Mn hollow cathodes. No blank reading was observed. An optical system employing a Glan-Taylor calcite polarizer was used. A Beckman D.B. was used to compare the two polarized beams. Sensitivities ranged from about 10^{-11} g for solid samples and 10^{-10} g/ml for liquid samples.

The second feature covered was the development of an analytical method for analyzing for microtrace concentrations of Ag in snow, hail or water. The method involved preconcentration of the Ag by solvent extraction and its subsequent analysis by furnace atomic absorption (FAA). The extractant was a dithizone- CCl_4 solution. Two hundred twenty five snow and four hail samples were analyzed by this method. A comparison between flame boat AA, neutron activation analysis and furnace AA was presented. The results obtained by the boat technique were quite different than those obtained by the other two methods. Where neutron activation analysis is $\pm 30\%$ reproducible, FAA's reproducibility is $\pm 5\%$. The concentration ranges involved were on the order of 5×10^{-11} gm/ml. The sensitivity for the FAA method was 5×10^{-13} gm/ml.

INTRODUCTION

Our environment and the quality thereof is the concern of every man, woman, and child on this planet. With the development and application of reliable and sensitive analytical methods, chemists have been able to monitor trace element concentrations and their influence on the inhabitants of the earth. Furnace atomic absorption spectroscopy (FAA) is perhaps one of the most revolutionary analytical techniques at the present time. It has the sensitivity capability to compete with neutron activation analysis, while at the same time being as reproducible as flame atomic absorption, these two features coupled with the fact that solid, liquid, or gas samples can be analyzed make FAA a potentially powerful tool in the fields of pollution control, weather modification, medicine, and geochemistry as well as chemistry.

Within the past two years, several large instrument companies have made available non-flame atomic absorption attachments for their commercial atomic absorption spectrophotometers. In general, these systems are quite different than the furnace. Most commercial models flash evaporate the sample by heating the entire system each time a sample is introduced. The furnace, on the other hand, remains at a constant temperature as samples are inserted into it for atomization. The commercial non-flame units are about two orders of magnitude more sensitive than flame AA, while furnaces are about four orders of magnitude more sensitive than flame AA.

The more prominent workers in the field of non-flame AA are: L'vov in Russia, ^(1, 2, 3) Massman in West Germany, ⁽⁴⁾ Kahn and Manning in this country, ^(5, 6) Amos in Australia, ⁽⁷⁾ and Woodriff also in this country. The system developed by L'vov is undisputedly the most sensitive, but is neither practical nor convenient as far as the routine analysis of samples is concerned.

This thesis deals primarily with two aspects of FAA, the first being the development of a background correction technique which can be applied to any double beam atomic absorption system. The second aspect covered is the application of FAA to the analysis of metals in real samples, namely, silver in snow. This is currently the best method for analyzing for microtrace concentrations of silver in either snow or water.

STATEMENT OF THE PROBLEM

Background Correction

In atomic absorption spectrophotometry, background absorption occurs from solvent matrix effects, from light scattering in the optical pathway, or anything else other than the sample which absorbs light from the hollow cathode source. There are various methods for eliminating the relative effects of background absorption. One of these techniques is to compare the hollow cathode radiation with some continuous source such as a hydrogen or deuterium lamp⁽⁸⁾. This is usually done in the ac mode, that is, the photomultiplier alternately detects the monochromatic radiation and the continuous radiation. The output is the net difference between the two. A second technique involves the same principle except that the photomultiplier compares the line emitted from two different hollow cathodes or elements⁽⁹⁾. A more recent method developed by Rains, involves a vibrating sector placed inside the entrance slit⁽¹⁰⁾. The sector optically compares the monochromatic radiation on and off the line. This technique is simple and holds great promise.

It was thought that a system using plane polarized light could be used as a background correction technique⁽¹¹⁾. If the reference radiation is polarized perpendicular to the sample radiation, the two could be compared either in the ac or dc mode. In the ac mode, the output is the net difference between the two sources. In the dc mode both sources can be observed independently⁽¹²⁾. The

system discussed involves the use of the ac mode. The technique will work quite well if the two polarized beams can be effectively separated.

Analysis of Silver

Seeding clouds with silver iodide crystals is one of the oldest and most widely used types of weather modification. In theory, the silver iodide crystal is quite similar in structure to a snow crystal. It should therefore serve as a nucleating agent for a snow crystal in a supersaturated cloud. Many millions of dollars and man hours have been devoted to the study of silver iodide and its effect on cloud physics and precipitation. Under laboratory conditions in a cold chamber set up to model a supersaturated cloud, seeding with silver iodide is quite effective. The technique involves counting snow flakes to determine if seeding occurred. This method when used in the field, although it is quite cumbersome and time consuming, has had some degree of success⁽¹³⁾. Another more practical method is to measure the silver concentration in seeded and unseeded snow and make some sort of correlation between increased snow pack and increased silver concentration. During the past five years there have been two accepted techniques for measuring Ag in snow. The first and most widely accepted is neutron activation analysis⁽¹⁴⁾. This technique requires large samples (1 to 10 liters of melted snow), a source of neutron flux, much money (ca. \$50 per sample), and has poor precision in the region of the Ag concentration

in snow. Another even less precise method has come into existence recently. This method, however, is cheap. It is a flame atomic absorption technique involving a micro-sampling boat⁽¹⁵⁾. The claimed detection limit for this technique ranges from 10^{-10} gm/ml to 5×10^{-11} gm/ml of silver. These reported limits incorporate a preconcentration step and a 10X recorder scale expansion. Ordinary flame AA has been used for the silver analysis in seeded snow, but the procedure lacks reliability⁽¹⁶⁾. The values reported by these methods are, to say the least, quite questionable.

Background concentrations for silver in snow range from 4×10^{-11} gm/ml to 2×10^{-12} gm/ml. Seeded samples contain from 6×10^{-11} gm/ml to 6×10^{-10} gm/ml of silver.

The sensitivity of FAA for silver is on the order of 5×10^{-13} gm/ml with a 10X preconcentration step and no recorder scale expansion. The reproducibility of the method in the 5×10^{-11} gm/ml range is +5% as compared to +30% with neutron activation analysis. FAA should be an excellent method for micro-trace silver analysis⁽¹⁶⁾. There are, however, many problems involved in handling such small concentrations of silver. Untreated aqueous silver solutions are unstable, especially if the silver concentration is below 10^{-8} gm/ml. Silver is adsorbed onto the surface of the container wall, therefore the solution must be stabilized. Contamination is another problem. Most containers,

solvents, and reagents are contaminated with silver at this concentration level. The method developed, and the procedure used for handling the samples will be discussed.

EXPERIMENTAL

Background Correction

The apparatus used for this study can be separated into three categories: the furnace, the optical system, and the detection system.

The Furnace

The furnace design illustrated in figure 1 depicts a second generation furnace. This furnace is somewhat different than that used previously^(17, 18). The heater tubes are 15.2 cm long, 10 mm o.d., and 7 mm i.d. The heat sink in the center holds the heater tubes, the shield tube, and also acts as the sample inlet. At the outer ends, the heater tubes are held by copper chucks. The chuck is attached to a spiral copper tube (figure 2) which acts as an end cooling plate. The spiral tubing is flexible to allow for expansion of the heater tubes. The furnace is flushed with argon gas to prevent the oxidation of the graphite. The argon enters at the sample port, passes down the side tube, and out the heater tubes. The hot gas escapes from the furnace through the copper cooling coils and is monitored with flow meters.

Solid, liquid, and gas samples can be introduced into the furnace for analysis. Solids are placed on a graphite cup, ashed if necessary, screwed on to an 1/8 in. graphite rod and inserted through the side tube. Liquid samples can either be evaporated on a cup, or nebulized directly into the furnace. Gases could be analyzed by introducing the gas in place of the argon at a constant

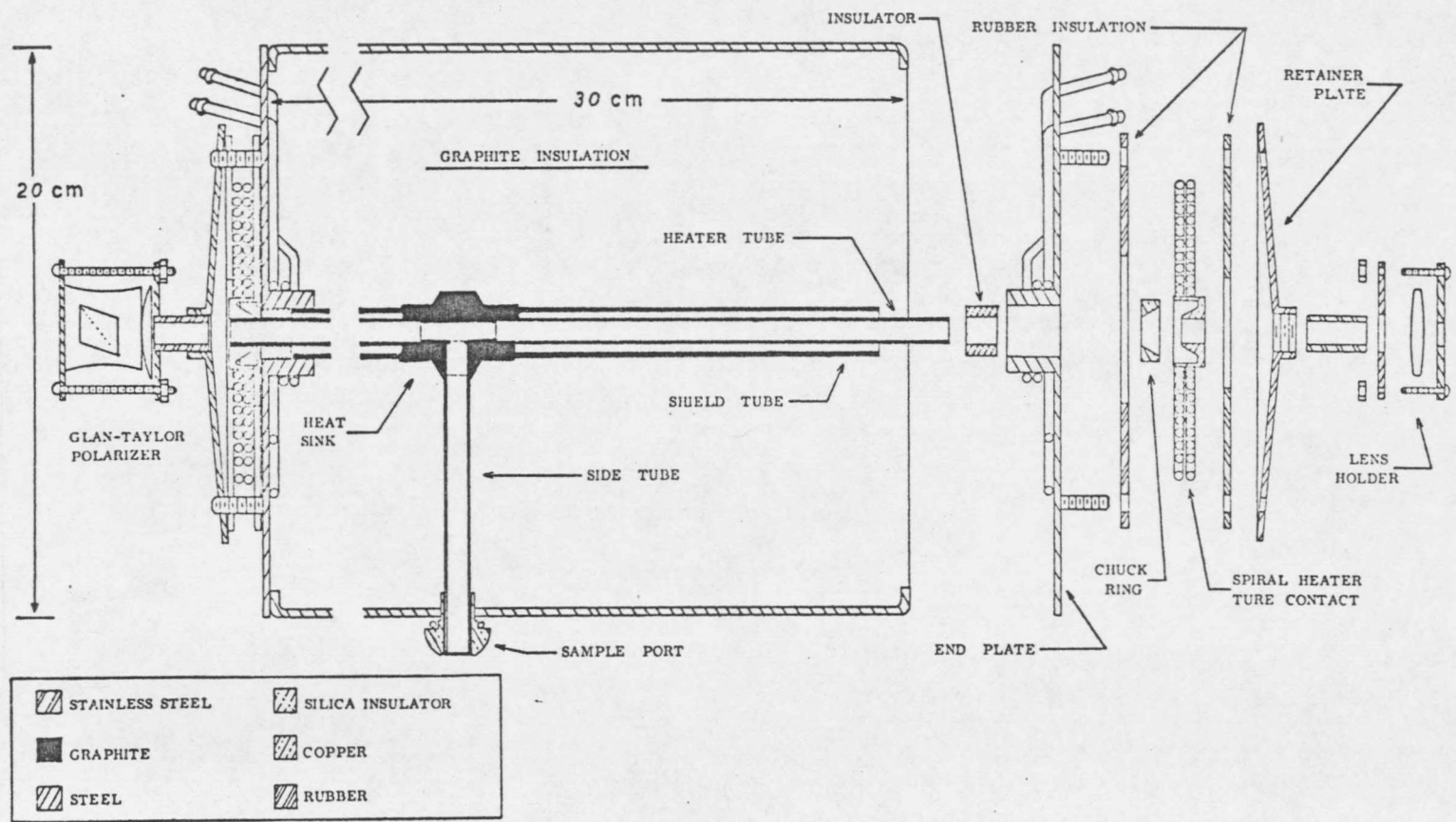
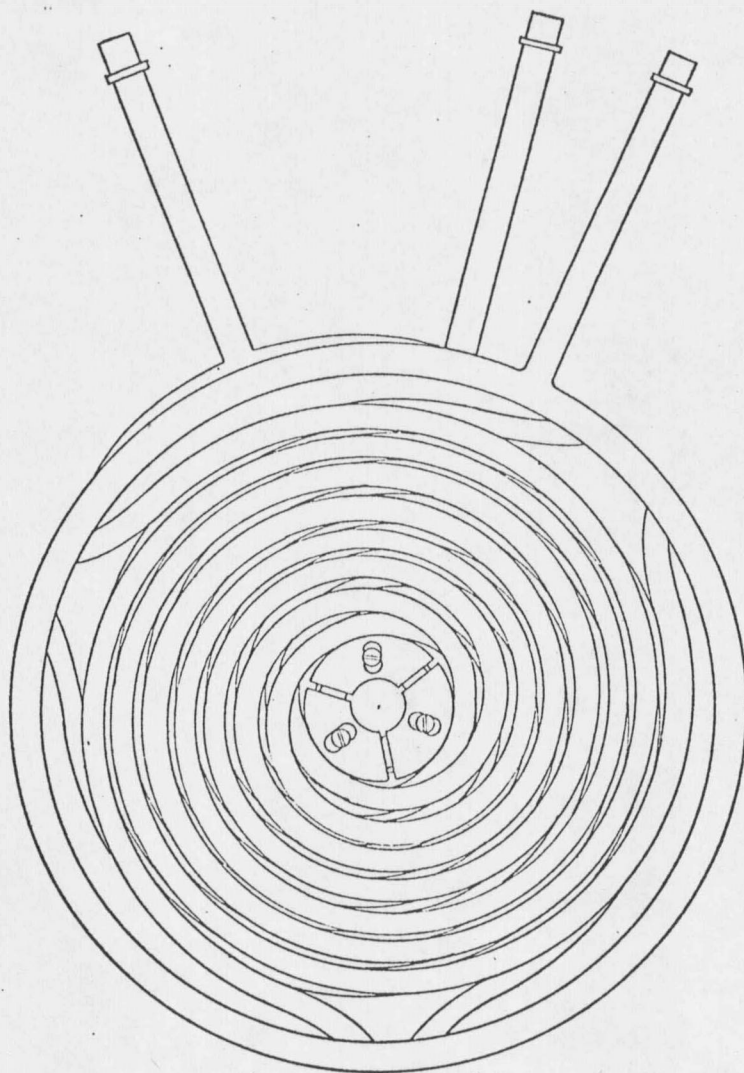


Figure 1: The Furnace (a second generation model)



SPIRAL HEATER TUBE CONTACT

Figure 2: Copper cooling coil and electrode chuck

flow. Liquid samples were analyzed for this study using both techniques mentioned above.

Attached to the sample port is a Vycor 18/9 socket used to aid sample introduction. The furnace temperature was measured with an optical pyrometer.

The Optical System

The optical system (figure 3) consists of a Glan-Taylor air spaced calcite light polarizer, two Glan-type prism polarizers placed in the instrument sample compartment and a quartz collimating lens. Two light sources are needed: a hollow cathode and a hydrogen lamp which is used as a continuous background source.

The hollow cathode light is polarized by the Glan-Taylor polarizer before it passes through the furnace. The hydrogen lamp light enters the polarizer through the side window at a 7° angle to the normal to the optical axis. Two polarized beams from the hydrogen lamp emerge from the polarizer. One is polarized perpendicular to the hollow cathode light while the other is an extraordinary ray and is polarized parallel to the light from the hollow cathode. The extraordinary ray is removed by merely positioning the polarizer so that only the beam which is polarized perpendicular to the hollow cathode light passes through the furnace. The extraordinary ray is absorbed into the furnace wall.

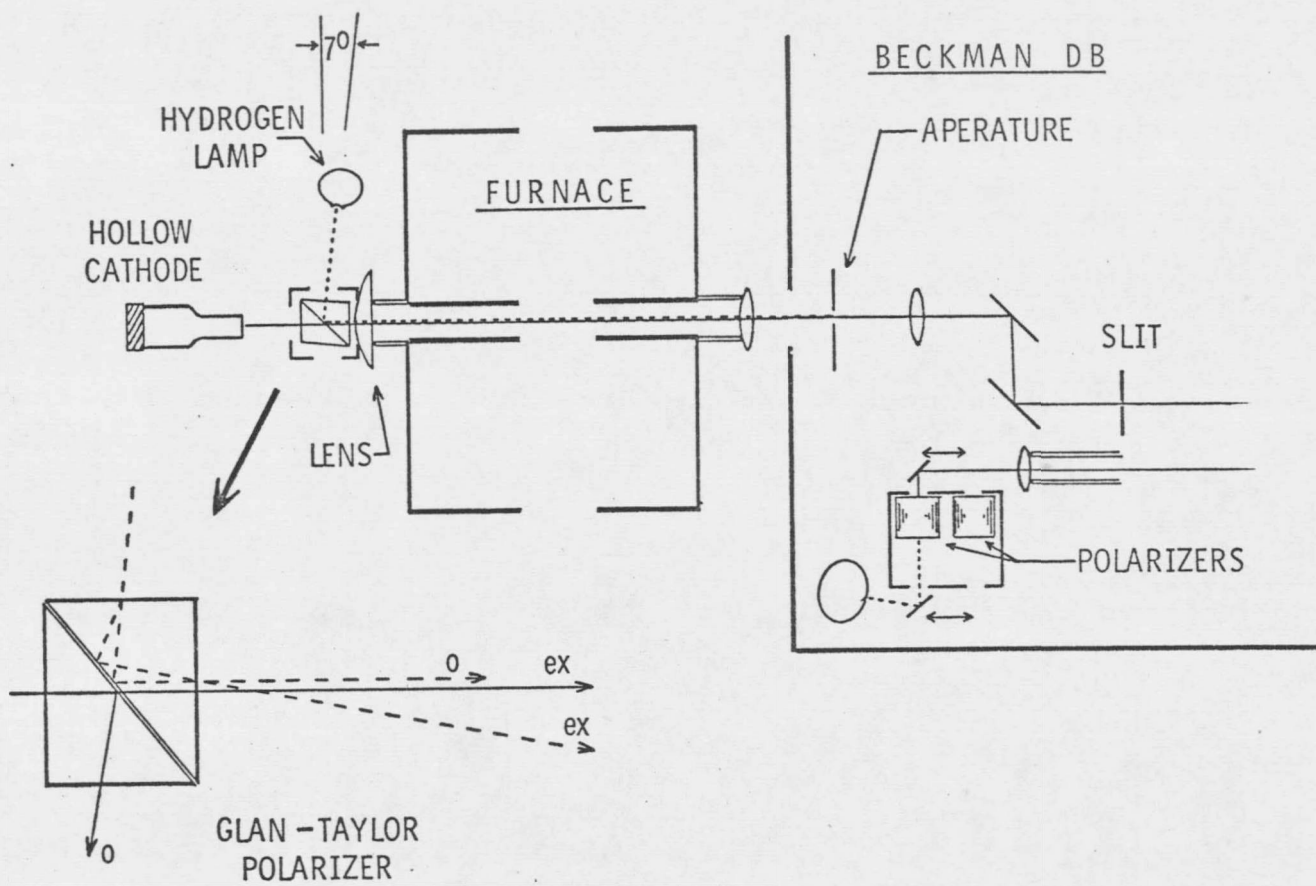


Figure 3: The Optical System

The angle between the two hydrogen lamp beams is about 10° . The extraordinary ray from the hollow cathode, which is transmitted, is polarized parallel to the optical axis of the calcite and the ordinary ray from the hydrogen lamp is polarized perpendicular to the calcite's optical axis.

Both collimated beams proceed through the furnace and come to focus on the aperture placed just inside the entrance to the Beckman D. B. spectrophotometer.

The Detection System

The monochromator and read-out for this system is a Beckman D. B. spectrophotometer. A D. B. is a double beam ratio recording instrument. After the two polarized beams go through the furnace and come to focus on the aperture in the D. B. they proceed to the instrument slit, then on through the monochromator. After passing through the monochromator the beam comes to focus on a vibrating mirror which alternately reflects the light through one of the two polarizers located in the sample compartment. One polarizer transmits only the background light and the other only the hollow cathode light. After passing through the polarizers the light falls on the photomultiplier and the net absorbance is recorded. A Beckman model 93506 linear and log potentiometric 6 in. recorder was used to record the results.

Sample Preparation

The two types of standard solutions used were solid and liquid standards. Solid standards are standards that have been evaporated on a graphite cup, and liquid standards are nebulized directly into the furnace. The solid standards were prepared from salts of the metal to be investigated. The standards were made by diluting a 10^{-7} gm/ml solution of the metal. Fifty μ l portions of the standards were pipetted into a graphite cup and evaporated to dryness. The cups (6 x 11 mm) were screwed onto a 1/8 in. graphite rod and inserted into the furnace for analysis. After the signal was recorded, the cup was cooled in the Vycor entrance tube before being placed back in a dessicator where the cups remained when not being used.

Liquid standards, which are to be nebulized, are aqueous or dilute acid solutions of a salt of the metal to be investigated. The solutions were diluted to the working concentration range with distilled methanol. In this case, the working range was on the order of 10^{-7} - 10^{-9} gm of metal/ml of methanol. In solutions containing less than 10^{-8} gm Ag/ml the Ag exhibited a tendency to become adsorbed on the walls of the beaker if the solution was left to set in the beaker for more than 15 minutes. Complexing the silver with EDTA seemed to slow down the rate of this adsorption.

Sample Nebulization

Nebulization of the sample solution is carried out using an ultrasonic nebulizer^(19, 20) (figure 4). The solution is pumped across the silvered face of a vibrating piezoelectric crystal (1.3 MHz) at a rate of 2.32 ml/min. The nebulized vapor is then pushed through the furnace with argon gas. The amount of vapor flowing into the furnace is .465 ml/min. This indicates that 20% of the sample gets into the furnace. The remaining 80% of the sample is discarded. The size of the methanol droplets is on the order of 1.0 μ .

Various coatings for the piezoelectric transducer have been studied^(19, 20). At the present time a coating which is capable of withstanding frequencies on the order of 1-5 MHz and is also resistant to concentrated acids and/or bases has not been developed.

The flow meters attached to the cooling coils on the outer ends of the furnace indicated that the argon flow out of the furnace was about 1 liter/min. Gas flow into the nebulizer chamber was on the order of 500 ml/min.

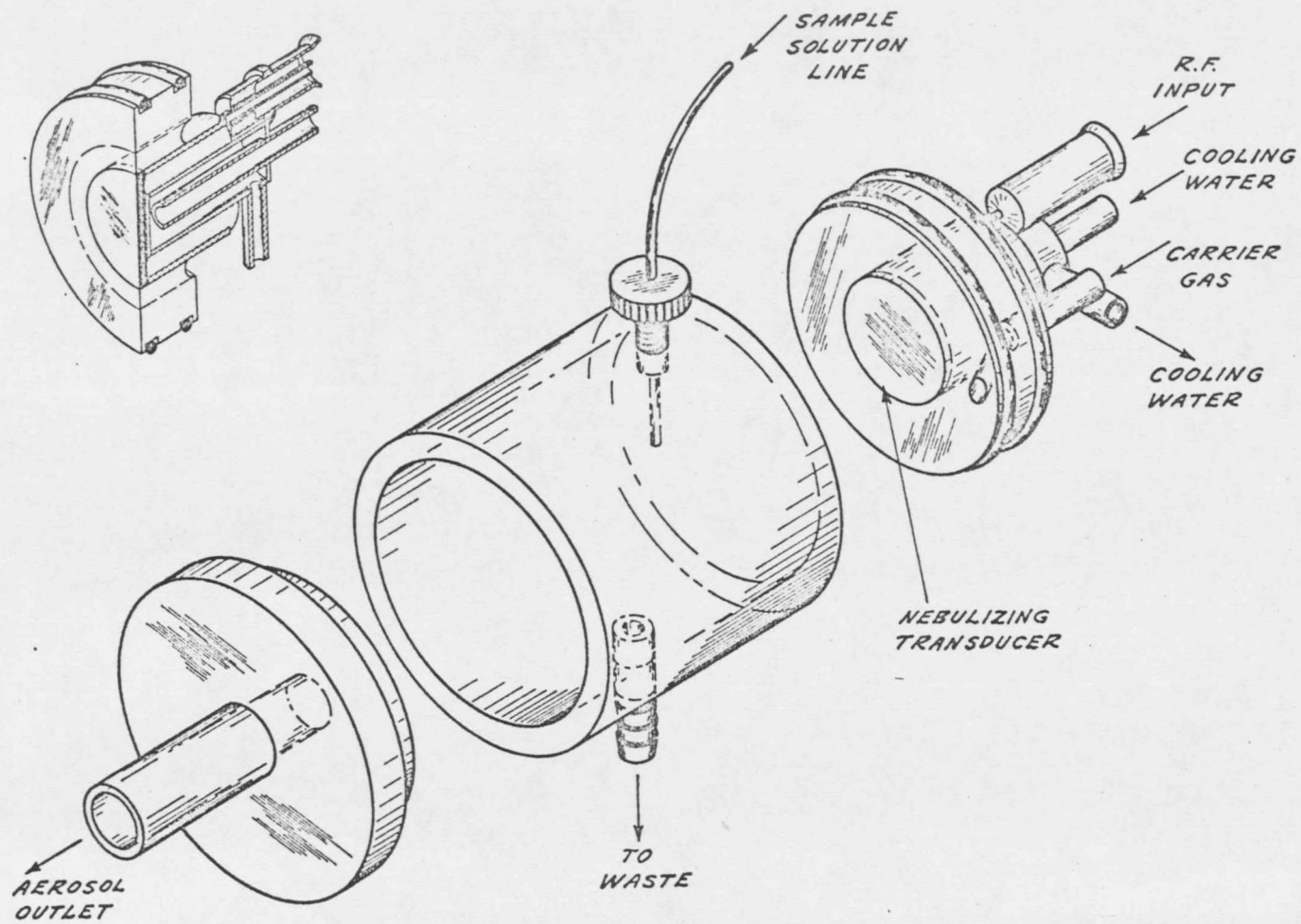


Figure 4: A Direct Impingement Ultrasonic Nebulizer

RESULTS AND DISCUSSION

Background Correction

The optical system using plane polarized light proved to be very advantageous in reducing the effects of the background absorption. Typical recorder readings for solid samples and liquid samples are shown in figure 5 (a) and (b). Calibration curves for Ag, Cr, and Co were obtained (figure 6).

The lack of reproducibility of the blank, especially with solid samples, has been a source of error in trying to determine the absolute sensitivity for elements using graphite tube furnace technique⁽¹⁸⁾. When cups are inserted into the furnace and butt against the retainer inside the heat sink, small flakes of carbon occasionally will fall through the light path and cause absorption of some of the hollow cathode radiation. If any organic matter is on or in the cup, it will pyrolyze to form free carbon particles which also cause background absorption. Using the polarized light optical system, an equal amount of the continuous background light is also absorbed, balancing out the hollow cathode absorption so that the net absorption is zero. The optics must be aligned so that the two collimated polarized beams coincide throughout the entire length of the furnace. If this is not the case, unequal portions of the polarized beams will be absorbed, making the technique less efficient.

Blank cups were inserted into the furnace using the following hollow cathodes: Cu, Co, Cr, Mn, Mg, Al, and Dy. No net blank was observed for

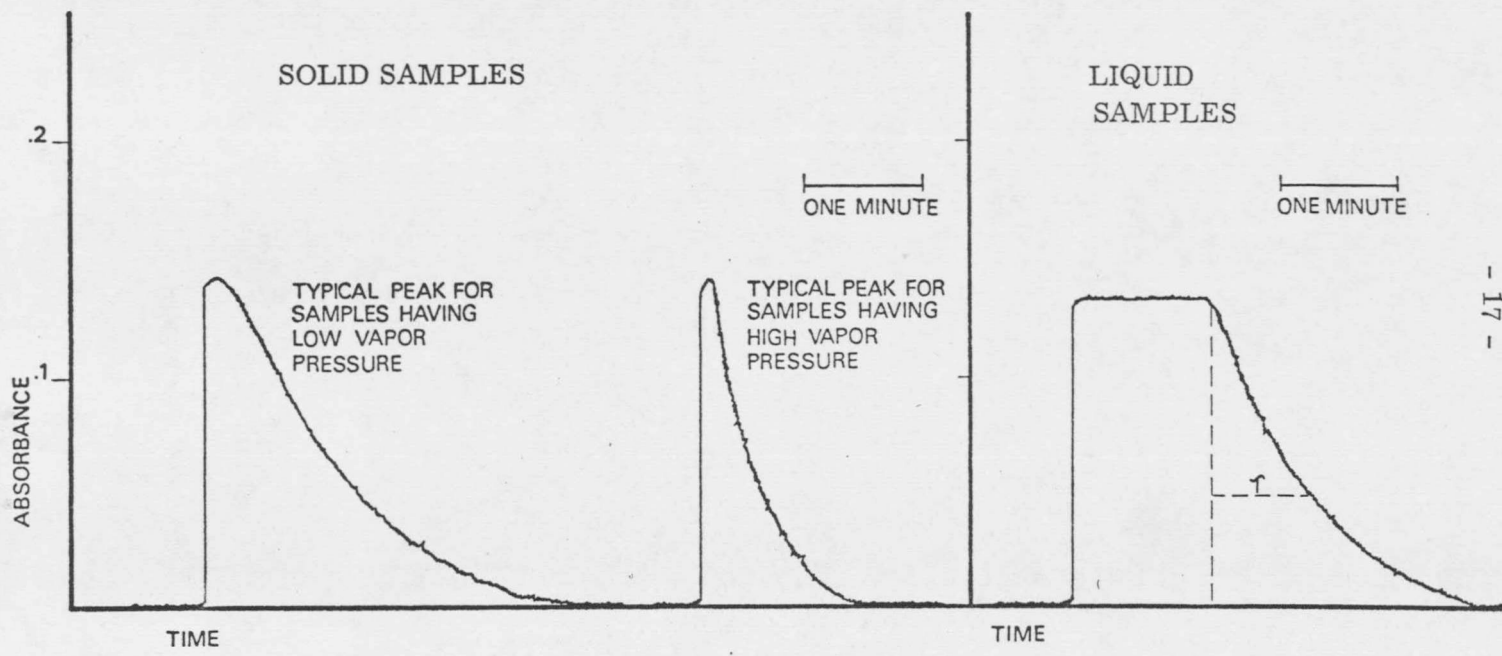


Figure 5: Typical Recorder Traces

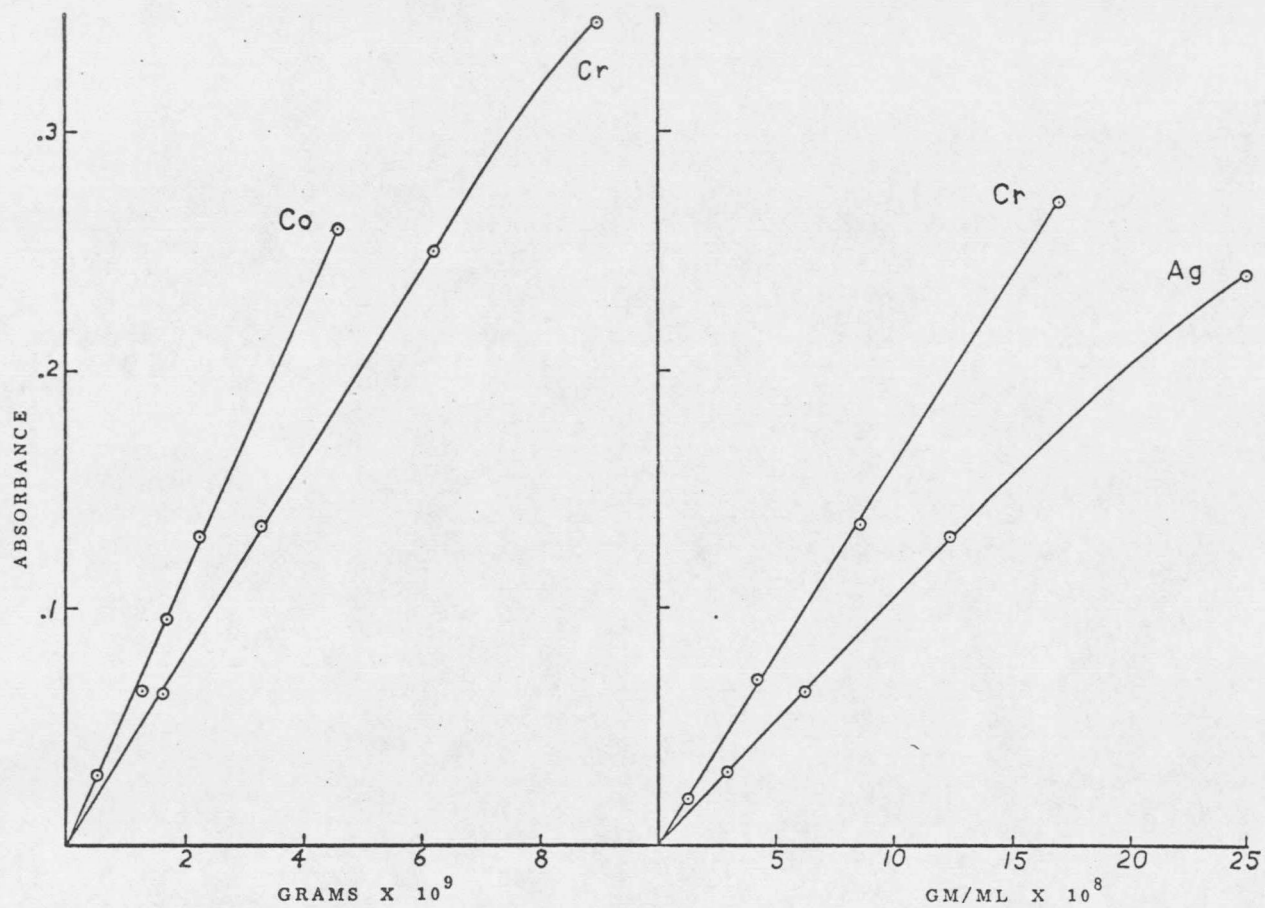


Figure 6: Calibration curves

any of these elements. It should be emphasized, however, that because of the rather crude instrumentation 100% scale deflection was not always obtainable. Below 2400 Å the calcite in the Glan-Taylor polarizer began absorbing light and, due to alignment difficulties, above 4100 Å blackbody radiation from the furnace walls interfered. Using better instrumentation and recording technique coupled with improved optics, these problems could be alleviated. Calibration curves for Co and Cr using the cup technique are presented in figure 6 (a).

Nebulizing liquid samples into the atomization source, whether it be a flame, plasma, or furnace, is of greater interest to analytical chemists than introducing solid samples into the atomization source. The technique described looks very promising for routine analysis of trace elements. Calibration curves for Ag and Cr were obtained (figure 6 (b)). Once the sample solution is pumped over the face of the piezoelectric crystal it requires approximately 3 seconds to reach maximum absorption. A steady state condition is then reached.

It was observed that the time constant of the sample decay curves could be directly related to sample concentration. This is because the decay curves fall off exponentially and are quite consistent. The decay curve is dependent upon: furnace temperature, the vapor pressure of the element, and somewhat on gas flow rate. If the first and last of these parameters are held constant, it is reasonable that a standard curve (concentration vs. time constant) could be

obtained. At high concentrations of sample (95% scale deflection +) a saturation point is reached and a Beer's law plot begins to flatten out making peak height a less reliable measure of concentration. At these higher concentrations the time constant could be a more precise measure of concentration. For smaller concentrations, however, the time constant is usually too short to get precise measurements.

TABLE I: Sensitivity Data for Elements

| Element | Wavelength (Å) | Sample Phase | Furnace Temperature (°C) | Sensitivity |
|---------|-------------------|-----------------|--------------------------------|-----------------------------|
| Co | 2407.3 | solid | 2400 | 1.1×10^{-10} gm |
| Cr | 3578.7 | solid | 2200 | 8.0×10^{-11} gm |
| Cr | 3578.7 | liquid | 1850 | 3.0×10^{-10} gm/ml |
| Ag | 3280.7 | liquid | 1600 | 4.5×10^{-10} gm/ml |

The sensitivities of the calibration curves obtained are listed in Table I. Calculated absorbance readings corresponding to 1% absorption determine the sensitivities for the elements tested.

The system described can be applied to any double beam spectrometer.

It should work quite well with flame atomic absorption instruments. Furnace atomic absorption is more advantageous than flame atomic absorption, because it confines the sample in a small volume of longer path length with a nonturbulent inert atmosphere in which absorption can take place. With improved instrumentation trace element analysis down to 10^{-12} g/ml for some elements could be commonplace.

EXPERIMENTAL

Silver Analysis

This section can be separated into four main categories: preparation of the glassware and reagents, the furnace, the procedure, and the detection system.

Preparation of the Glassware and Reagents

One set of Pyrex glassware is kept specifically for the analysis of silver. It consists of: 6-400 ml beakers, 6-150 ml Teflon stoppered separatory funnels, 1-100 ml graduated cylinder, 1-50 ml graduated cylinder, 1-10 ml graduated cylinder, and 2-500 μ pipettes. All the glassware was purchased new, and not used for any other purpose. A solution consisting of:

- 1 liter of distilled water
- 1 liter of concentrated hydrochloric acid
- 50 ml of concentrated hydrofluoric acid
- 50 ml of 30% hydrogen peroxide

was used for cleaning all the glassware. The glassware was rinsed in this solution. After this initial cleaning, the separatory funnels were kept filled with 1.0 N HNO₃ between uses. The beakers and graduated cylinders were periodically soaked in 1 N HNO₃, then rinsed 6 to 8 times with doubly distilled water.

The reagents used were dithizone (diethylthiocarbazon), carbon tetrachloride, and nitric acid. The dithizone is reagent grade and was recrystallized

five times to insure its purity. The carbon tetrachloride was distilled as was the nitric acid. All reagents were independently checked for silver. The water used for rinsing the glassware and making dilutions was doubly distilled in Pyrex.

The Furnace

The furnace used in this study was a third generation furnace (figure 7). It is essentially the same basic design as a second generation furnace with one major exception — the outside jacket is double walled stainless steel for water cooling. The shield tube and heat sink was constructed from one piece of graphite. These two features seemed to have greatly increased the lifetime of the heater tubes. One particular pair lasted 10 months without burning out. Previous to that, the expected lifetime was one or two months. The furnace temperature was measured through the side tube with an optical pyrometer. Furnace temperatures can be varied from 200°C to 2800°C. The temperature for the silver analysis was either 1650°C or 1800°C. The power dissipated to acquire these temperatures was about 2500 to 3000 watts. The furnace is powered with a GE dc arc welder.

The Procedure

The snow samples were collected in plastic bags placed at the various collection sites. They were kept frozen at all times until just prior to the

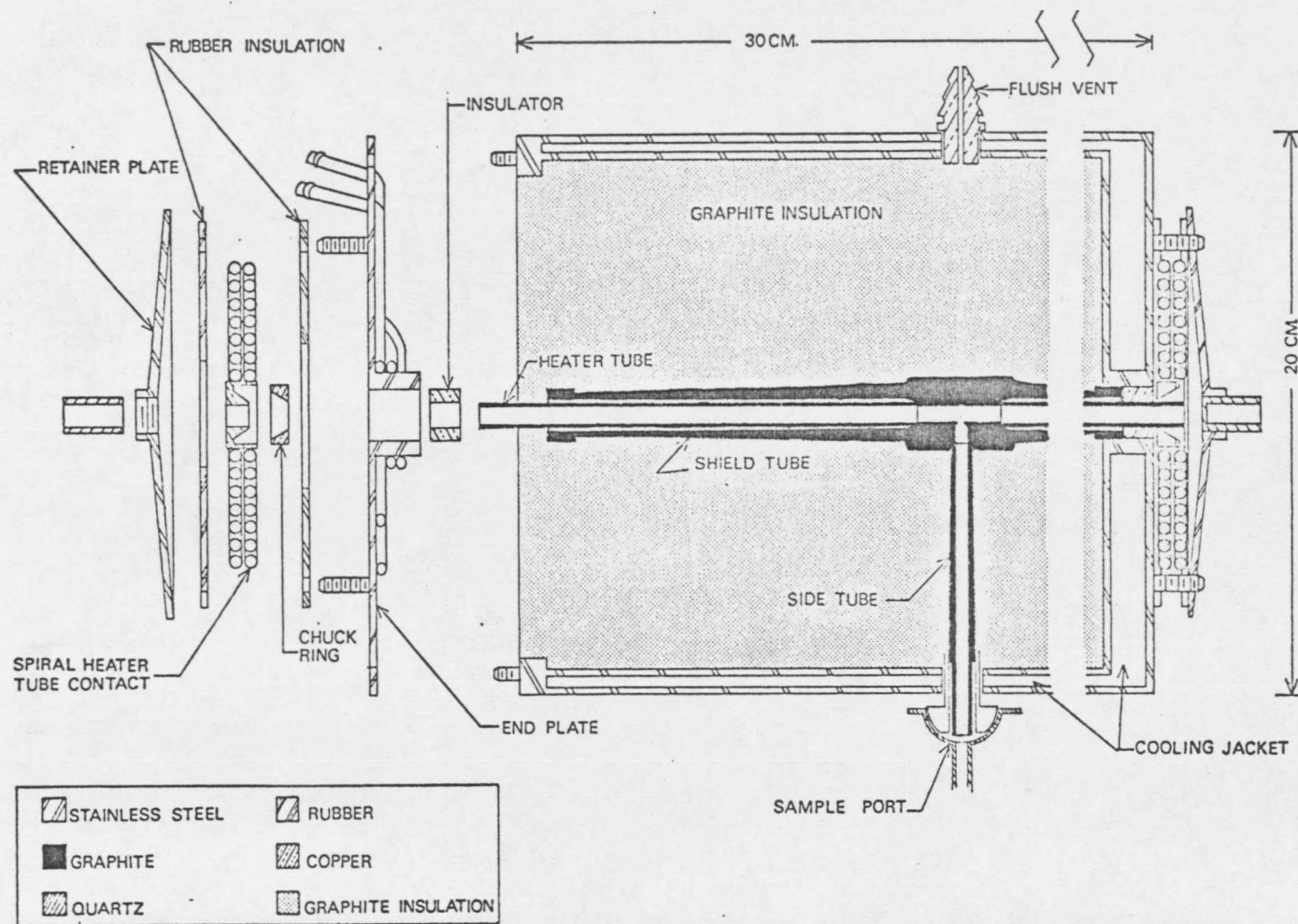


Figure 7: The Furnace (a third generation model)

extraction step. The men collecting the samples were carefully instructed how to handle the bags to avoid any possibility of contamination. Most of the samples were collected weekly either by snowmobile or helicopter. The sample size varied from 500 ml of snow up to 4 or 5 liters. The method is as follows:

1. Break up sample in bag and mix thoroughly.
2. Fill a 400 ml beaker with snow and melt on a hot plate.
3. Immediately after the snow has melted add 1 ml of .1 N HNO₃ to 100 ml of the melted snow sample (sample is at pH 3).
4. Pour the sample into a separatory funnel and add 5 ml of 10⁻⁵ M dithizone-CCl₄ solution. Shake the funnel vigorously for about 45 seconds.
5. After the layers have separated, transfer a portion of the organic phase to a 5 ml holding bottle. The sample may be stored for one day in the bottle in a refrigerator with no appreciable losses of Ag.
6. Using a 100λ Eppendorf pipette, evaporate 500λ of the organic phase onto a graphite cup under an infra-red lamp. The volume of a cup is about 120λ. Duplicate cups for each sample are run.
7. After the sample is on the cup, it can be analyzed immediately or several days later. The cups are stored in a dessicator. To analyze, the cups are screwed onto a 1/8 inch graphite rod and inserted

into the furnace.

The results are reported as grams of Ag/ml of melted snow. The normal concentration range for silver in snow is on the order of 10^{-11} gm/ml, (10^{-6} gm/ml = 1 ppm).

The Detection System

A picture of the instrumentation is on page 27. The major components of the system are: the furnace, a Spex 3/4 meter Czerny-Turner Spectrophotometer, a Princeton Applied Research (PAR) HR8 lock-in amplifier and light chopper, a Honeywell 6 inch recorder, and the associated electronics (Hewlett Packard and Fluke power supplies, Tektronix oscilloscope, etc.).

The Spex monochromator was set on the most sensitive of the two silver resonance lines. The line is at 3280 \AA . The photomultiplier in the Spex is an RCA IP28. The hollow cathode light was chopped at 400 hertz, and the PAR amplifier was locked-in on that frequency. The signal from the photomultiplier was monitored by the oscilloscope as it went into the PAR.

The recorder records the signal, and its chart speed was set at 2 min/in. Figure 5 shows a typical trace.

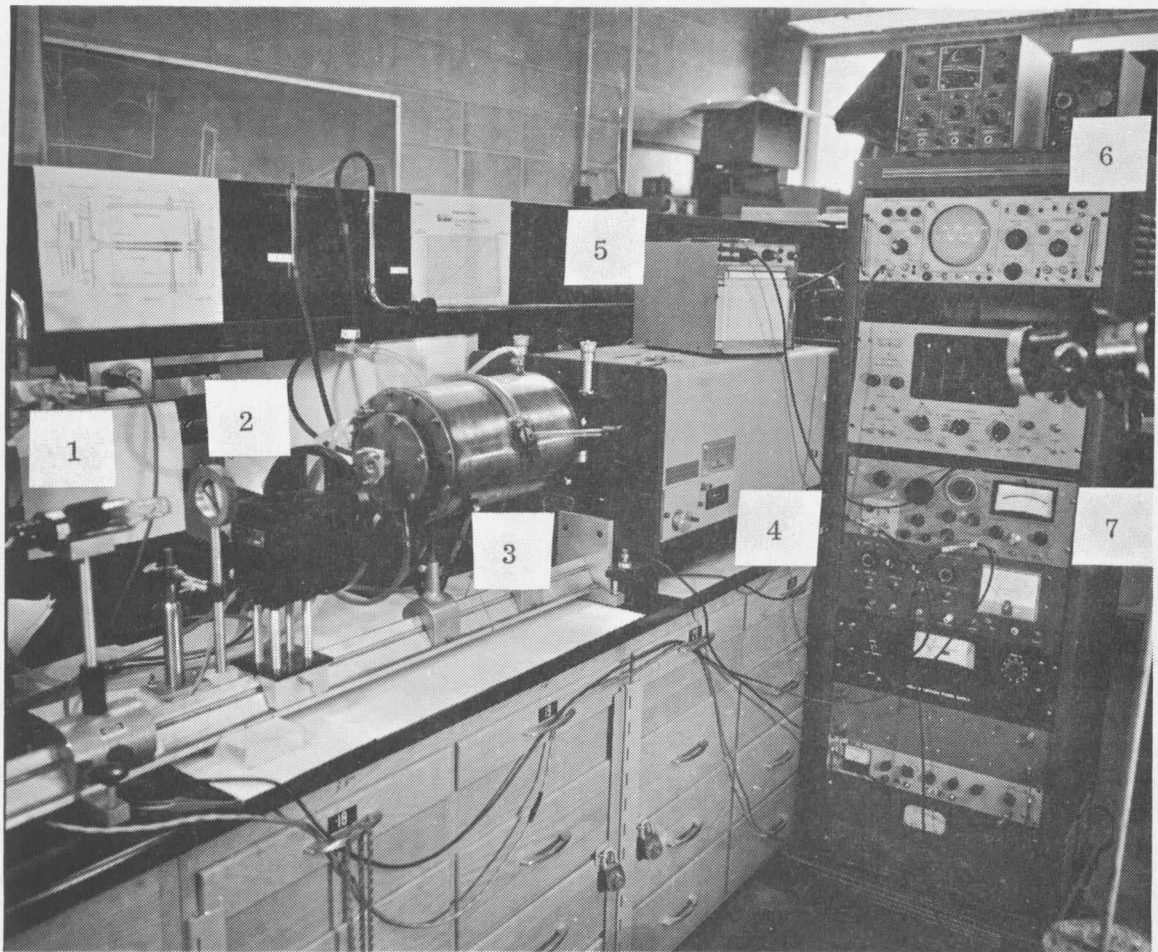


Figure 8: Picture of the instrumentation

1. The hollow cathode
2. PAR model BZ-1 light chopper
3. The Furnace - a third generation model
4. Spex 3/4 meter Czerny-Turner spectrophotometer
5. Honeywell 6 inch recorder
6. Techtronics type RM 503 oscilloscope
7. PAR HR8 lock-in amplifier

RESULTS AND DISCUSSION

Silver Analysis

Several possible methods of sample preparation for silver concentrations in the picogram to nanogram range have been studied by workers in our laboratory⁽²¹⁾ as well as others^(14, 15, 16). Some of the methods were: coprecipitation of the silver with a carrier and subsequent centrifugation into a cup for analysis, preconcentration of the silver using an anion-exchange column⁽¹⁴⁾ electroplating the silver onto a Pt or Ir filament for emission spectroanalysis in a RF induced discharge,⁽²¹⁾ and extraction of the silver into an organic solvent with some chelating agent for preconcentration. After carefully studying these methods, the latter was chosen as the simplest, most reliable, and practical method.

Dithizone (diethylthiocarbazon) was chosen as the best chelating agent for silver because it has a high degree of specificity for silver over a wide pH range. The primary silver dithizonate, which is formed at pH's below 7, is soluble in organic solvents and practically insoluble in water. Chloroform is the usual solvent for dithizone because metal dithizonates are most soluble in chloroform. The silver concentration in chloroform, however, was too high (ca. 10^{-9} gm/ml) for it to be used. Several attempts were made to remove the Ag from the chloroform, but none were successful. Carbon tetrachloride was then selected as a solvent, and proved to be quite free from silver after being distilled once.

The first attempts to extract the silver involved extracting 50 ml of melted snow into 5 ml of 10^{-5} M dithizone in carbon tetrachloride and evaporating all 5 ml on a graphite cup. The background peaks were off scale using this technique. The sample size was cut in half to 25 ml, but the background peaks were still too high. Another problem encountered with this technique was high blanks due to the contamination of the glassware. Blank peaks ran between 20% and 50% scale deflection and were inconsistent. The glassware could not be completely cleaned of silver. Silver seems to slowly leach out of the glass over a period of weeks or months. This problem pertained mostly to the separatory funnels. Keeping the funnels filled with 1 N HNO_3 between uses seemed to decrease the problem over a period of time, but did not entirely eliminate it.

The two methods mentioned above were in essence putting 50 and 25 ml of melted snow on the cup. The Ag concentration was too high. An alternative method was developed. This new method not only decreased the Ag concentration to within the right range but also eliminated the blank problem from the glassware, and saved time.

The method involved taking a larger sample (100 ml), but only evaporating 1/10 of the extractant onto a cup (.5 ml). This technique is equivalent to evaporating 10 ml of melted snow on a cup while at the same time cutting the blank one order of magnitude. The working range was 3×10^{-12} gm/ml up to about 3×10^{-10}

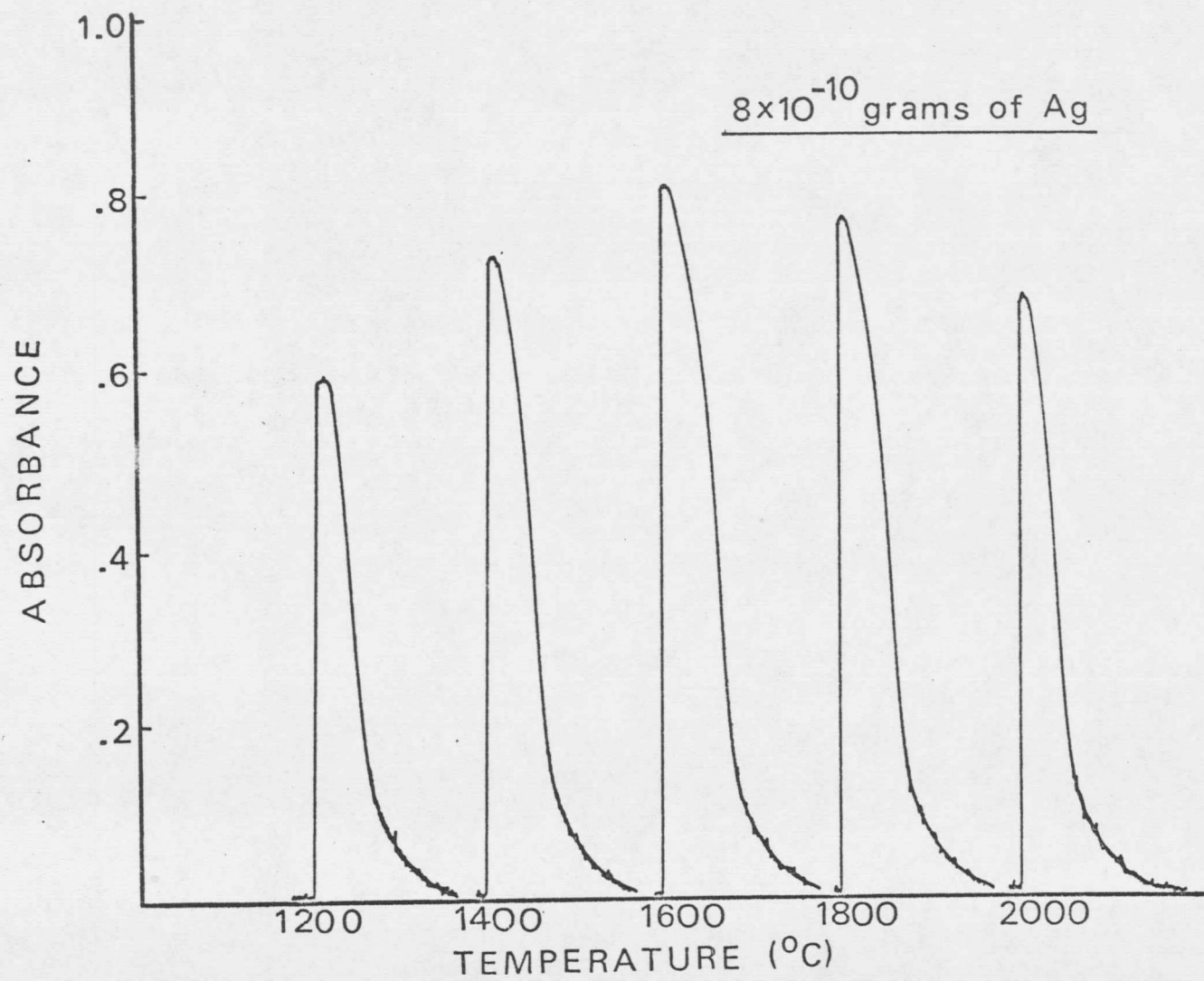
gm/ml. Some highly seeded samples still went off scale, but a smaller portion of the extractant (200λ), which was held in the holding bottle, was evaporated on another pair of cups and rerun immediately.

Another problem encountered in handling samples containing such minute quantities of silver is that of surface adsorption. Silver has a tendency to adsorb onto container walls if the solution is not properly treated^(22,23). This is why it is necessary to acidify the sample as quickly as possible after it has melted. Once the sample is acidified the silver will stay in solution for a short time (ca. 1/2 hour). The silver was always extracted immediately to avoid this problem.

The optimum furnace temperature to analyze silver was determined. Figure 9 shows that maximum sensitivity is achieved somewhere between 1400°C and 1800°C. Two Ag standard curves were run, one at 1650°C and the other at 1800°C (figure 10). Although the 1650°C curve is obviously more sensitive, the 1800°C curve is more linear over a wider concentration range. Both curves were made by running standard silver solutions through the extraction procedure.

Some Results

Over 225 snow samples and 4 hail samples were analyzed using the above mentioned method. Nineteen of these samples were triplicated and sent



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Figure 9: Temperature Calibration Curve for Silver

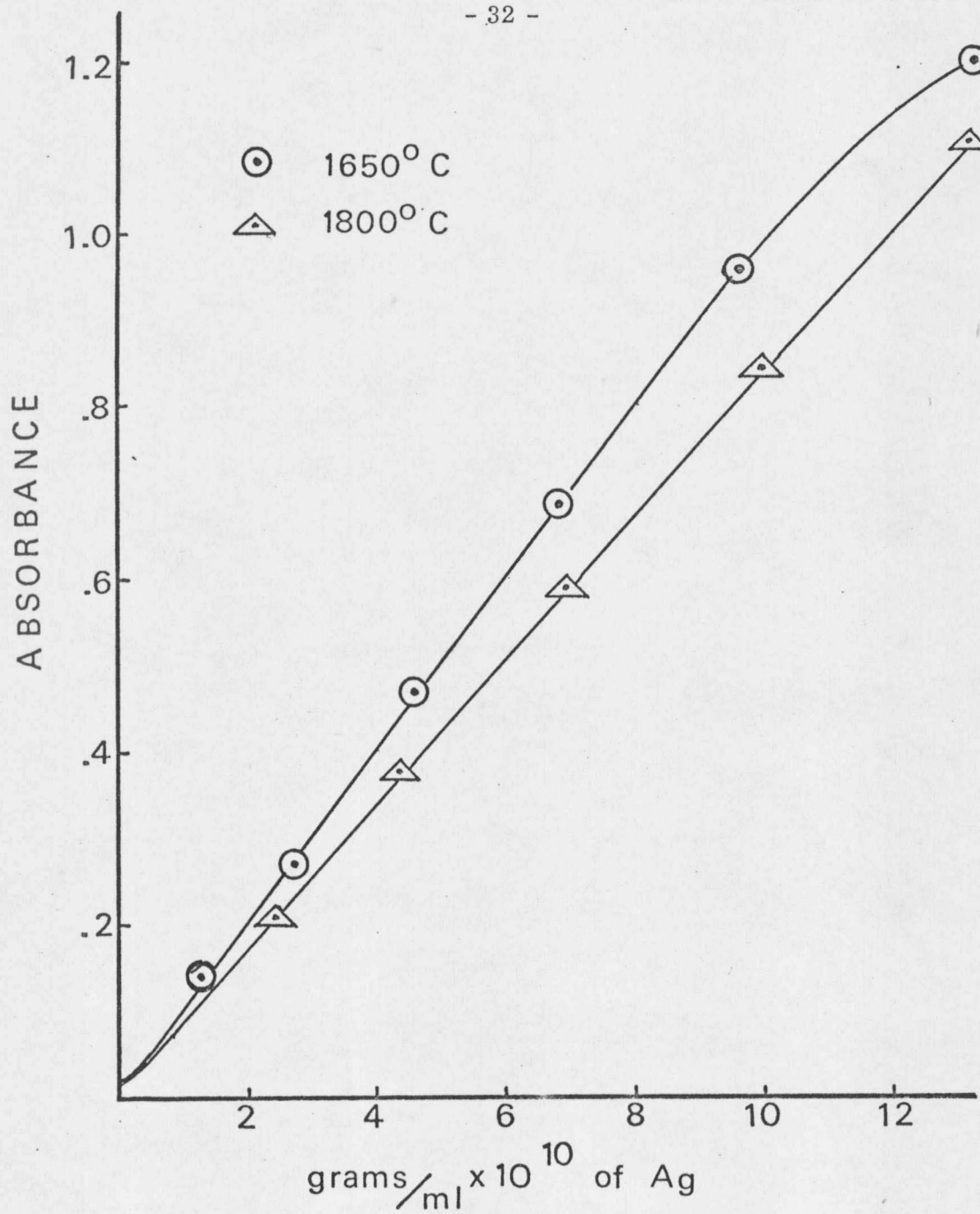


Figure 10: Silver Standard Curves

to two other laboratories, Bureau of Reclamation Laboratory in Denver, Colorado, and Desert Research Institute near Reno, Nevada. In Denver, the samples were analyzed using a flame AA boat technique. The samples sent to DRI were done by Warburton using neutron activation analysis. Table II shows some results of these methods as compared to the furnace technique. The results of the samples done in Denver are questionable. In most cases the samples analyzed at DRI are in good agreement with the furnace method. Using the furnace, some samples were found to have a 35% silver gradient from one end of the sample to the other. This necessitates thorough sample mixing. The triplicate samples sent to the various mentioned laboratories were not the same sample. They were carefully taken from the same location, but were not portions of the same sample. These two facts could account for some of the variation between this method and that done by neutron activation analysis. The boat technique is not even competitive with the other methods.

Of the samples analyzed, 22 were unsatisfactory (i. e., the duplicates were quite different). These samples were reanalyzed. Some of the results are shown on table III. The tags were changed to insure honesty on the part of the chemist. Every one of the reanalyzed samples were either almost equal to one of the other two earlier results or fell between the two earlier results.

TABLE II: Comparison of FAA with other Analytical Methods

(results in $\text{gm/ml} \times 10^{-10}$ of Ag)

| Snow Sample | boat AA (Salman) | NAA (Warburton) | FAA (Culver) |
|-------------|------------------|-----------------|--------------|
| 301 | 3.7 | 0.6 | 0.5 |
| 302 | 2.4 | 0.4 | 0.3 |
| 303 | 1.5 | 0.9 | 0.7 |
| 304 | 1.0 | 0.8 | 0.6 |
| 305 | 13.0 | 0.3 | 0.3 |
| 307 | lost | 0.2 | 0.8 |
| 308 | 0.6 | 0.2 | 0.5 |
| 309 | 3.8 | 1.7 | 0.8 |
| 310 | lost | 0.3 | 0.7 |
| 311 | 1.4 | lost | 0.1 |
| 312 | lost | 0.2 | 0.5 |
| 313 | 0.6 | 0.1 | 0.5 |
| 314 | 1.4 | 0.5 | 0.6 |
| 315 | 0.7 | 0.2 | 0.5 |
| 316 | 11.0 | 24.8 | 2.6 |
| 317 | 20.0 | 27.9 | 4.2 |
| 318 | 0.6 | 0.1 | 0.1 |

TABLE III. Comparison of Some Samples Analyzed on Different Days
(results in gm/ml x 10⁻¹⁰ of Ag)

| Sample | Analyses | | | | | |
|--------|----------|---------|------|---------|-------|---------|
| | #1 | date | #2 | date | #3 | date |
| 105 | 0.17 | 2/19/71 | 0.53 | 6/24/71 | *0.44 | 7/13/71 |
| 106 | 0.46 | 2/17/71 | 0.70 | 6/29/71 | *0.63 | 7/13/71 |
| 108 | 0.81 | 5/22/71 | 0.46 | 6/23/71 | 0.56 | 7/13/71 |
| 109 | 0.23 | 2/19/71 | 0.61 | 6/24/71 | 0.20 | 7/13/71 |
| 111 | 0.29 | 2/20/71 | 0.57 | 6/24/71 | 0.52 | 7/13/71 |
| 116 | | | 1.10 | 6/24/71 | 0.90 | 7/13/71 |
| 120 | | | 0.32 | 6/24/71 | 0.45 | 7/13/71 |

*results are the average of triplicate determinations

Four frozen hail samples taken in conjunction with the Northeast Colorado Hail Experiment (NECHE) were analyzed for background silver concentration. The results are listed in table IV. The silver background in hail appears to be one to two orders of magnitude higher than that of the snow, and varies so much that not much useful information could be obtained by analyzing hail for silver. Silver iodide is used by meteorologists for hail suppression work. The reason for the high background could be because hail storms are

generally quite turbulent and dust could easily contaminate the samples even though they are taken 30 feet above the ground. Most soil contains about .1 ppm of silver⁽²⁴⁾.

TABLE IV: Silver in Hail Samples

| Sample | Date Taken | Silver Concentration |
|--------|---------------|----------------------------|
| 1 | July 9, 1971 | 22×10^{-11} gm/ml |
| 2 | July 9, 1971 | 16×10^{-11} gm/ml |
| 3 | June 30, 1971 | 7×10^{-11} gm/ml |
| 4 | June 21, 1971 | 11×10^{-11} gm/ml |

Note: Samples 1 and 2 were taken during the same storm.

CONCLUSIONS

These investigations were undertaken to determine if:

1. Polarized light could be effectively used for a background correction technique using double beam spectrophotometers.
2. A practical, reliable, and inexpensive method for the silver analysis of snow could be developed.

The results show that polarized light can be used as a background corrector. Comparing a continuous background source of an elemental or hollow cathode source has been an effective way of removing the relative effects of extraneous light absorption and/or scattering. The polarized light technique proved to be a potentially useful extension of the method.

The method developed for analyzing silver in the picogram range proved not only to be practical, reliable, and inexpensive, but it is also fast and simple. This method is currently the best method for silver analysis in snow, hail, or water for concentrations below the nanogram/ml range.

NEED FOR FURTHER WORK

As was mentioned in the introduction, furnace atomic absorption is one of the most promising analytical tools for trace and microtrace metal analysis at the present time.

In medicine: It is conceivable to be able to do 50 quantitative elemental analyses on 1 ml of whole blood. It is known that many trace metals are instrumental in the cause or prevention of many human ailments.

In geochemistry: Ore deposits could be located by carefully analyzing ground water.

In weather modification: Analysis of elements in storms for possible control over hurricanes, hail or draught.

In pollution control: Monitoring trace elements in the air, water, animal and vegetable tissue.

With the sensitivity capability that the furnace has, many problems can be overcome by merely going around them as was done with the Ag in snow method. The furnace offers an inexpensive alternative to neutron activation analysis, while at the same time being simple if proper precautions are taken with reagents and handling technique.

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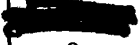
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