



Improvement and application of nonflame atomic absorption instrumentation
by Douglas Edmund Shrader

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree
DOCTOR OF PHILOSOPHY in Chemistry
Montana State University
© Copyright by Douglas Edmund Shrader (1973)

Abstract:

An optical system applicable to single beam instruments is presented to correct for background absorption found in atomic absorption spectroscopy. The optical system involves two Glan-Taylor air-spaced calcite polarizers.

The hollow cathode light is polarized perpendicular to the reference beam. The polarizers are used to combine and finally separate the two beams after passage through the furnace atomization device and a Beckman DU. Individual photomultipliers are used for the two beams, whose outputs are recorded individually and compared. An improved furnace design is presented. Representative signals for the two channels are presented. Calibration curves for Ag, Au, and Hg were obtained and sensitivities are given.

The design, construction, specifications, and operation of a new dual-wavelength spectrophotometer is presented. The instrument utilizes only one fixed grating and mobile exit slits with photomultiplier light sensors. Two wavelengths can be monitored simultaneously and both channels may be scanned independently. The spectrophotometer has been integrated into an atomic absorption system which includes a Woodruff furnace and Ithaco dual-channel lock-in amplifier. The two channels may be used separately (A and B) or may be ratioed (A/B). Taking the ratio of the intensity of a resonance line of interest and the intensity of a nearby nonresonant line allows background absorption corrections to be made. In the separate channel mode, two elements may be simultaneously determined in a single sample. Results are given for the determination of Ag and Pb in various sample types requiring background correction using the ratio (A/B) mode. Results are also given for the simultaneous determination of Ag and Pb in synthetic samples using the separate channel (A and B) mode. Calibration curves were obtained for the two most sensitive lines of both Ag and Pb.

Applications of furnace atomic absorption are presented. Trace element concentrations of different elements were determined in Various types of samples and the results are given and discussed. The average relative standard deviations of the results ranged from 3.1% to 15.4% for amounts of metals in the nanogram and sub-nanogram region. . Sensitivities for Ag, Pb, Au, Cd, Cu, Hg, and Mn are presented.

IMPROVEMENT AND APPLICATION OF NONFLAME
ATOMIC ABSORPTION INSTRUMENTATION

by

DOUGLAS EDMUND SHRADER

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

of

DOCTOR OF PHILOSOPHY

in

Chemistry

Approved:

Arnold C. Craig

Head, Major Department

Ray Woodruff

Chairman, Examining Committee

Henry L. Parsons

Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

August, 1973

ACKNOWLEDGMENT

I would like to thank my wife, Mary Ann, for her constant support during graduate school.

For his inspiration, advice, and help, thanks go to Dr. Ray Woodruff.

The support of this research and myself by Montana State University, the National Science Foundation, the National Aeronautics and Space Administration, and the U. S. Office of Education is greatly appreciated.

I wish to express my appreciation to Ithaco Inc. for their technical competence and generous help.

Also, thanks go to Dave Phelps for the part he played in the construction of equipment.

TABLE OF CONTENTS

	page
LIST OF TABLES	vi
LIST OF FIGURES	vii
ABSTRACT	ix
INTRODUCTION.	1
STATEMENT OF PROBLEM	4
 EXPERIMENTAL	
(Furnace Atomic Absorption with Reference Channel)	8
Optical System and Readout	8
The Furnace	12
Sample Preparation	14
 RESULTS AND DISCUSSION	
(Furnace Atomic Absorption with Reference Channel)	16
 EXPERIMENTAL	
(A New Dual-Wavelength Spectrophotometer)	25
Instrument Design	25
Total System	32
Sample Preparation and Methods	40
 RESULTS AND DISCUSSION	
(A New Dual-Wavelength Spectrophotometer)	47
 EXPERIMENTAL	
(Application of Furnace Atomic Absorption)	61
Sample Group I	61
Procedure	62
Sample Group II	63

	page
Procedure	64
Sample Group III	65
Procedure	65
Sample Group IV	66
Procedure	66
RESULTS AND DISCUSSION	
(Application of Furnace Atomic Absorption).	68
Sample Group I	71
Sample Group II.	78
Sample Group III	81
Sample Group IV	84
CONCLUSIONS	
	87
APPENDIX	
	89
BIBLIOGRAPHY.	
	102

LIST OF TABLES

Table	page
I. Sensitivity Data for Ag, Au, and Hg	24
II. Monochromator Specifications	32
III. Results of Water Determinations for Ag	52
IV. Results of Simultaneous Ag and Pb Determinations	53
V. Results of Determinations for Pb	55
VI. Results of Ag Determinations on Rock Samples	57
VII. Representative Sensitivities.	69
VIII. Surface Water Results (Teller).	73
IX. Surface Water Results (Teller).	74
X. Leachate Water Results.	76
XI. Burner Condensate Results	77
XII. Results of Determinations for Pb (Farnes)	79
XIII. Results of Determinations for Zn, Cd, and Ag (Farnes)	80
XIV. Results of Plant Samples (Weaver)	83
XV. Bozeman Area Surface Water Results	84
XVI. Hg Hollow Cathode Emission Lines	95
XVII. Pb Hollow Cathode Emission Lines	97
XVIII. Cu-Zn-Pb-Cd Hollow Cathode Emission Lines	99

LIST OF FIGURES

Figure	page
1. Optical System Diagram	9
2. Glan-Taylor Polarizers.	11
3. Drawing of the Furnace (third generation)	13
4. Absorption Spectra of the Glan-Taylor Polarizer	18
5. Representative Signals	20
6. Calibration Curve for Ag.	22
7. Calibration Curves for Au and Hg.	23
8. Monochromator System.	26
9. Monochromator (top view)	28
10. Monochromator (side view).	30
11. Monochromator Electrical Circuit.	31
12. Block Diagram of Components.	33
13. Improved Third Generation Furnace.	35
14. Spiral Heater Tube Contact	36
15. Transformer Regulator Circuit	38
16. Lock-in Amplifier Configurations	39
17. Calibration Curves for Ag	43
18. Calibration Curves for Pb	44

Figure	page
19. Current versus Temperature Curves	49
20. Current versus Voltage Curves	50
21. Extraction Efficiency Curves for Ag	70
22. Optical Bench and Accessories	90
23. Optical Bench and Accessories	91
24. Water Flow System	92
25. Gas Flow System	93
26. Hg Hollow Cathode Spectra.	94
27. Pb Hollow Cathode Spectra.	96
28. Cu-Zn-Pb-Cd Hollow Cathode Spectra.	98
29. Temperature versus Absorbance Curves	100
30. Representative Calibration Curves.	101

ABSTRACT

An optical system applicable to single beam instruments is presented to correct for background absorption found in atomic absorption spectroscopy. The optical system involves two Glan-Taylor air-spaced calcite polarizers. The hollow cathode light is polarized perpendicular to the reference beam. The polarizers are used to combine and finally separate the two beams after passage through the furnace atomization device and a Beckman DU. Individual photomultipliers are used for the two beams, whose outputs are recorded individually and compared. An improved furnace design is presented. Representative signals for the two channels are presented. Calibration curves for Ag, Au, and Hg were obtained and sensitivities are given.

The design, construction, specifications, and operation of a new dual-wavelength spectrophotometer is presented. The instrument utilizes only one fixed grating and mobile exit slits with photomultiplier light sensors. Two wavelengths can be monitored simultaneously and both channels may be scanned independently. The spectrophotometer has been integrated into an atomic absorption system which includes a Woodruff furnace and Ithaco dual-channel lock-in amplifier. The two channels may be used separately (A and B) or may be ratioed (A/B). Taking the ratio of the intensity of a resonance line of interest and the intensity of a nearby nonresonant line allows background absorption corrections to be made. In the separate channel mode, two elements may be simultaneously determined in a single sample. Results are given for the determination of Ag and Pb in various sample types requiring background correction using the ratio (A/B) mode. Results are also given for the simultaneous determination of Ag and Pb in synthetic samples using the separate channel (A and B) mode. Calibration curves were obtained for the two most sensitive lines of both Ag and Pb.

Applications of furnace atomic absorption are presented. Trace element concentrations of different elements were determined in various types of samples and the results are given and discussed. The average relative standard deviations of the results ranged from 3.1% to 15.4% for amounts of metals in the nanogram and sub-nanogram region. Sensitivities for Ag, Pb, Au, Cd, Cu, Hg, and Mn are presented.

INTRODUCTION

Since its introduction in 1955 ⁽¹⁾, atomic absorption spectroscopy has become a very useful analytical technique and is a part of almost every modern analytical lab. Atomic absorption theory, its application to numerous fields, and the problems involved in its use have been the subject of many publications and texts in the past.

Inherent in flame atomic absorption is a high noise level caused by turbulence in the flame and nebulized sample introduction. This imposes a limit on sensitivity and detection limit, thus relatively large samples are needed. Also, the samples need to be in relatively pure liquid form for aspiration into the burner head. These facts put the analyst at a disadvantage in many fields such as clinical, forensic, and environmental chemistry where the available sample is or should be very small, or in a solid or a complex, viscous form.

The recent concern over the environment and its quality has made necessary the development of new instrumentation in order to improve sensitivities and detection limits. Several nonflame atomization devices for atomic absorption have been introduced during the last few years ^(2, 3, 4, 5, 6, 7, 8, 9). These devices have the advantage of much greater sensitivity, allowing a smaller sample to be analyzed. Also, in some cases, solids, complex liquids,

and gases may be analyzed directly or with a minimum of sample preparation. This is extremely valuable if the sample size is or should be small, or in some form other than a relatively pure liquid. Even though many of the problems involved in the use of flame atomic absorption have been eliminated by the nonflame devices, more work needs to be done to perfect them.

Another problem found in atomic absorption spectroscopy is that of background absorption^(10,11). The cause of this background absorption is molecular absorption and/or scattering of light due to particles. This non-atomic absorption can cause erroneously high results if not compensated for. Several methods of correction for background absorption have been described^(12,13,14,15,16). These all involve the use of a hydrogen or deuterium continuum in various instrumental arrangements to measure the background absorption at the wavelength of interest and allow for correction. Also, the use of a nonabsorbing wavelength near the resonance line of interest for the purpose of background correction or reference has been reported in several publications^(10,17,18,19,20).

An additional problem, or rather disadvantage, of atomic absorption spectroscopy is that in practice it is generally only useful for single-element determinations. Several instrumental arrangements for the determination of more than one element have been published^(21,22,23). Very recently Fisher

Scientific Co. and Instrumentation Laboratory, Inc. have introduced spectrophotometers which can be used to determine two elements simultaneously by atomic absorption. These instruments can monitor two wavelengths. Perkin-Elmer, American Instrument Co., and Phoenix Precision Instrument Co. also have instruments with dual-wavelength capabilities but have not applied these to atomic absorption but rather to UV-Visible spectroscopy. In all but one case the instruments are composed of two grating monochromators. The Instrumentation Laboratory instrument utilizes one grating monochromator and an interference filter for the second channel.

This thesis deals with the improvement of instrumentation available for use in atomic absorption spectroscopy. Complete instrumental systems have been developed as well as improvements in the atomization device, the Woodruff furnace. The instrumental systems have been developed in order to provide a method of background correction to compensate for nonatomic absorption. The second instrumental system may also be used for the simultaneous determination of two elements. Applications of furnace atomic absorption have been developed and are part of this thesis. They show that the Woodruff furnace can be utilized to determine trace element concentrations in real samples, taken in connection with problems or projects of current interest, and that reproducible results in the nanogram and sub-nanogram region can be obtained.

STATEMENT OF PROBLEM

Briefly, the problem was to look into the improvement of instrumentation (complete systems as well as the furnace atomization device) available for use in atomic absorption spectroscopy. This improvement involves applications and evaluation of results with real samples.

As was stated previously, there are several problems which one encounters in atomic absorption spectroscopy. A major breakthrough in solving some of the problems associated with flame atomic absorption came about with the introduction of various nonflame atomization devices. The Woodruff furnace is such a device. Since its introduction to the public in 1966⁽²⁴⁾, various publications have presented sensitivities, detection limits, and some of the problems encountered in its use. Heater tubes had a very short life (15 hours)⁽⁴⁾. Blanks were many times irreproducible⁽²⁵⁾. A large portion of this was thought to be caused by furnace design and materials. The construction of a second generation furnace with enclosed ends and improved chucks for end cooling and electrical conduction seemed to increase the life of the heater tubes⁽¹⁴⁾. On this basis it was decided that the furnace design needed additional improvement, not only with the goal of increased life of heater tubes and other graphite parts, but also with the goals of increasing reproducibility of results and the development of a design which would promote

safety, simplicity, and efficiency. A third generation furnace and an improvement of it were constructed and are discussed.

The problem of background absorption caused by the scattering of light by particles in the optical path and/or molecular absorption needed to be confronted. The instrumental arrangements previously used to correct for background absorption are in some cases very complicated and either give only the net absorbance or individual absorbances at different times or on different samples. It was thought that a system of background correction involving plane polarized light could be useful. By using two polarizing beam splitters, reference and sample radiation, polarized perpendicularly to each other, could be combined into a single beam and, after passage through the furnace, could be separated and monitored. The use of DC electronics would allow a continuous and simultaneous record of both hollow cathode and hydrogen lamp radiation to be obtained.

Along the same lines but more versatile was an idea for a dual-wavelength monochromator. It would have one fixed grating and two mobile exit slit and photomultiplier tube assemblies. Being able to monitor two wavelengths would allow one to use a nonresonant line, close to the resonant line of interest, as a reference and thus be able to compensate for background absorption. A simultaneous record of both reference and sample beams could

be obtained or the outputs from the two channels could be ratioed, giving the net absorbance. Also, it would have the capability of simultaneously determining two elements by atomic absorption. The versatility would be greater and the construction would be simpler than commercially available dual-wavelength spectrophotometers.

Both instrumental arrangements were developed and incorporated into atomic absorption systems involving a Woodruff furnace. The instruments are presented and discussed.

Finally there arises the problem of applications. Techniques for determining very small amounts of metals are in great demand due to the current emphasis on the environment and its quality. A technique such as furnace atomic absorption can fulfill the requirement of being very sensitive. It is in fact 3 or 4 orders of magnitude more sensitive than conventional flame atomic absorption. However, with this technique, as well as any other technique, real samples need to be analyzed in order to determine its applicability to routine analysis. Applications of nonflame devices available from different instrument companies have been the subject of various publications^(26,27,28,29,30). The Montana State University group has published only two applications to real samples^(31,32). The opportunity to become involved in the analysis of samples from various

research projects presented itself and was accepted. The methods used and the results obtained in these projects are presented.

EXPERIMENTAL

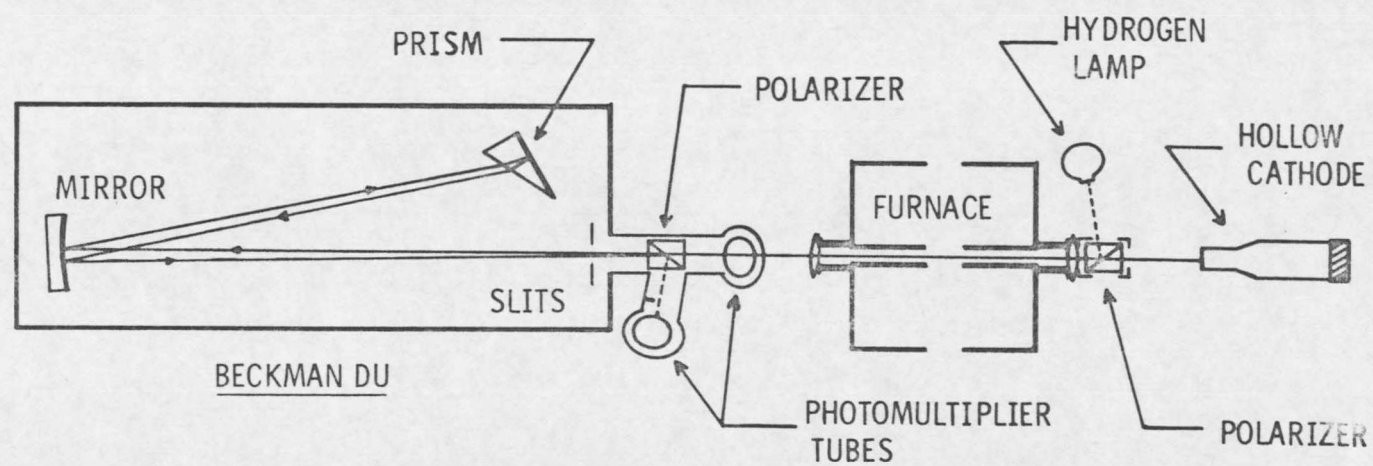
Furnace Atomic Absorption with Reference Channel

Systems mentioned earlier to compensate for background absorption employ alternating sample-reference observation and give only the difference between the two signals or measure the sample signal and reference signal at two times relatively far apart or on two samples. The system described here gives a continuous, simultaneous record of both signals.

Optical System and Readout

Figure 1 shows the optical system which was used. The hollow cathode light enters the primary Glan-Taylor polarizer and is polarized parallel to the optical axis of the polarizer. The polarized hollow cathode light then passes down the optical path of the furnace. The hydrogen lamp light enters the primary polarizer through the side window and is divided into two perpendicularly polarized beams which are reflected in such a manner that the portion which is polarized perpendicular to the optical axis of the polarizer follows the same optical path as the beam from the hollow cathode. The other portion of the hydrogen lamp beam leaves the optical path and is absorbed. Before passage through the furnace, the two beams of interest are collimated by means of a quartz lens placed between the polarizer and the furnace.

Both beams, the hollow cathode beam polarized horizontally and the



-6-

Figure 1. Optical System Diagram.

hydrogen lamp beam polarized vertically, after passing through the furnace are focused on the slit of the Beckman DU with a second lens placed on the end of the furnace. After passing through the monochromator, the combined beams pass through the second slit and fall on the secondary Glan-Taylor polarizer. The polarizer separates the two perpendicularly polarized portions of the beam. The hollow cathode portion is transmitted straight through the polarizer and falls on a photomultiplier tube. The hydrogen lamp portion is reflected through the side window of the polarizer and falls on a second photomultiplier tube.

Enlarged diagrams of both the primary and secondary polarizers are shown in Figure 2. The polarization of the hollow cathode and hydrogen lamp beams is indicated. A horizontally polarized portion is reflected through the side window of the secondary polarizer at a slightly different angle than the vertically polarized hydrogen lamp beam of interest. This portion is kept from striking the reference photomultiplier tube by placing a baffle between the polarizer and photomultiplier tube (see Figure 1). A drawing of the optical bench and accessories which were constructed is shown in the Appendix, page 90.

After the hollow cathode light and hydrogen lamp light fall on their respective photomultiplier tubes (RCA IP28's), the signals are recorded

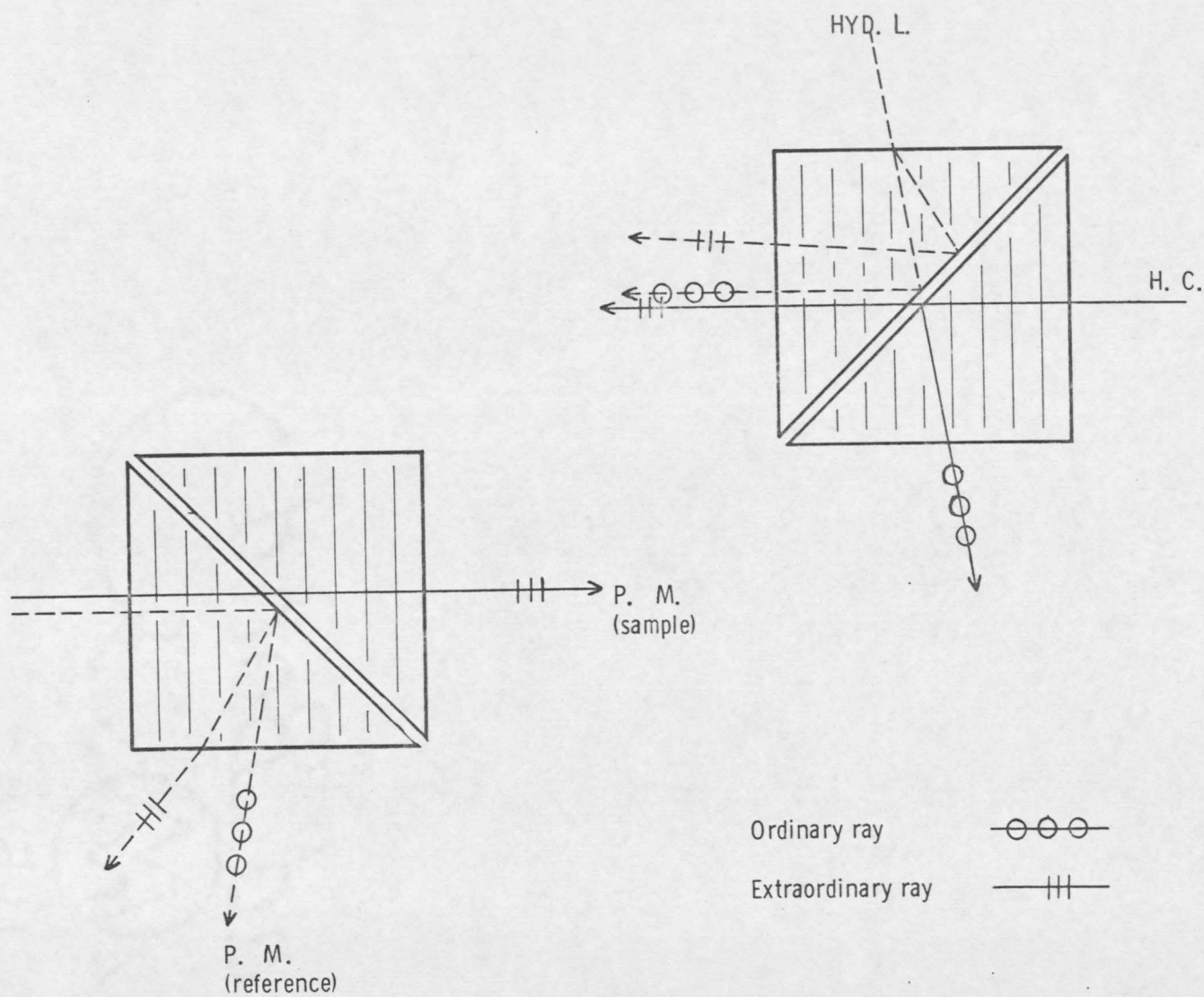


Figure 2. Glan-Taylor Polarizers.

individually. Two Heath Servo-recorders, Model EUW-20, were used to record the results. The two simultaneous records, sample and reference, are then available for comparison.

The Furnace

Previous furnace designs have been published^(4, 14). The furnace used in this study was a third generation furnace. A schematic drawing of the improved furnace design is shown in Figure 3. The heater tubes are 15.2 cm long, 10 mm o.d., and 8 mm i.d., and make contact in the center with the one-piece combination heat sink and shield tube. The outer ends are connected to a spiral copper tube which fulfills the dual purpose of electrode contact and cooling⁽¹⁴⁾.

The shield tube prevents the graphite felt insulation from coming into contact with the heater tubes and also helps reduce heat loss from the heater tubes to the rest of the furnace. The one-piece heat sink and shield tube makes the optical path more stable and gives a better heat capacity for volatilization of the sample. This change in shield tube design from the previous three-piece construction also gives more uniform temperature by allowing more efficient heat conduction to the central part of the furnace.

The side tube, through which samples are introduced, is 6 mm i.d., is very thin-walled next to the heat sink to reduce heat conduction away from

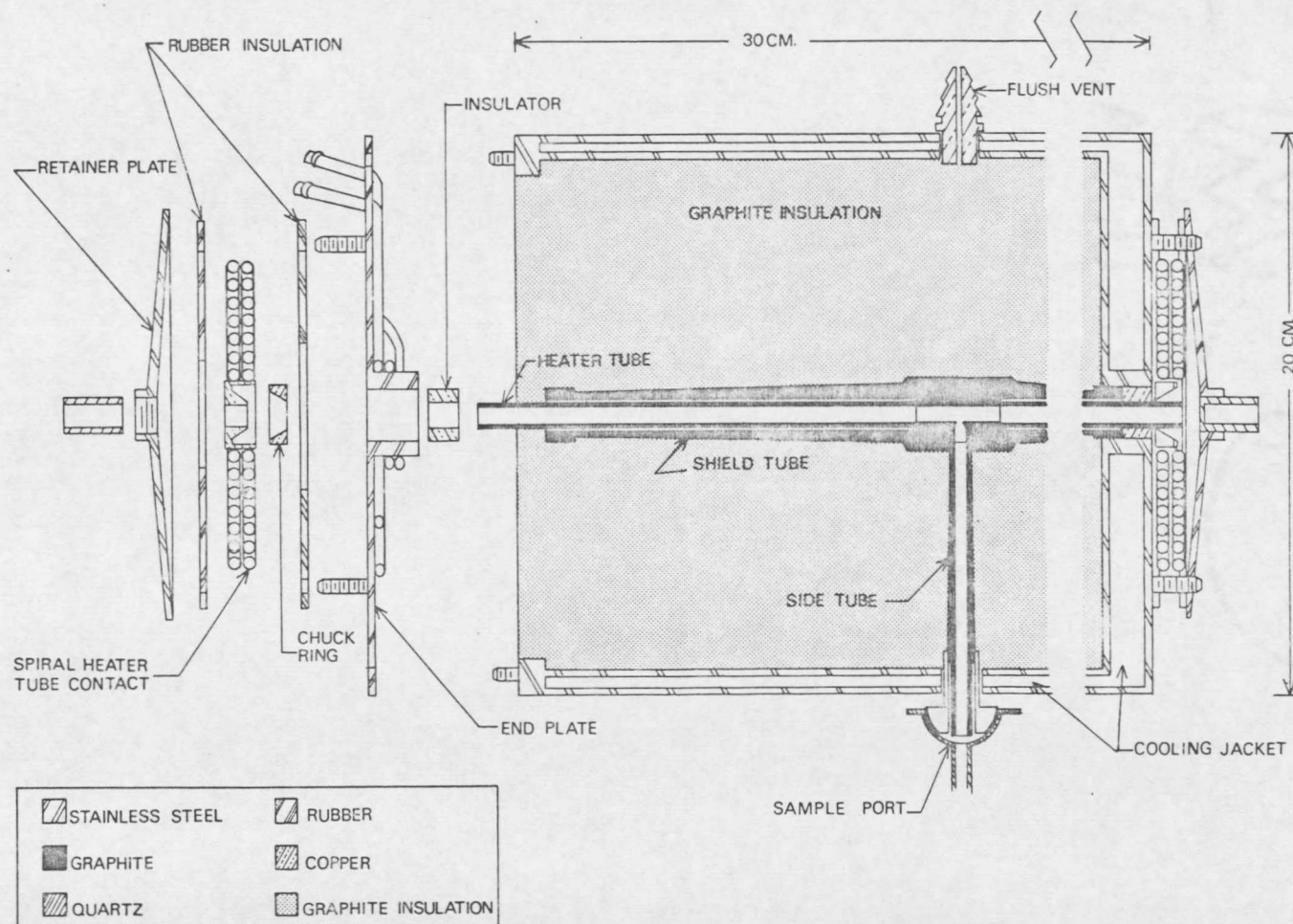


Figure 3. Drawing of the Furnace (third generation).

the interior, and has a thick lip approximately 4 cm from the outer end to hold a spring which provides constant tension on the side tube as it expands or contracts with changing temperature. Argon gas enters the sample port and side tube through small aligned holes in both. A Vycor 18/9 socket is attached to the sample port through which samples are introduced.

In addition to other improvements, this furnace is double-walled to provide effective cooling (with water) of the entire furnace. The furnace is also made of stainless steel rather than iron. This design has proved very satisfactory. Heater tubes needed to be replaced every month or two with the second generation furnace. Sets of heater tubes in this furnace have been used for periods of up to ten months without replacement.

Sample Preparation

Standard solutions were prepared from salts of the metal to be investigated. The solutions were made with doubly-distilled water to 10^{-7} g of metal/ml and diluted to 10^{-8} g of metal/ml when necessary. The solutions were kept acidic (pH ca. 2) to reduce the amount of adsorption of metal on the walls of the container^(33,34,35). This was true of all standard or sample solutions used at any time. In order to prepare calibration curves, 10- to 100- μ l portions of the appropriate solutions were placed into cups made of high-density graphite and dried under a heat lamp.

Samples are placed into the cups and, after drying or ashing as needed, are inserted directly into the furnace. The cups (6 x 16 mm), either for cleaning or sample introduction, are screwed onto a threaded 1/8 in. carbon rod and inserted through the Vycor socket and side tube into the furnace so that they rest against the heat sink. Any sample present in the cup vaporizes quickly, enters the optical path, and a reading is recorded.

RESULTS AND DISCUSSION

Furnace Atomic Absorption with Reference Channel

Some problems were encountered in the use of polarized light in the optical system. These were, to an extent, based on the properties of polarized light. The Glan-Taylor polarizers used are of the birefringence or double refraction type. A double refraction polarizer divides an incident beam into two perpendicularly polarized components and reflects either one or both of them towards the side of the polarizer⁽³⁶⁾. This was no problem with the hollow cathode light but caused alignment problems with the hydrogen continuum.

Another problem encountered was the mixing of the two perpendicularly polarized light beams. It was not possible to completely isolate the two beams. This was probably due to the following facts⁽³⁶⁾:

- (a) Most polarizers have some depolarizing tendencies.
- (b) There is partial linear polarization produced when light is passed through a slit. The electric vector tends to align itself with the slit. This would affect light polarized perpendicular to the slit.
- (c) Prisms, mirrors, and gratings have some partial polarization tendencies.

Thus, partial polarization (or depolarization as the case may be) occurs in the prism instrument itself, which has previously been reported^(37,38), and the

secondary polarizer may cause some mixing. The partial polarization produced in prism instruments has been reported to vary extensively and cyclically with wavelength⁽³⁹⁾. It was found that the least amount of mixing occurred when the secondary polarizer was rotated from 20-45° out of plane with the primary polarizer, depending upon the elemental wavelength being used. The small amount of mixing remaining after alignment to peak both signals (approximately 5%) did not seriously affect the results obtained.

A slight limitation is imposed by the use of calcite polarizers in the optical system. As shorter wavelengths are approached, the polarizers tend to absorb increasing fractions of the incident light. Figure 4 shows the absorption curve of one of the polarizers, obtained with the Cary 14 UV-Visible instrument. The signal throughput decreases making necessary increased voltages to the photomultiplier light sensors and/or increased current to the hollow cathode. However, only analyses involving resonance lines such as Pb (217.0 nm), Se (196.0 nm), and As (193.7 nm) would be seriously affected by this property.

The optical system described worked very well in eliminating errors due to background absorption. If the sample exhibits broad-band absorption because of anions or carbonization of organic material, equal light fractions are absorbed from both the hollow cathode beam and the reference beam which

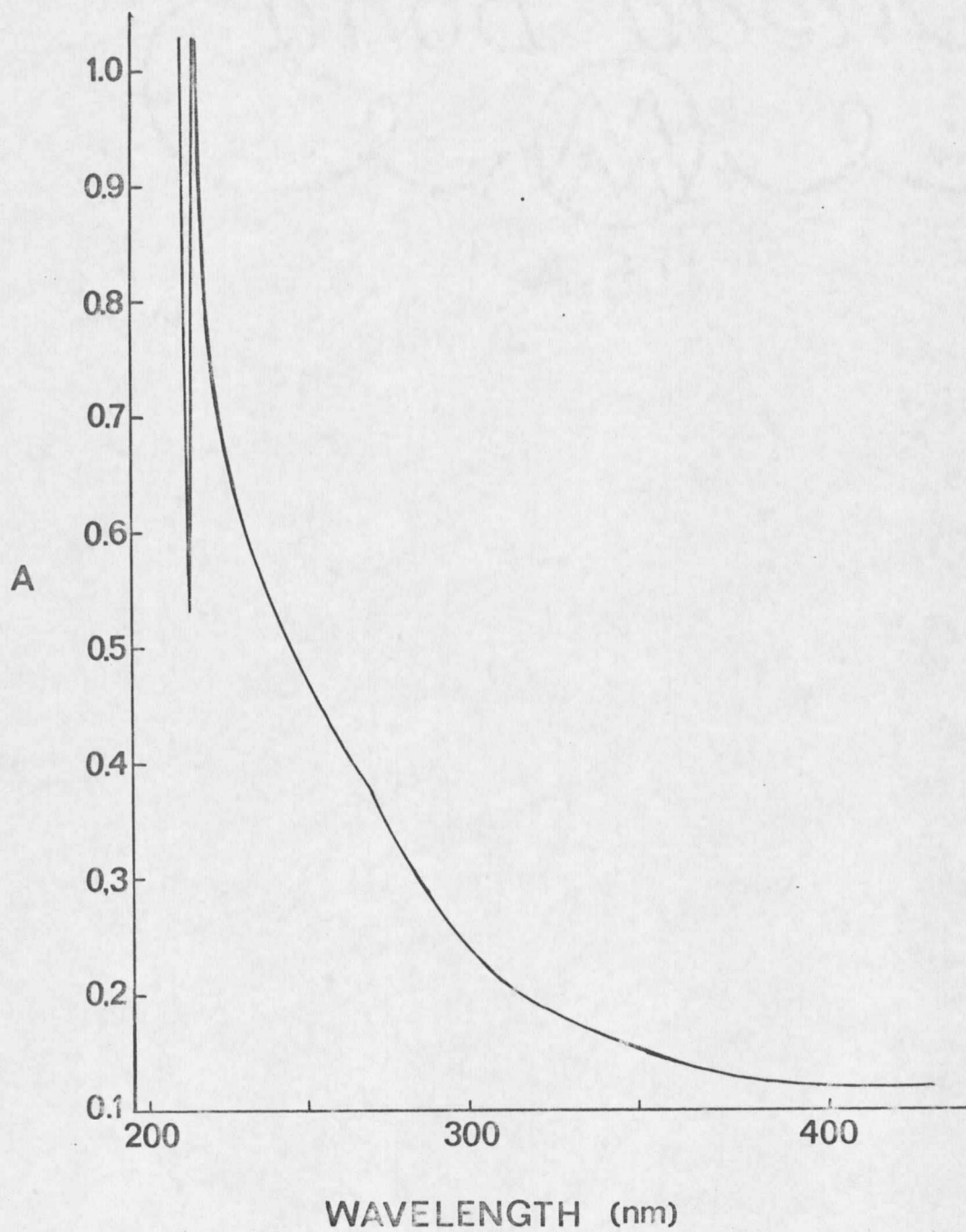


Figure 4. Absorption Spectra of the Glan-Taylor Polarizer.

can then be taken into account. Individual recorders permitted complete quantification of each beam, sample and reference. Different types of samples were run qualitatively to determine the background absorption which may occur.

Many organic samples such as drugs and tissues pyrolyze and give broad-band absorption before the trace elements present are volatilized. An example of the two signals recorded in such a case is illustrated in A of Figure 5. The opposite behavior is shown in B. This type of curve is obtained with Hg in organic matrices under proper conditions. The Hg volatilizes and diffuses into the light path more rapidly than the pyrolyzed organic material. The most common behavior is one where the trace element and the broad-band absorbing material are simultaneously present in the light path as shown in C. If the peak separation in A and B is sufficiently large, and the particular peak due to the element being analyzed is known, determinations may be made without background correction. Even in these cases, the broad-band absorption is ordinarily wide enough to cause some error.

The reproducibility of the blank, especially with solid samples, has been a problem with using the graphite tube furnace technique^(4, 25). This problem was encountered initially with Ag. It was found that the interior of the furnace (insulation and side tube) was heavily contaminated. The same was true with the sample cup holders and desiccators. The contamination

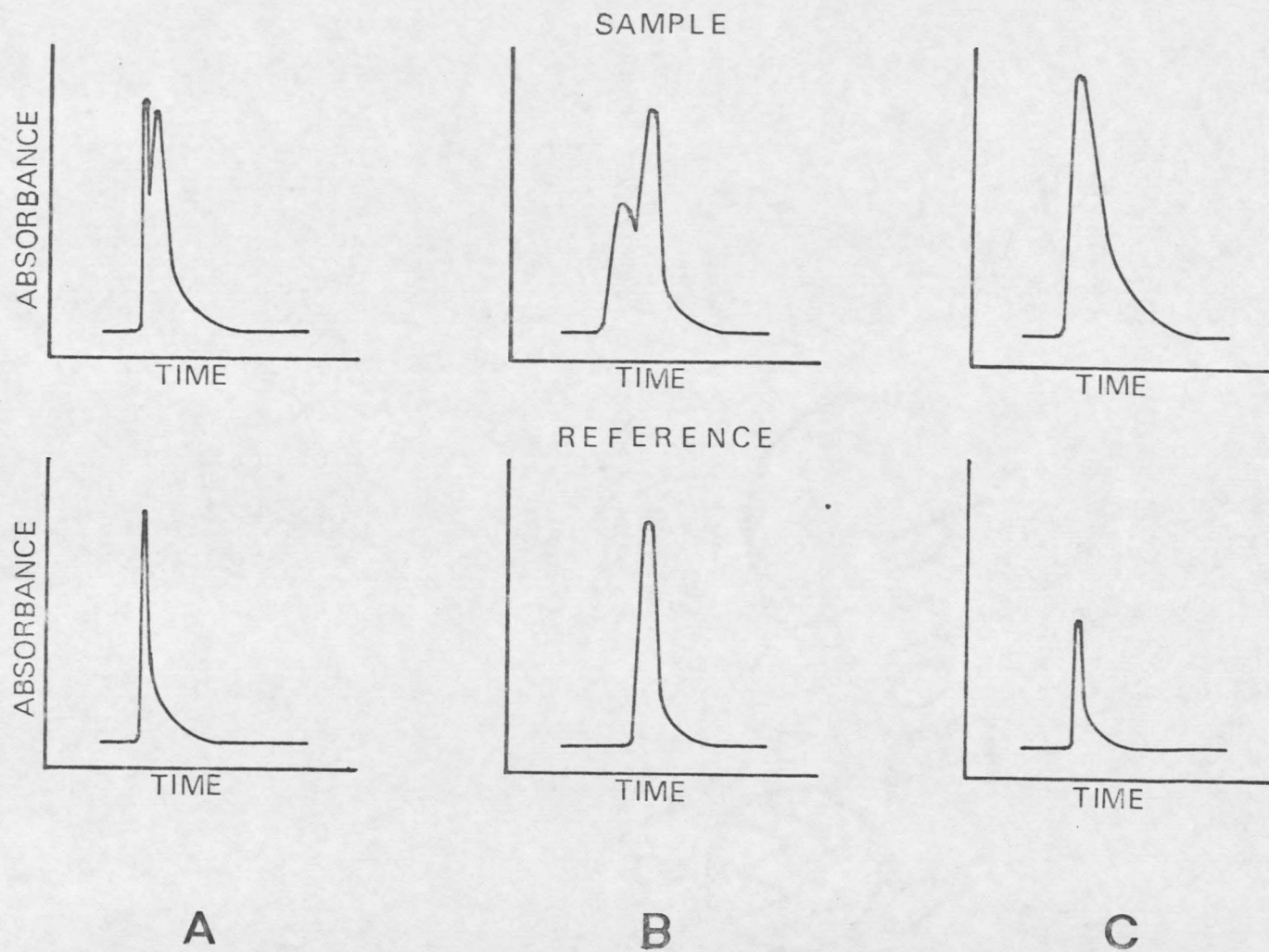


Figure 5. Representative Signals.

problem was reduced in several steps. First graphite felt rather than graphite flake was used for insulation. The felt seemed to be much cleaner. Then the entire furnace was cleaned by prolonged heating, while flushing with large volumes of argon. Second, improved sample preparation was instituted. All cup holders, desiccators, and the Vycor socket are now cleaned regularly with a solution of sodium thiosulfate and/or a mixture of concentrated HNO_3 and H_2SO_4 , and rinsed with doubly-distilled water. The third step was standardizing the sample cups. Very reproducible blanks were finally obtained. Fifteen blanks run on different days were obtained for Ag whose standard deviation equaled an absorption of 0.0022. Defining the detection limit as the amount of element required to give a signal twice the standard deviation of the blank, $A = .0044$, it can be seen that the calculated detection limit for this procedure is approximately equal to the measured sensitivity.

Calibration curves were obtained for Ag, Au, and Hg. These curves are shown in Figures 6 and 7. It was found that the reproducibility depended to a great extent upon the size of the sample and the cups used for the samples. The precision for samples of 10^{-10} grams might be greatly improved by better sampling technique, the use of a set of standardized cups, and improved electronics and optics. The precision for larger samples (ca. 5×10^{-9} grams) was approximately 1-2%.

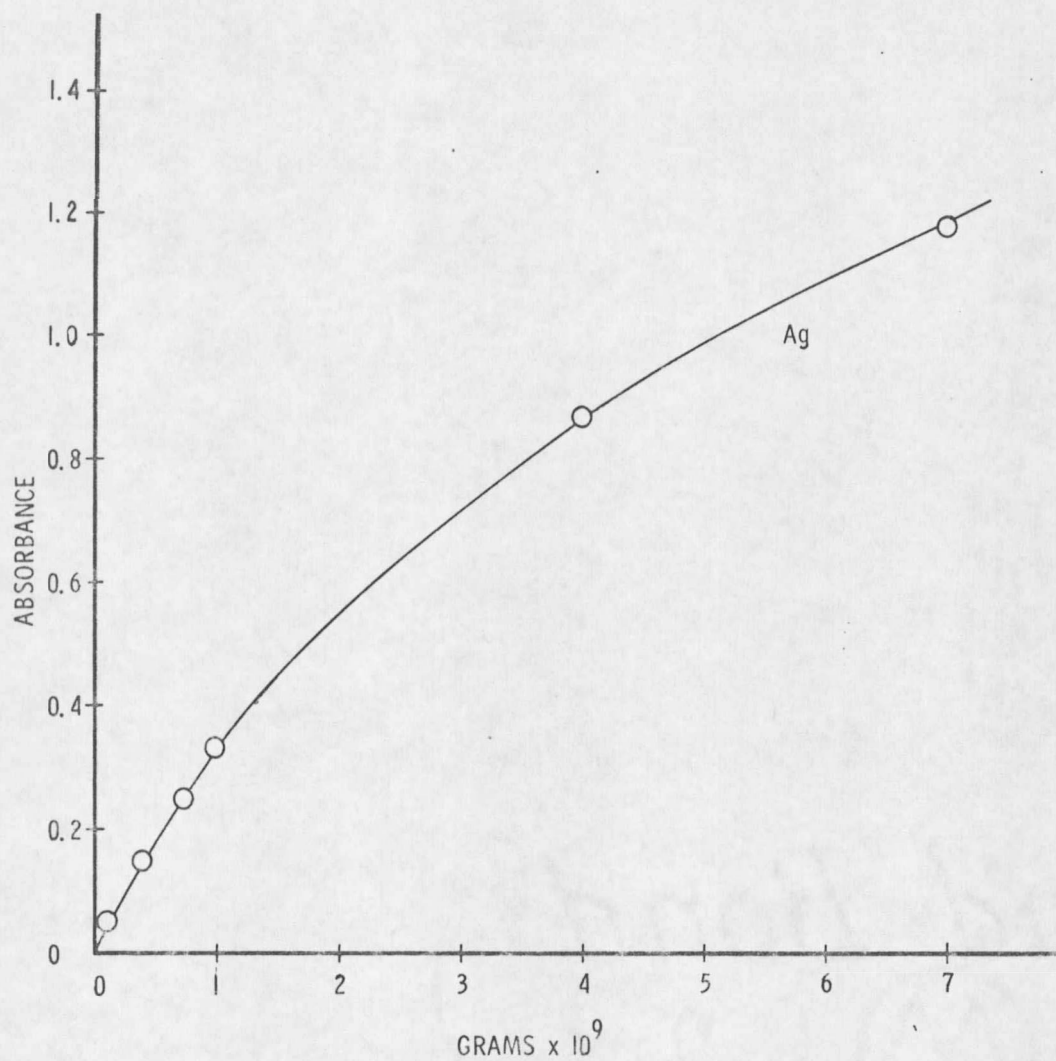


Figure 6. Calibration Curve for Ag.

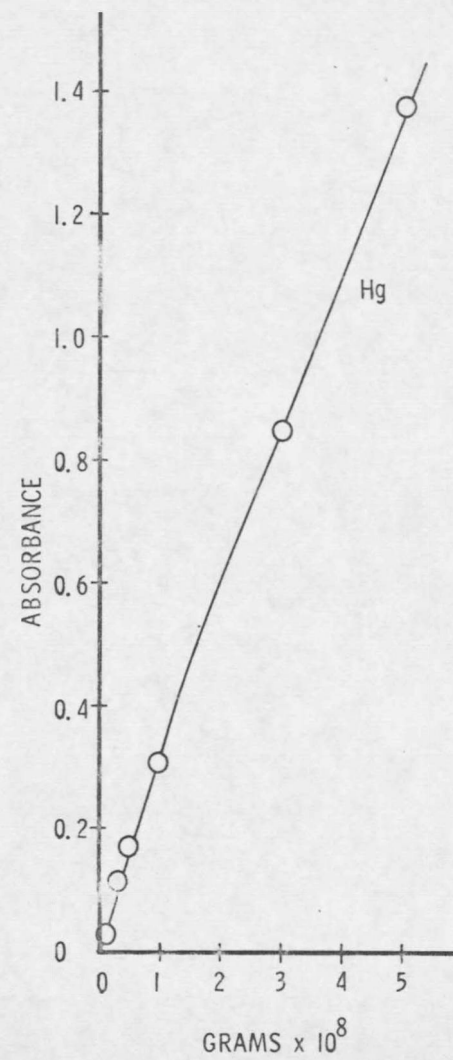
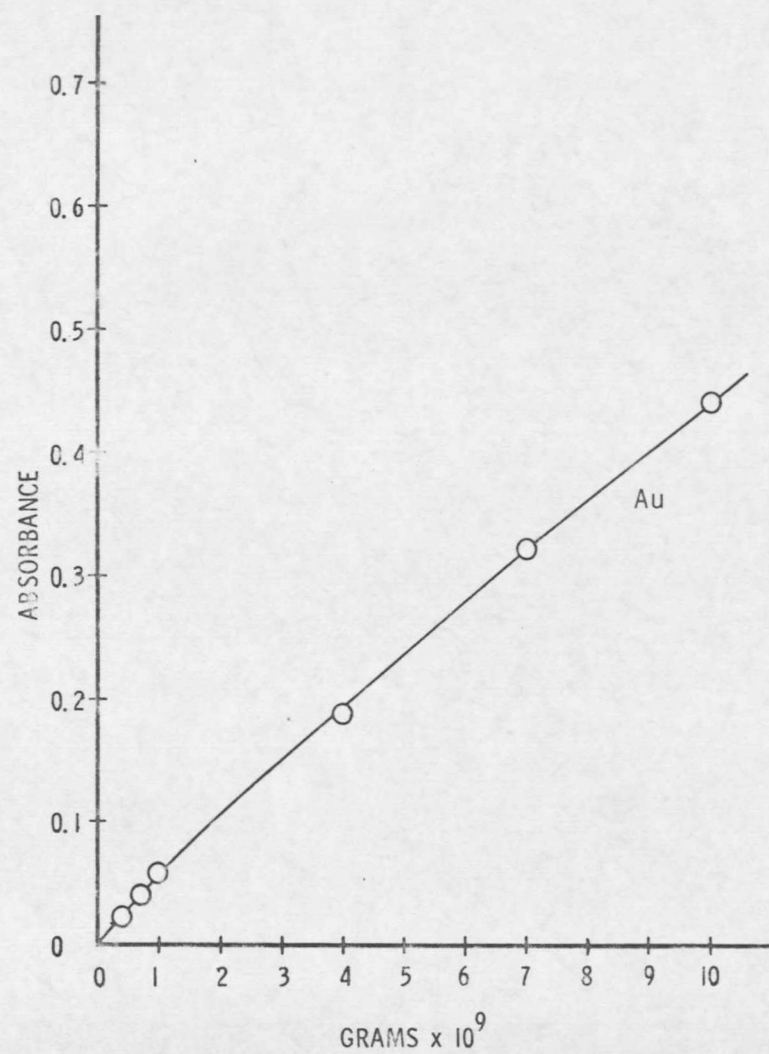


Figure 7. Calibration Curves for Au and Hg.

Table I shows pertinent data for each element including the measured sensitivity. The sensitivity corresponds to the amount of metal which would give a 1% absorbance reading. As was stated previously, the detection limit of this method is approximately equal to the sensitivity.

Table I: Sensitivity Data for Ag, Au, and Hg.

Element	Wavelength (nm)	Furnace temperature (°C)	Sensitivity
Ag	328.1	1800	8×10^{-12} grams
Au	242.8	2150	7×10^{-11} grams
Hg	253.7	1050	1×10^{-10} grams

This continuous, direct current system is applicable to any single-beam instrument. It can be applied to either flame or furnace atomic absorption. The greatly increased sensitivity of furnace atomic absorption over flames permits the analysis of very small samples, and with a minimum of sample preparation, provided any broad-band absorption is corrected for. The equipment involved in the system is comparable to flame atomic absorption with regard to complexity and cost of operation. It is comparable to neutron activation analysis with regard to sensitivity and its precision is much greater

(54)

EXPERIMENTAL

A New Dual-Wavelength Spectrophotometer

This dual-wavelength monochromator has the capability of correcting for background absorption and also the simultaneous determination of two elements by atomic absorption spectroscopy. In comparison to other dual-wavelength instruments, the monochromator utilizes only one grating. This spectrophotometer has a fixed grating and mobile exit slits with photomultiplier light sensors. The design utilizes the property of concave diffraction gratings whereby light reflected from the grating comes to focus on the Rowland circle. The design and operation of the monochromator as well as the components of the total atomic absorption system and its applications are discussed.

Instrument Design

As stated previously, this new dual-wavelength spectrophotometer is a concave diffraction grating instrument capable of sensing two different wavelengths reflected from one grating, simultaneously and independently. The grating is fixed and there are two mobile exit slits with photomultiplier housings encasing two Hamamatsu R106 photomultiplier tubes.

Figure 8 diagrammatically shows the monochromator system. The entrance slit and grating are positioned directly opposite each other on the

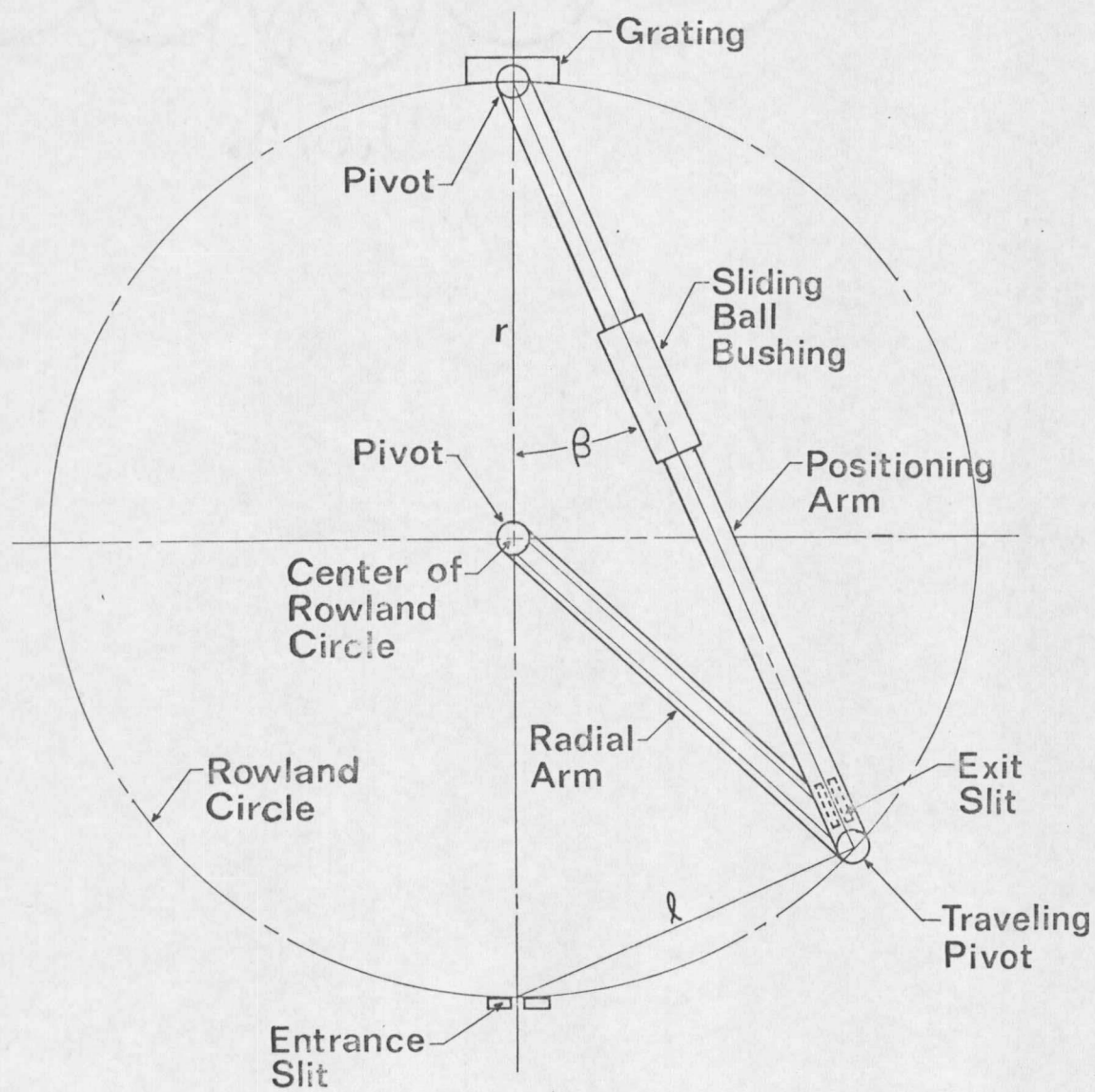


Figure 8. Monochromator System.

Rowland circle. The detected wavelength (λ) reflected from the concave grating is directly proportional to the sine of the angle β .

$$\pm n\lambda = d(\sin \alpha + \sin \beta)$$

The angle of incidence $\alpha = 0$. β includes the line from the grating to the exit slit, positioned near the traveling pivot, and the line from the grating through the center of the Rowland circle. The diameter (r) is constant and is the hypotenuse of the right triangle formed which includes the angle β . Thus, an incremental change in the distance l will produce a corresponding change in wavelength.

The radial arm has one end fixed at the center of the Rowland circle but free to pivot. Its length is equal to the radius of the Rowland circle. Thus, the free end of the radial arm is always on the focus point of the grating. The positioning arm is collapsible and is attached at the end of the radial arm and beneath the center of the grating, and is free to pivot. An exit slit and photomultiplier tube and housing placed on the positioning arm, parallel to it, are always facing the grating and the slit is maintained at the focus point (see Figures 9 and 10).

Figure 9 shows a top view of the monochromator and the mechanical parts of one of the two channels. The grating, slits, photomultiplier tube housings, and mechanical linkages are shown. The ball screw drive assembly

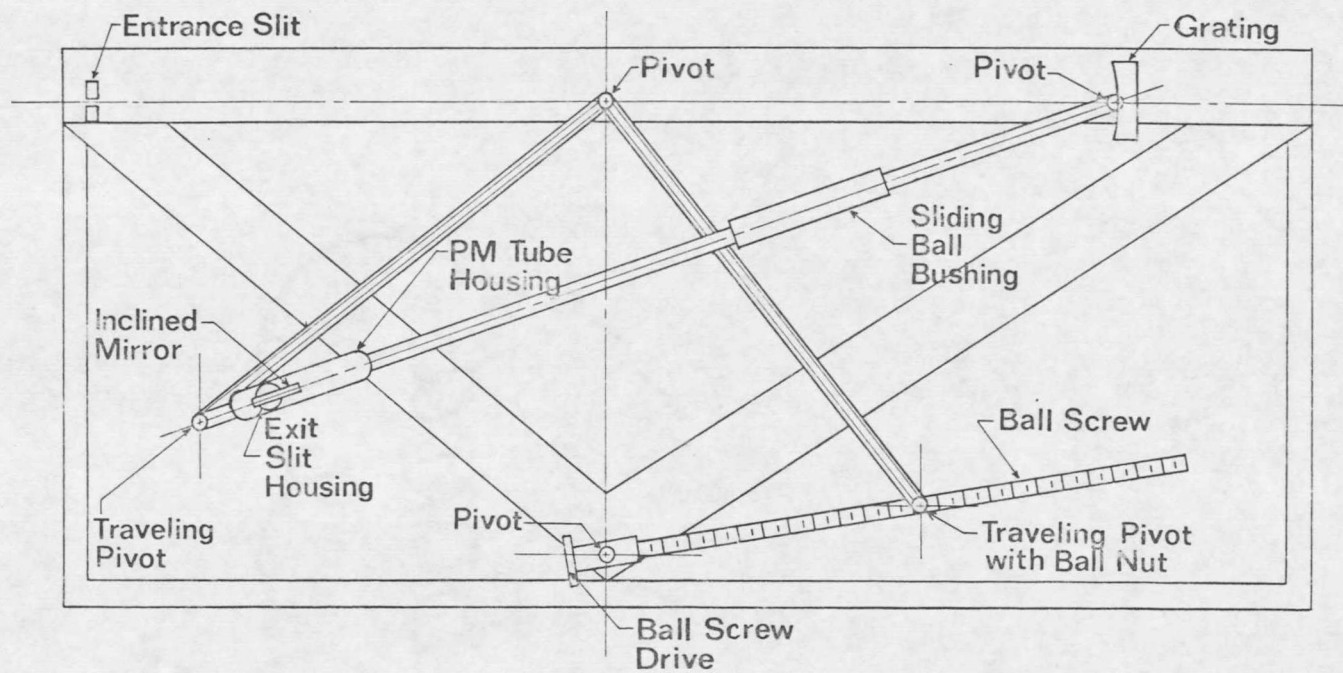
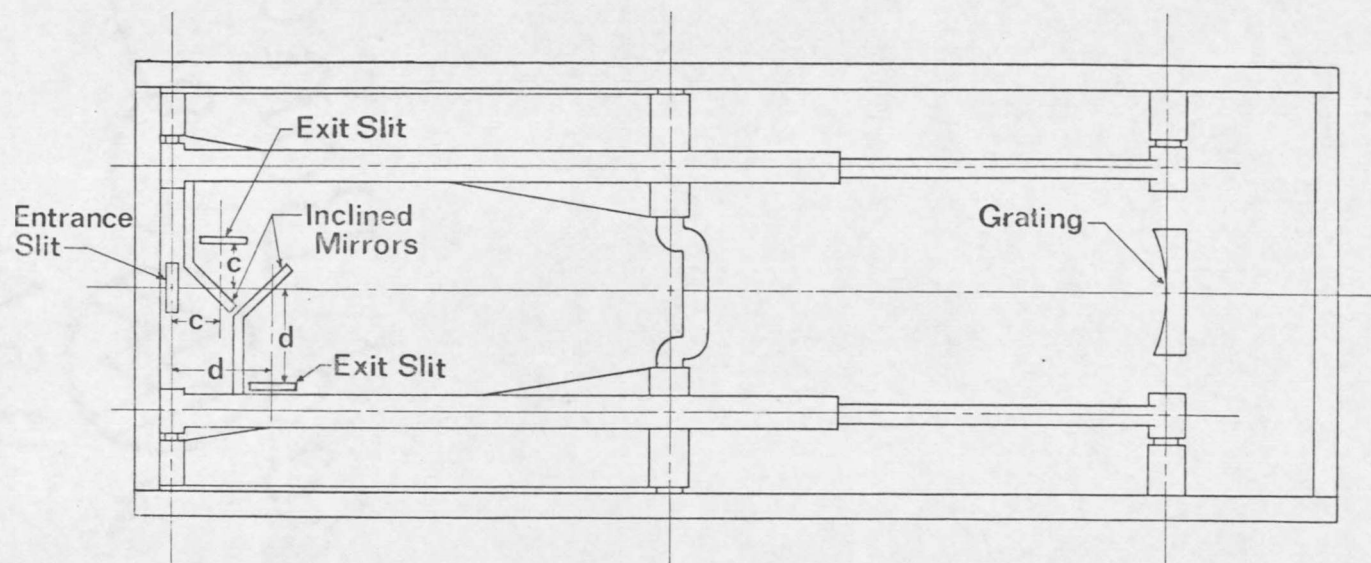


Figure 9. Monochromator (top view).

is driven by a small DC motor. The ball screw was machined so that 1 turn corresponds to a wavelength change of $10 \text{ \AA}$. This allows a mechanical counter connected to the ball screw with an automobile speedometer cable to be used to denote the wavelength.

Figure 10 shows a side view of the monochromator and the physical placement of both channels. To allow the two radial arms with their sensing devices and associated mechanical parts to pass one another, one above the other, front-silvered mirrors are positioned as shown. The exit slits are positioned at the distances c and d such that they are always at the focus point of the grating. In addition, this leaves the Rowland circle clear for the placement of photographic film or photomultiplier tubes for spectrographic or direct reader applications. How close two wavelengths may be and still be monitored successfully depends upon the width of the inclined mirrors used. In the present model, the two wavelengths can be within 5 nm of each other before any significant amount of signal is lost in the second channel.

Figure 11 shows the electrical circuit used to power the scanning mechanisms of each channel. The monochromator is powered by AC rectified to DC. A switch allows either channel to be scanned. The scan speed can be varied with a rheostat. Additional switches on each channel allow forward and reverse scan of each channel independently. Limit switches are included at



-30-

Figure 10. Monochromator (side view).

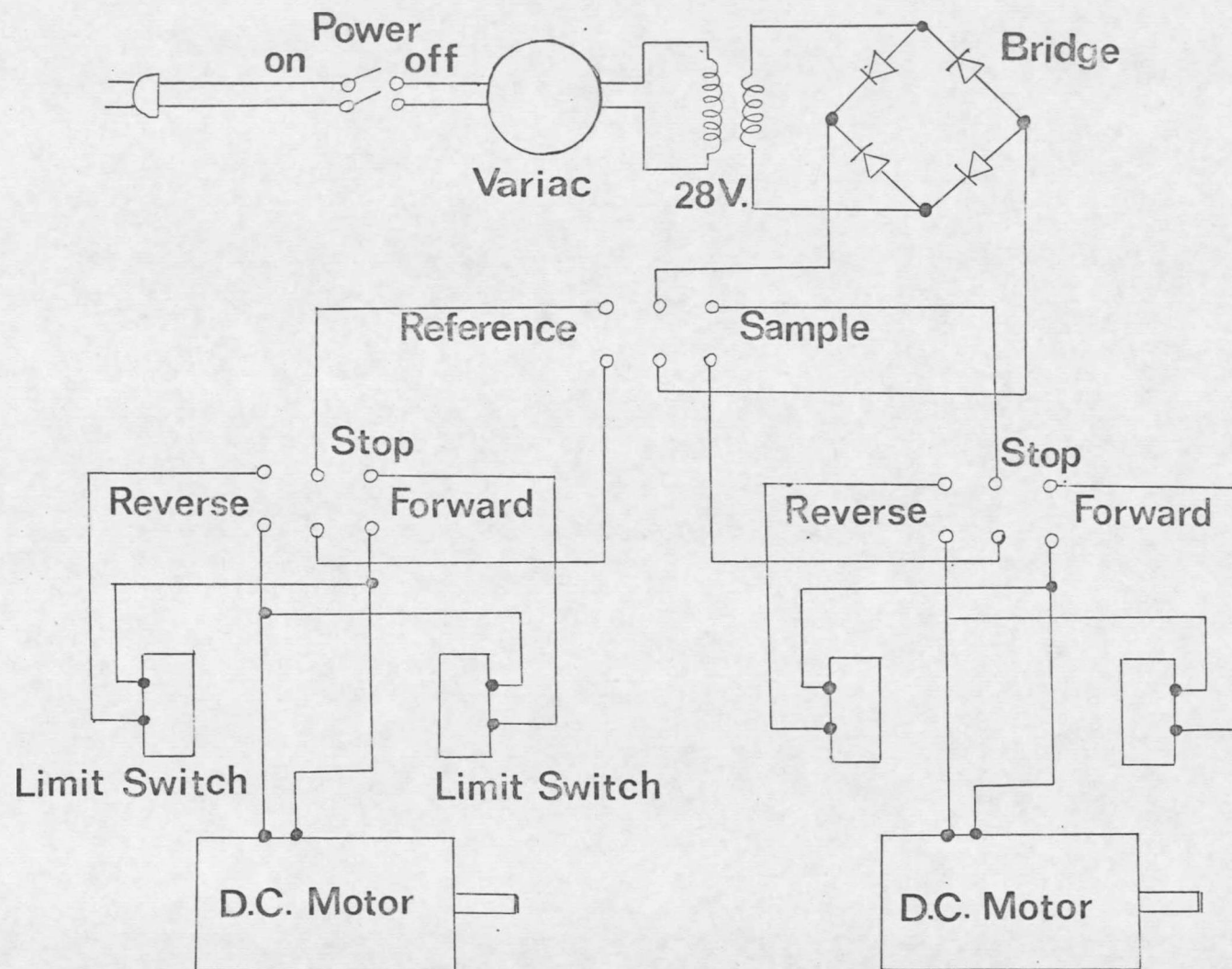


Figure 11. Monochromator Electrical Circuit.

the ends of the scan range to automatically stop each channel. Although the two channels are labeled sample and reference in Figure 11, they will be designated as A and B, respectively, for future reference.

Table II gives the monochromator specifications as calculated or measured. Some of the specifications may not be optimum since the monochromator is a prototype model and was built utilizing a concave grating available in the laboratory and easily obtainable materials. Size, weight, aperture, and dispersion could be improved and made more practical for general usage by using a different grating, lighter materials, and shorter, finer ball screws.

Table II: Monochromator Specifications

Grating: concave, 50x85 mm, 600 lines/mm

Focal length: 0.5 m

Aperture: f/7

Reciprocal linear dispersion: 1.7 nm/mm

Wavelength range: 185-1100 nm

Scan speed: continuously variable at 3-110 nm/min

Outside dimensions: 1.2 x 0.6 x 0.4 m

Weight: 64 kg

Total System

The dual-wavelength monochromator was integrated into an atomic absorption system. A block diagram of the components is shown in Figure 12.

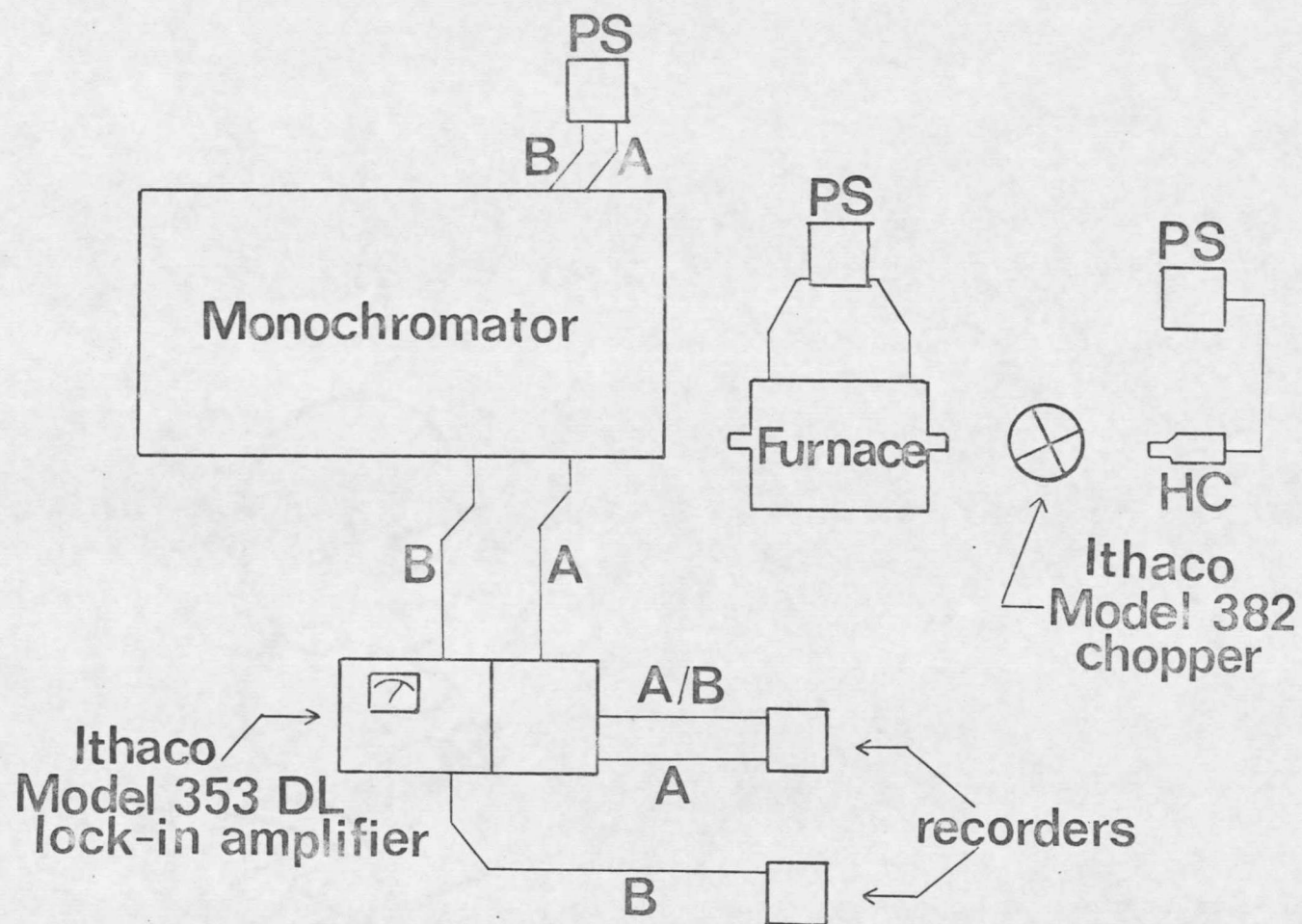


Figure 12. Block Diagram of Components.

A drawing of the optical bench and accessories constructed is shown in the Appendix, page 91. Being primarily concerned with trace element analysis in the lab, and since a nonflame atomization device has been developed over a period of years^(4, 14, 25, 31, 32, 40), a Woodruff furnace was included in the system. The furnace is basically like the third generation furnace previously described but with a few improvements. Figure 13 shows a schematic drawing of the furnace.

The cooling jacket design was simplified to make construction easier and improve the cooling characteristics. Rather than having the side tube held against the shield tube by spring tension, it is threaded and screwed into the shield tube, giving a better seal and simplifying the sample port construction. Both gas vents are included in the separate, threaded sample port, decreasing construction costs. The sample port is concave rather than convex, aiding cup introduction and reducing breakage of the Vycor socket. Pages 92 and 93 of the Appendix show diagrams of the water flow and gas flow systems of the furnace.

The spiral heater tube contact was simplified. Figure 14 shows the new design. The chuck ring is one piece of copper with a tapered hole in the middle rather than the previous more complicated design involving two rings and three screws⁽¹⁴⁾. The heater tubes are made with the same taper (12°)

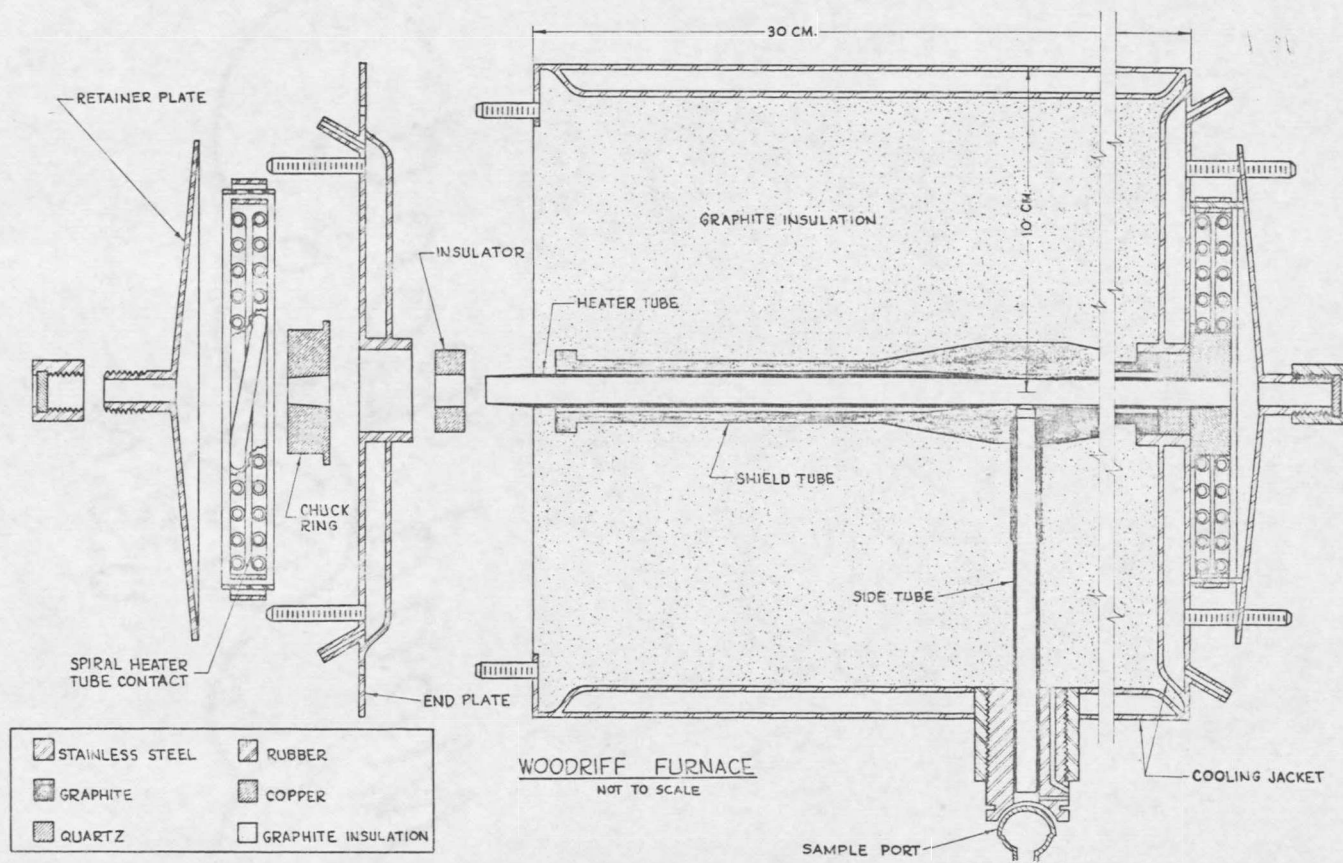


Figure 13. Improved Third Generation Furnace.

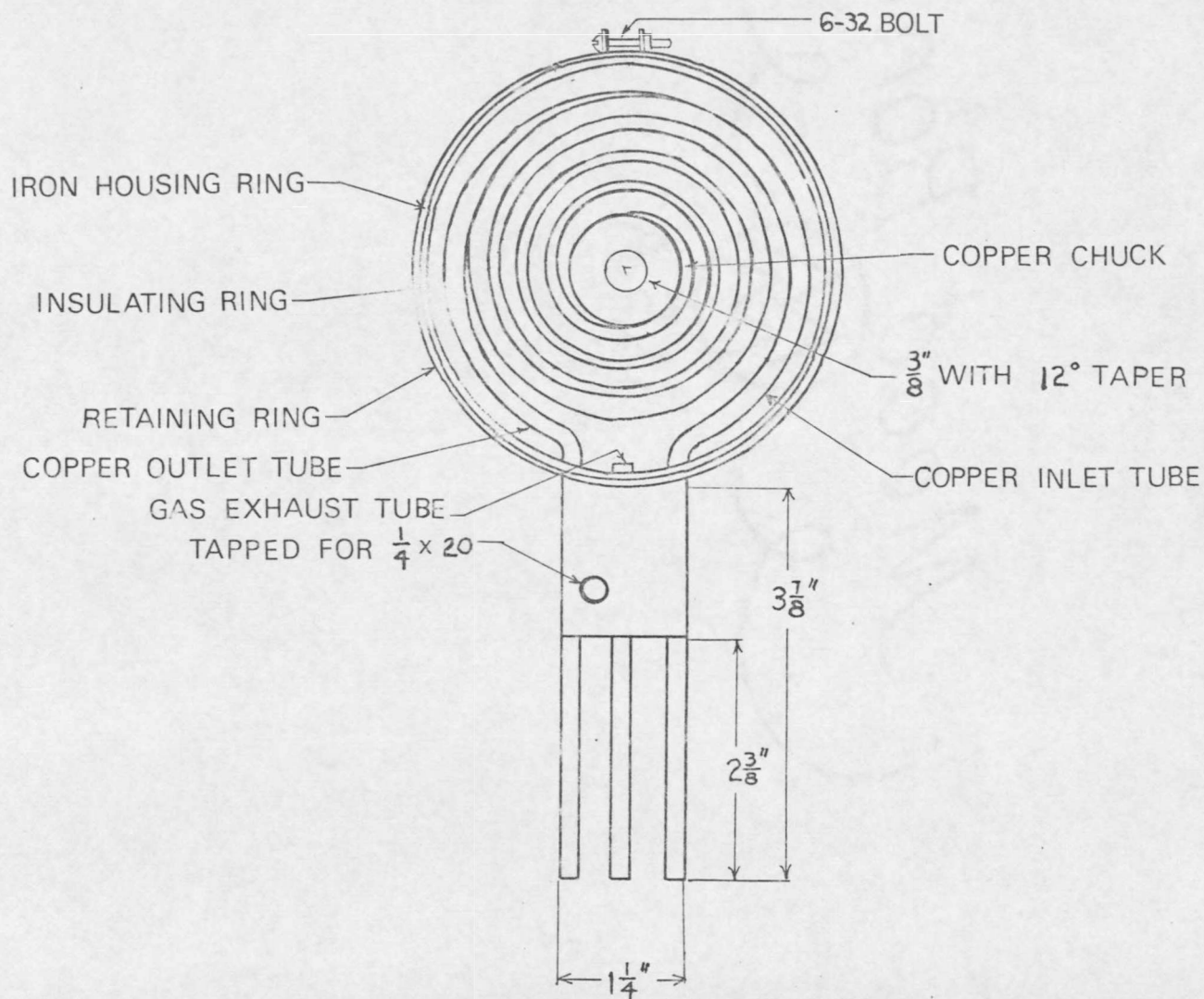


Figure 14. Spiral Heater Tube Contact.

on both ends and pressure fit to allow electrical conduction through the furnace.

The power supply for the furnace is a GE dry-type 5KVA transformer. Previously, electric welders had been used for power. An electronic control circuit is used to regulate the transformer output. A diagram of the circuit is shown in Figure 15. By adjusting the transformer output, the temperature of the furnace can be optimized for the element or elements to be determined.

One high-voltage power supply, an Atomic Instrument Co., Model 312, is used for both photomultiplier tubes to assure that any slight voltage variations would cause similar changes in their responses. Both photomultiplier tubes have approximately the same response characteristics. The power supply used for the hollow cathode lamp is a Lambda, Model C-281, regulated power supply.

An Ithaco Model 353 DL lock-in amplifier and Model 382 chopper were incorporated into the set-up. This provides the electronics to utilize the dual-wavelength capability of the monochromator. The Model 353 DL lock-in amplifier system consists of two independent log (or linear) lock-in amplifier systems sharing a common cabinet, power supply, and meter. It may be used as two separate channels (A and B) or as a ratiometric system (A/B). Figure 16 shows the conformations of the lock-in amplifier system which were used or could be used.

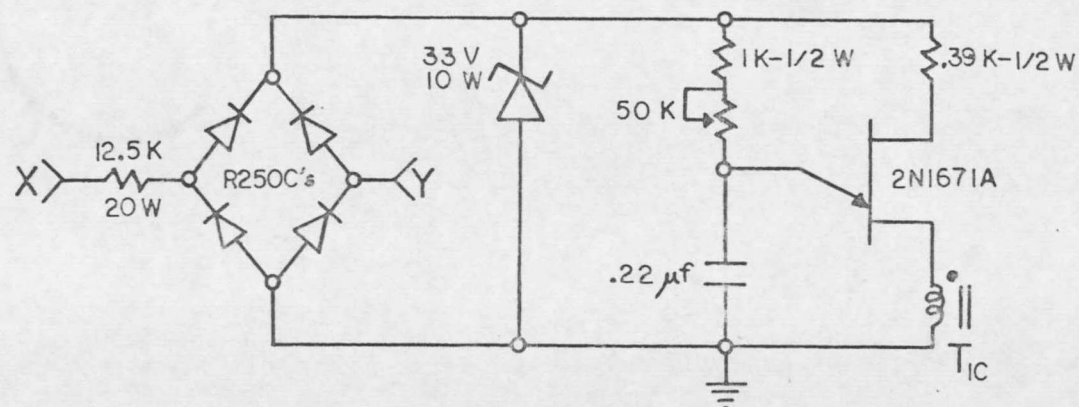
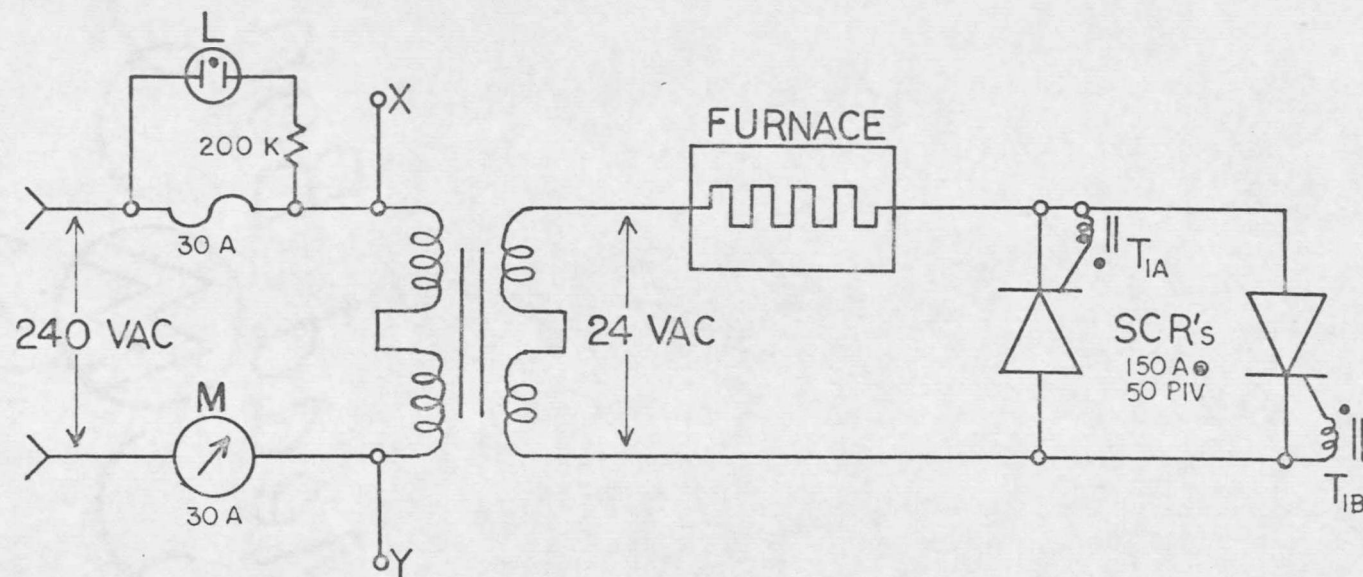


Figure 15. Transformer Regulator Circuit

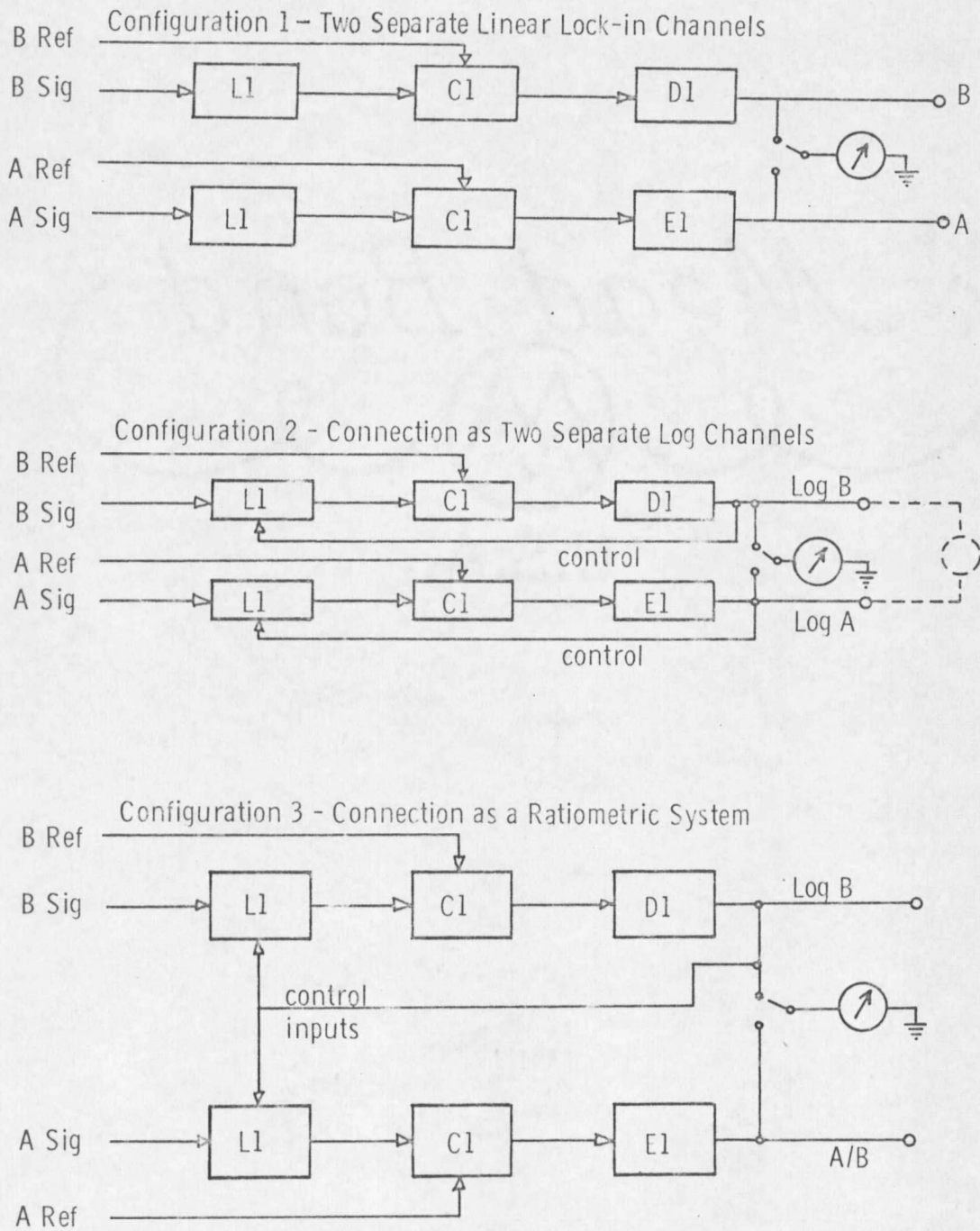


Figure 16. Lock-in Amplifier Configurations.

Either one or two recorders may be used as readout devices. One recorder was used for A/B measurements. Measurements in the separate channel mode were made by monitoring channel A with a recorder and reading the response of channel B from the meter on the lock-in amplifier. Following the dirty water and simultaneous determination of Ag and Pb results, the first types of samples run on the arrangement, a second recorder was borrowed and some of the later results were monitored with two recorders as shown in Figure 14. A Linear Instruments Corp., Model 232, dual-pen recorder has been acquired which allows a chart record of both channels independently or in the A/B mode utilizing only one recorder. This recorder is currently being used.

Sample Preparation and Methods

The dual-wavelength spectrophotometer was used to determine Ag and Pb in several different types of samples. The first group of determinations were performed on a water sample which was one of a large number of samples which have been analyzed for Ag in conjunction with a hail suppression study being carried out by Colorado State University. This particular sample was very dirty, containing much suspended sediment of both inorganic and organic nature. Earlier attempts to determine the Ag concentration by a solvent extraction procedure⁽³¹⁾ presented problems which were finally eliminated by

including filtration and acid digestion steps prior to the solvent extraction.

The Ag concentration of this sample was later determined without prior preparation other than filtration using the dual-wavelength spectrophotometer in the ratiometric (A/B) mode. Channel A was set on the most sensitive Ag line (328.1 nm) and channel B was set on a nearby nonresonant line emitted by the hollow cathode. By taking the ratio of the responses of the two channels, any effects of background absorption caused by molecular absorption or light scattering by particles is corrected for. As will be seen later, the results of these determinations corresponded very well with the results obtained previously.

The second group of determinations were performed on synthetic samples containing both Ag and Pb. The Ag and Pb were determined simultaneously by using the dual-wavelength spectrophotometer in the separate channel (A and B) mode. Channel A was set on the most sensitive Ag line (328.1 nm) and channel B was set on the most sensitive Pb line (217.0 nm). A Pb hollow cathode was used rather than a multielement hollow cathode since it was found that a very strong Ag signal was emitted along with the Pb signal.

A third set of determinations (for Pb) was performed on a standard orchard leaf sample obtained from the National Bureau of Standards. This was done to check the accuracy and precision of the technique used.

A fourth set of determinations (for Pb) involved a "sodium vitamin" and a "sulfur drug" obtained from Hoffmann-LaRoche Inc. Again, these determinations were performed to check the accuracy and precision of results obtained employing the dual-wavelength spectrophotometer and furnace in the ratiometric (A/B) mode. In all cases, orchard leaves, "sodium vitamin," and "sulfur drug," channel A was set on the Pb 283.3 nm resonance line and channel B was set on a nearby nonresonant line.

The final set of determinations (for Ag) was performed on standard rock samples from the Nonmetallic Standards Committee of the Canadian Association for Applied Spectroscopy. The first type of sample was a syenite rock, composed of different silicates, and the second type was a sulfide ore. The most sensitive resonance line of Ag was used.

Calibration curves were prepared and are shown in Figures 17 and 18. Stock standard solutions of Ag and Pb were diluted with doubly-distilled water to 10^{-8} g of metal/ml. Five- to 150- μ l portions of the solutions were placed into high-density graphite cups and dried under a heat lamp. The cups were then inserted directly into the furnace. Using the separate channel (A and B) mode permitted the simultaneous running of calibration curves for the Ag 328.1 nm and 338.3 nm resonance lines or for the Pb 217.0 nm and 283.3 nm resonance lines.

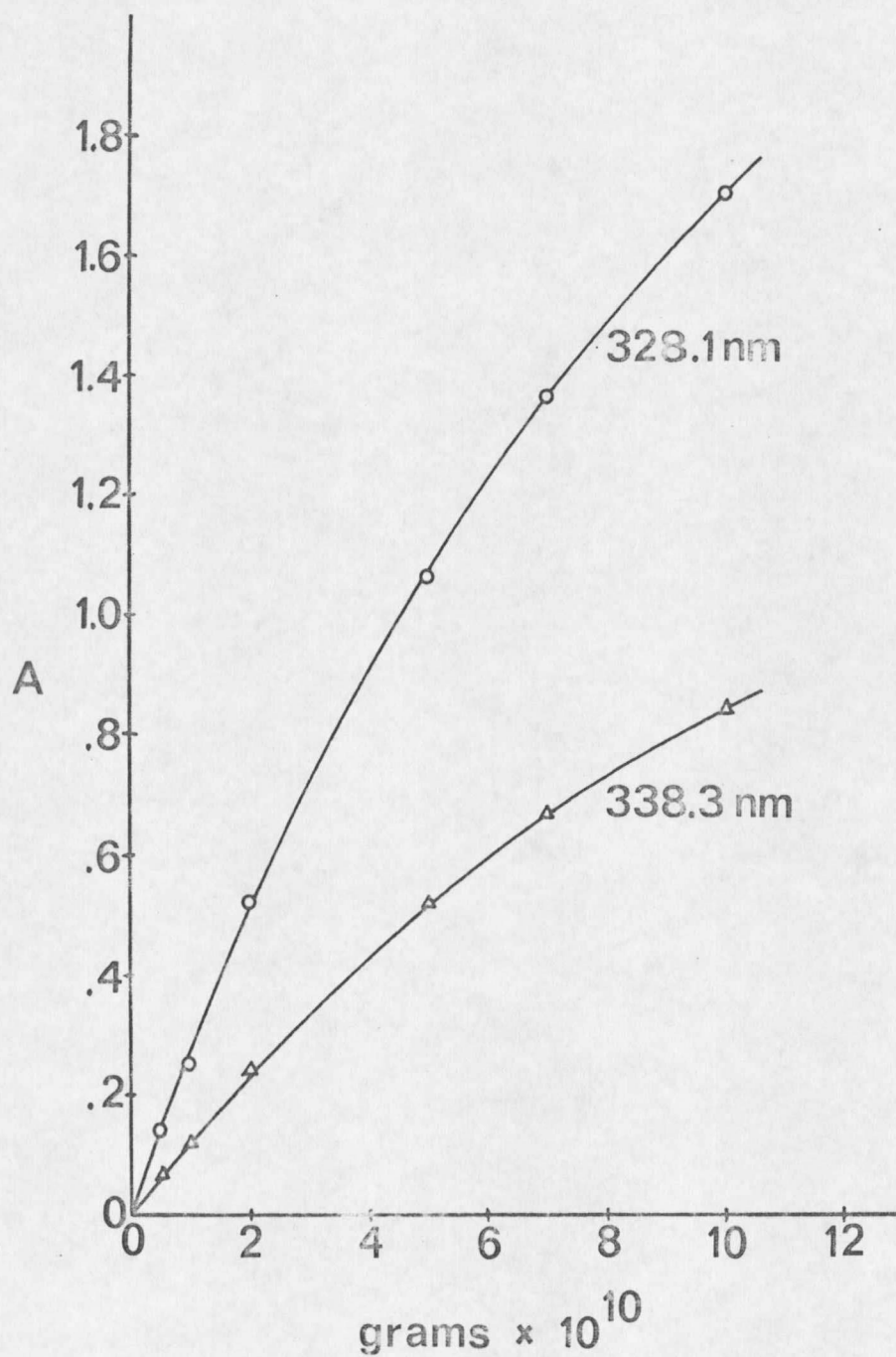


Figure 17. Calibration Curves for Ag.

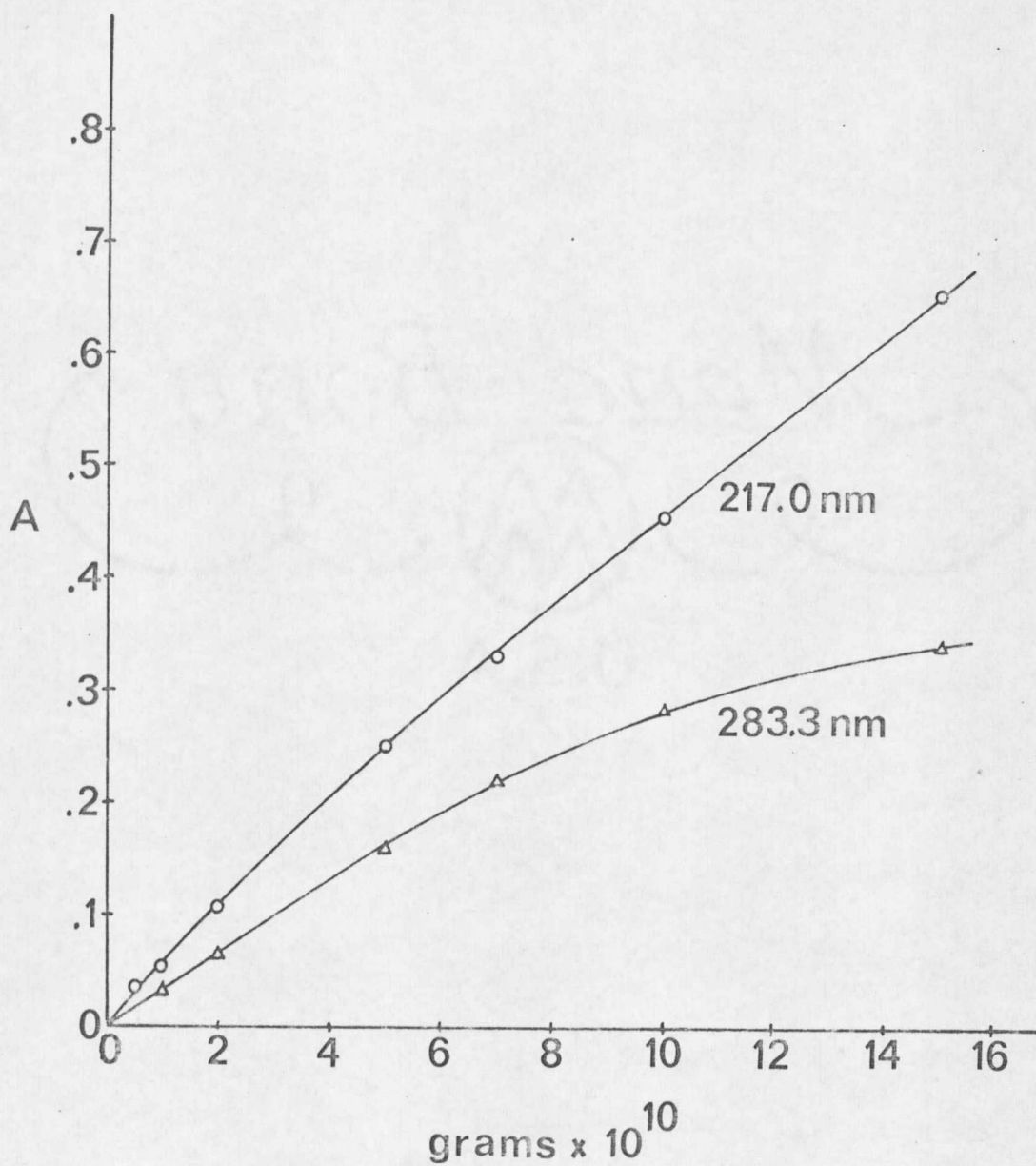


Figure 18. Calibration Curves for Pb.

Synthetic samples for the simultaneous determination of Ag and Pb were prepared by placing appropriate volumes of both Ag and Pb solutions into cups. The dirty water samples were prepared by placing 100-, 200-, and 300- μ l portions into cups without prior preparation other than filtration. In both cases the cups were dried under the heat lamp and inserted into the furnace. The furnace temperature for all determinations was 1825°C. This is approximately the optimum temperature for the determination of both Ag and Pb.

The orchard leaf sample was prepared as follows: 250 mg of sample was weighed; 10 ml of concentrated HNO₃ and approximately 10 ml of doubly-distilled water were added to the sample and heated; the resultant solution was diluted to 100 ml with doubly-distilled water. Ten- μ l portions were placed into cups, dried, and inserted into the furnace.

In the case of both the "sodium vitamin" and "sulfur drug," 1-2 mg portions of the samples were accurately weighed into cups. One hundred μ l of 30% H₂O₂ was added to each "sodium vitamin" sample. One hundred μ l of concentrated HNO₃ was added to each "sulfur drug" sample. After drying under a heat lamp, they were inserted into the furnace.

Both the syenite rock and sulfide ore were prepared in the same manner. Five hundred mg of sample was weighed and digested in 25 ml of concentrated HNO₃ + 10 ml of 48% HF. The resultant solutions were diluted to 65 ml with

doubly-distilled water. Either 5- μ l or 10- μ l portions of the solution were placed into cups, dried, and inserted into the furnace.

RESULTS AND DISCUSSION

A New Dual-Wavelength Spectrophotometer

When the dual-wavelength spectrophotometer was first incorporated into an atomic absorption system, many small adjustments and alterations needed to be made. The alignment of the components on the optical bench was a major task. The exact placement of the exit slit housings and alignment of both exit slits and entrance slit were determined by maximizing the signal from the photomultiplier tubes. Noise levels were found to be higher than one would want them to be so all power supplies and connections were thoroughly checked. In order to balance the outputs of the two channels, variable load resistors had been installed on the original RCA IP28 photomultiplier tubes. This circuit seemed to be a source of noise so was completely rewired, changing to a system of variable input voltage rather than variable output, and the photomultiplier tubes were replaced with Hamamatsu R106 photomultiplier tubes. The above steps improved the noise to a usable level.

It had been noticed earlier that the furnace power supply setting needed to produce a particular furnace temperature would seem to change with time. Also, it was wondered how the temperature produced varied with current. Power supplied in an AC circuit is equal to EI . The energy delivered to the furnace should be proportional to the product of the voltage and current.

With the secondary current and voltage meters available with the new power supply and furnace, it was decided to study the above. Temperature versus current curves were obtained over a period of six months. These curves are shown in Figure 19. Voltage versus current curves are shown in Figure 20. From these curves it can be seen that the current needed to produce a given temperature does decrease with time. Also at a given current the voltage increases with time. This means that the resistance of the heater tubes increases. This is borne out by the fact that the longer a heater tube has been used, the thinner the walls become. Also it can be seen from the curves that the temperature produced in the furnace is a linear function of the current on any given day. EI calculations showed that the temperature is not directly proportional to the power. At higher temperatures heat losses increase, causing heating efficiency to decrease.

The dual-wavelength spectrophotometer worked very well in the modes of operation which were investigated. The Woodriff furnace, like other non-flame devices, is very sensitive. This allows the direct determination of low concentrations of trace elements without preconcentration. By providing some means of correcting for background absorption in samples containing relatively high concentrations of salts or organics, most sample preparation can be omitted.

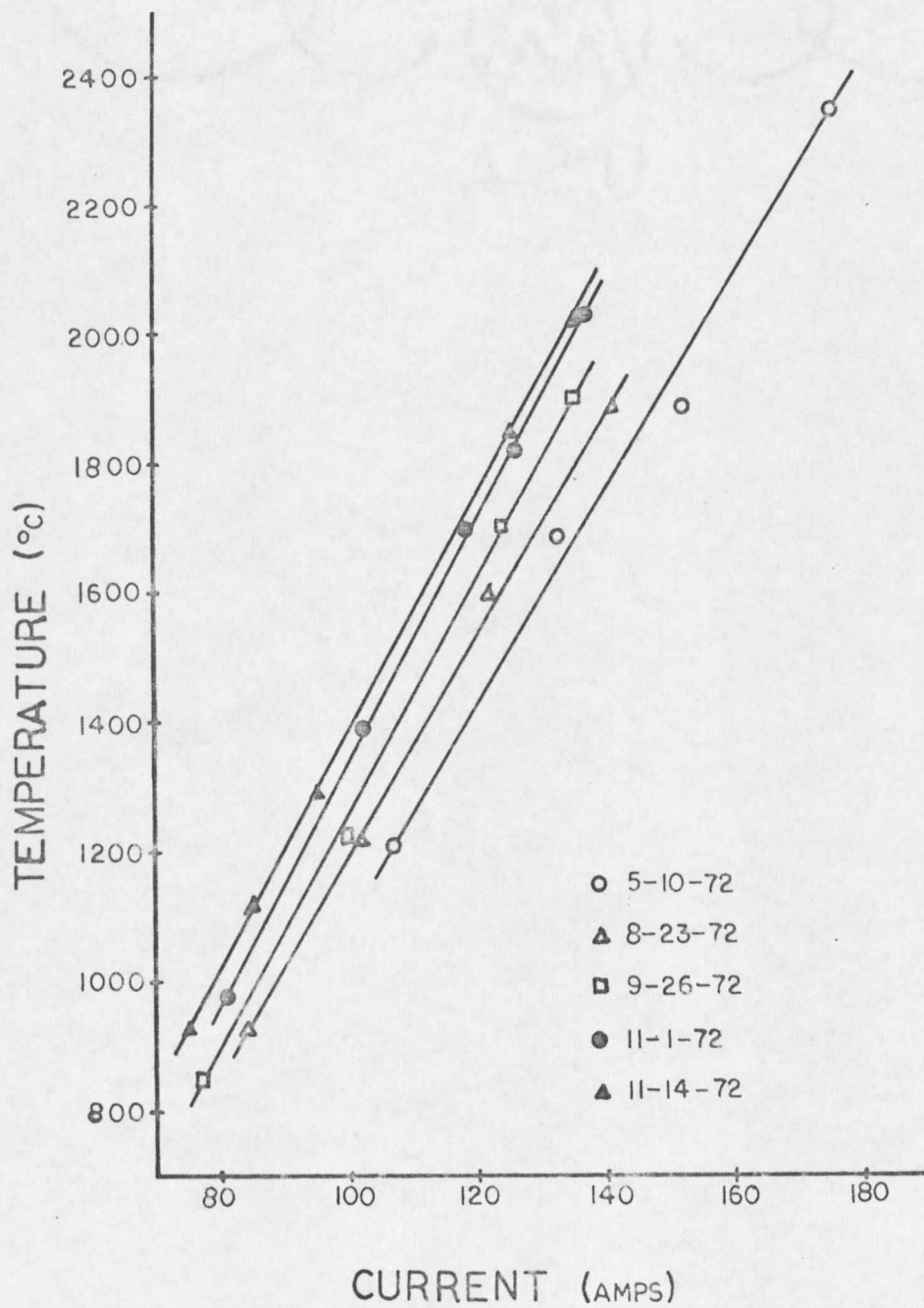


Figure 19. Current versus Temperature Curves.

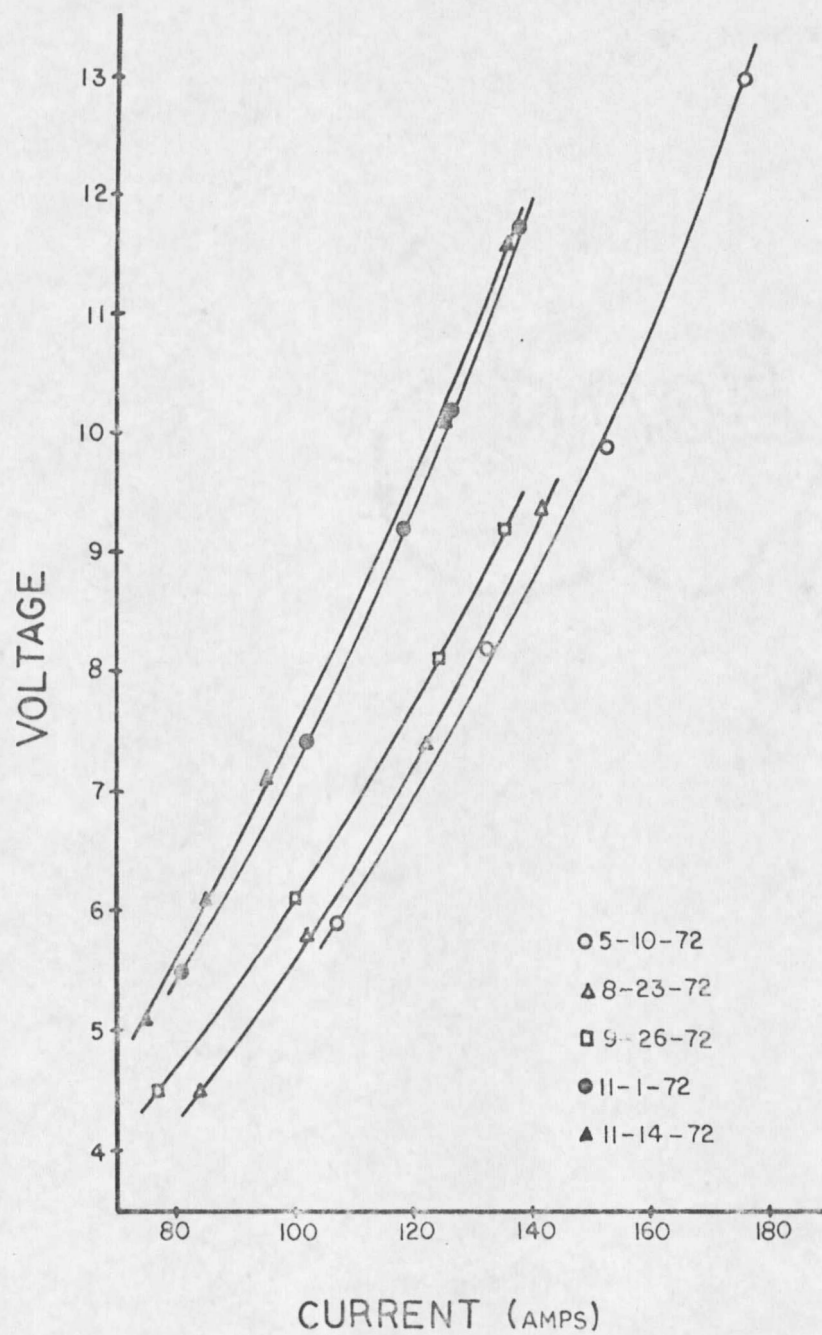


Figure 20. Current versus Voltage Curves.

In order to get some comparison between running the complex water sample with and without background correction, duplicate sets of samples were run first in a single channel (A) mode and then in the dual-channel (A/B) mode. One hundred-, 200-, and 300- μ l samples of water were determined for Ag. When only the Ag resonance line was monitored, the absorption values increased out of proportion with respect to the increase in sample size. This indicated that some sort of background absorption was occurring. When the Ag line and a nearby nonresonant line were both monitored and the ratio of their responses taken, the absorption values increased in close correlation with the increase in sample size. Also the absorbances were more reproducible in the A/B mode. Table III gives the results of the Ag determinations on the dirty water sample. The concentration values in the A/B mode agree quite well with the previously determined concentration of Ag utilizing an acid digestion-solvent extraction procedure. The concentration values in the A mode do not. There appears to be a slight decrease in values of the A/B mode which could indicate a tendency for the spectrophotometer system to overcompensate for background absorption as sample size increases. However, this may also indicate that the larger sample takes longer to volatilize completely, producing a slightly lower absorbance than would be expected. This effect has been demonstrated by Winefordner and co-workers in other

systems. Using the integrated signal absorption rather than peak absorption corrects almost completely for this effect when a background corrector is used.

Table III: Results of Water Determinations for Ag.

Sample size	A mode		A/B mode	
	Concentration (g/ml)	RSD*	Concentration (g/ml)	RSD*
100 μ l	3.20×10^{-10}	31.7%	1.40×10^{-10}	18.5%
200 μ l	5.70×10^{-10}	11.6%	1.35×10^{-10}	20.8%
300 μ l	6.73×10^{-10}	51.5%	1.23×10^{-10}	5.1%
Average	5.21×10^{-10}	31.6%	1.33×10^{-10}	14.8%

Concentration determined by acid digestion-solvent extraction procedure:
 1.29×10^{-10} g/ml.

*RSD = relative standard deviation using the standard deviation =

$$\left[\frac{\sum (x - \bar{x})^2}{N-1} \right]^{\frac{1}{2}}$$

The results for the simultaneous determination of Ag and Pb in synthetic samples are given in Table IV. The correlation between amounts expected and amounts found for both Ag and Pb is quite good, especially considering the amounts being determined. The Pb results are not quite as good as the Ag results which in part would be due to the fact that the meter on the

lock-in amplifier was used as the readout. A recorder would improve these results somewhat. The system needs to be used with other combinations of elements. Multielement hollow cathode lamps are available for this purpose containing any compatible combination of interest.

Table IV: Results of Simultaneous Ag and Pb Determinations*

Sample	Ag expected (g)	Ag found (g)	Pb expected (g)	Pb found (g)
1	10.0×10^{-10}	10.5×10^{-10}	1.0×10^{-10}	0.90×10^{-10}
2	7.0×10^{-10}	6.9×10^{-10}	2.0×10^{-10}	1.7×10^{-10}
3	5.0×10^{-10}	4.9×10^{-10}	5.0×10^{-10}	5.4×10^{-10}
4	2.0×10^{-10}	2.0×10^{-10}	7.0×10^{-10}	6.5×10^{-10}
5	1.0×10^{-10}	0.95×10^{-10}	10.0×10^{-10}	10.2×10^{-10}
6	0.50×10^{-10}	0.45×10^{-10}	15.0×10^{-10}	14.6×10^{-10}

*The Pb results were read from a meter and were not as accurate as the recorder results for Ag.

One problem involved in the use of multielement lamps however is that of spectral interference⁽⁴¹⁾. Although multielement lamps are slightly less efficient than single-element sources, they offer convenience in handling and savings in equipment cost. As the number of elements increases, the spectra of the lamp becomes more complex, and the possibility of spectral interference

increases. Thus, multielement lamps must be checked to see that the lines emitted by different elements do not overlap to any great extent. Even single-element hollow cathodes many times emit lines of elements other than the element of interest. Generally these do not cause problems and may allow the use of single-element lamps for multielement determinations. Pages 94-99 of the Appendix show chart paper records and data from photographic film of two single-element lamps and one multielement lamp, demonstrating the ideas mentioned above.

One objection which has been made to dual-wavelength instruments for simultaneous determination of two elements by atomic absorption is that it is difficult to get two elements which behave the same in a flame. The use of a furnace or other nonflame device eliminates much of this objection since the complex flame gas mixture is replaced with a single inert gas. Chemical reactions are minimized and nonoptimum temperatures which might be used for a particular element can be compensated for by running the calibration curve at the same temperature.

The results obtained for the determination of Pb in the standard orchard leaf sample, "sodium vitamin," and "sulfur drug" are shown in Table V. As can be seen, they compare quite well with the reported values^(42, 43).

The solution obtained after digestion for the orchard leaves was not

Table V: Results of Determinations for Pb*

Sample	Preparation	Results		
		Pb reported (ppm)	Pb found (ppm)	RSD (%)
Orchard leaves (NBS)	HNO ₃ digestion of 250 mg; diluted to 100 ml; 10 microliters placed on cups; dried.	44	43.2	8.4
"Sodium vitamin" (H-L)	1-2 mg weighed into cups; 100 microliters of H ₂ O ₂ added; dried.	1	1.04	8.3
"Sulfur drug" (H-L)	1-2 mg weighed into cups; 100 microliters of HNO ₃ added; dried.	1	0.98	16.5

*The Pb 283.3 nm line was used. Each sample after preparation contained on the order of 10^{-9} g of Pb.

clear; however, this was expected. The most generally used common acid mixture for wet digestions is a combination of nitric, sulfuric, and perchloric acids in the ratio of about 3:1:1⁽⁴⁴⁾. Using only nitric acid was much easier and safer, and the chance of reagent contamination was reduced. This non-complete digestion would account for the relative standard deviation being slightly higher than might be hoped.

It was found that good accuracy and precision were obtained by merely

adding 100 μ l of 30% H_2O_2 to the "sodium vitamin" sample in the cup. Along with reducing the background somewhat, it changed the form of the sample sufficiently that no powdered sample was lost during introduction to the furnace. The relative standard deviation obtained reflects the weighing procedure used in the sample preparation.

The "sulfur drug" presented considerably more problems in analysis than did the "sodium vitamin." The addition of 100 μ l of 30% H_2O_2 to the drug did not seem to affect it and upon insertion into the furnace, large amounts of smoke and H_2S were evolved. It was found that the addition of 100 μ l of concentrated HNO_3 reduced these problems sufficiently for the analyses to be performed. A large amount of background absorption was present which varied greatly depending upon the nonresonant line used for reference. Evidently, a large amount of molecular absorption, rather than scattering by particles, was occurring⁽¹¹⁾. This problem was overcome by plotting wavelength versus background absorption on both sides of the resonance line and interpolating an average background absorption/mg of sample. This was done both with the nonresonant lines emitted from the hollow cathode and with a hydrogen continuum lamp. Using this technique, the result reported in Table V was obtained.

The somewhat larger relative standard deviation in this case stems

from three facts. Errors are introduced in the weighing of 1-2 mg of sample, there was much more background absorption due to relative nondestruction of the drug before analysis, and background absorption for a particular sample size is not always the same. The latter is dependent upon the way in which the material leaves the cup and enters the optical path. Thus, using an average background absorption will give accurate results but will decrease the precision.

The results obtained for Ag in syenite rock and sulfide ore are shown in Table VI. The results obtained compare quite well with those reported⁽⁴⁵⁾. The procedure used for preparation is somewhat simpler than

Table VI: Results of Ag Determinations on Rock Samples

Sample	Date	Sample size	Results					
			Ag found (ppm)	RSD (%)	Ag reported (ppm)			
Syenite rock	May 16	5 μ l	0.78	18.1	<1	<1	<1	<1
					0.3	0.5	0.5	1.0
		10 μ l	0.78	11.2	1.4	1.9	5.7*	
					mean		1.6	
		average	0.78	14.6	mean		0.9	
Sulfide ore	May 16	5 μ l	5.2	5.4	range			
	April 28	10 μ l	4.8	3.3	2 - 6			
		average	5.0	4.3	mean		3.9	

*This outlier was discarded in the second syenite mean.

that generally used for silicate rocks. Silicates are generally prepared for atomic absorption analysis with an HF-H₂SO₄-HCl procedure, an HF-HClO₄-HCl procedure, or a Na₂CO₃ fusion-HCl procedure which may or may not include HF and H₂SO₄ before fusion^(46,47,48). Occasionally other reagents are added. The procedure generally involves 4 to 8 individual steps, which are sometimes quite complicated, in order to get the sample into solution. Sulfide ore samples have previously been brought into solution by using a nitric acid and/or sulfuric acid mixture followed by the addition of tartaric acid, nitric acid-hydrochloric acid-diethylenetriamine, or nitric acid followed by filtration with the residue being treated with a nitric acid-hydrofluoric acid mixture and mercuric nitrate^(46,49). Using fewer reagents and steps simplified the procedure and reduced the possibility of contamination.

The Ag results obtained for the syenite rock fall in the reported range and, if the obvious outlier reported⁽⁴⁵⁾ is discarded, compare almost exactly with the average value given. The Ag results obtained for the sulfide ore fall well within the reported range and the agreement among ore samples prepared at different times is quite good.

The relative standard deviations show that the accuracy of pipetting 5- μ l portions of solution is not as great as for 10- μ l portions. The average relative standard deviations reflect the incomplete dissolution of the

silicate rock.

The determination of elements with the dual-wavelength spectrophotometer in samples requiring background correction or the determination of elements simultaneously yield results which compare very well with those reported or expected. These results show great promise for the instrument. It is much simpler in construction than commercially available dual-wavelength systems. The wavelength reproducibility is good indicating a quite stable construction. The use of a concave grating introduces some aberrations; however, some of this is compensated for by simplicity and lower light losses. The only reflecting surfaces are the grating and one small front-silvered mirror for each channel. No lenses or collimating mirrors are used. The effect of stray light is minimized since the exit slits are parallel to the optical plane. A similar type of system should be adaptable to the Czerny-Turner and Ebert mounts which would allow the use of a less expensive plane grating and decrease some of the aberrations inherent to a concave grating. However, this would also increase the light losses since two additional reflecting surfaces would be introduced into each channel and the additional expense of spherical collimating and focusing mirrors would be introduced. An improvement which should be made on the spectrophotometer is the installation of a narrower front-silvered mirror on the channel which

passes in front of the second channel. This would allow wavelengths much closer together to be monitored.

Additional uses could possibly be made of the spectrophotometer. The extension of working curves could be accomplished by monitoring two different resonance lines of an element, giving different sensitivities; i.e., for Ag use 328.1 nm and 338.3 nm. There is room to place film along the Rowland circle allowing photographic recording. Alternately this space could be used to place fixed photomultiplier tubes and slit assemblies along the Rowland circle which would produce a direct reader for several different elements while simultaneously maintaining the dual-wavelength scanning feature. The scanning capability of both channels can be used in numerous ways. It is felt that this instrument is extremely versatile and will have many applications in emission spectroscopy or atomic fluorescence spectroscopy as well as in atomic absorption spectroscopy.

EXPERIMENTAL

Application of Furnace Atomic Absorption

In order to show that furnace atomic absorption can be used for routine analysis, trace element concentrations of different elements were determined in various types of samples. These sample groups (excepting one) were analyzed in conjunction with different research projects being carried out by personnel at Colorado State University, the U. S. Soil Conservation Service, and Montana State University.

The instrumentation used for the determinations in this section has been previously described⁽³¹⁾. The major components of the atomic absorption system used were: the Woodruff furnace (described in the first section), a Spex 3/4-meter Czerny-Turner Spectrophotometer, a PAR HR8 lock-in amplifier and chopper, a Honeywell 6-inch recorder, and associated electronics.

Sample Group I

The first large group of samples were obtained from Dr. H. L. Teller, Colorado State University, Fort Collins, Colorado. Before commencement of the 1971 cloud seeding program of the National Hail Research Experiment, he and Dr. D. A. Klein, also of CSU, were contracted to study silver disposition and environmental impact in the seeding target area^(50, 51). Surface water samples collected from the target area were sent to Montana State University

for the determination of Ag. Leachate samples and burner condensate samples were also analyzed.

Procedure

Water samples were collected by CSU personnel from both banks of streams, depth-integrated samples being taken by lowering and raising sample bottles through the depth, on the end of a pole. The two samples were combined into a single composite. The samples were acidified with nitric acid (to pH ca. 2), frozen, and shipped to Bozeman, packed in dry ice, via air freight. The samples were kept frozen until just prior to analysis.

Soil-core leachate samples, obtained from infiltration studies, were acidified, frozen, and shipped to Bozeman just as the surface water samples were.

Burner condensates were obtained by burning an unknown concentration of NaI, AgI, and acetone with propane. These were acidified, frozen, and shipped to Bozeman. In all of the above cases, samples were collected and stored in polyethylene bottles.

The analysis technique used for the surface water samples and leachate samples was basically the same as that developed earlier, a dithizone- CCl_4 extraction of Ag from the water sample. The samples were melted in the bottles shipped, the pH checked, and adjusted if necessary. Surface water

samples only, were then filtered, removing much of the sediment from the sample. One hundred ml of either sample was then extracted and the organic extractant determined for Ag as previously reported⁽³¹⁾.

Burner condensate samples were melted in the bottles shipped, the pH checked, and adjusted if necessary. Ten ml of the sample was heated several minutes with 10 ml of 0.2 M NaCN solution until all particulate matter was dissolved, leaving a homogeneous solution, which was then made up to 100 ml with doubly-distilled water. Before determination, a 1-1000 dilution was made, and 20- μ l portions of the resultant solution placed into cups for analysis.

Sample Group II

A second group of samples was obtained from P. E. Farnes of the USDA Soil Conservation Service, Bozeman, Montana. During the 1971 snow season, it was decided that snow samples should be analyzed for various trace elements to determine if elements being deposited with the winter snowfall would indicate trends of man's activities and explain an apparent increased precipitation trend noted in the mountains of Southwestern Montana⁽⁵²⁾. Snow samples collected were sent to Montana State University for qualitative survey and quantitative determination of Cd, Zn, Pb, and Ag.

Procedure

Snow-core samples were obtained by SCS personnel with a Federal snow sampler. The sampler consists of a silicone coated duralumin tube. The fifth core obtained at a particular snow course was that which was sent for analysis. The snow-core was placed in a polyethylene bottle and kept frozen until just prior to analysis.

The analysis technique used depended upon the element being determined. In all cases, however, the sample was first melted in the polyethylene bottle and acidified to ca. pH 2 with nitric acid. Cd determinations were made by placing 20- to 100- μ l portions of the sample on cups, and after evaporation of the water, inserting them directly into the furnace. Zn determinations were made, not with the furnace arrangement, but rather with a conventional flame atomic absorption unit (a Beckman DB). This was done since the Zn concentrations were such that the sample would need to be diluted before analysis by furnace atomic absorption. Pb determinations were made by placing 20- to 100- μ l portions of the sample on cups as in the Cd case. Ag was determined by two methods. Eleven of the samples were determined by placing 400- to 500- μ l portions on cups, drying them, and inserting them into the furnace. The remaining samples were determined for Ag using the solvent extraction procedure previously developed⁽³¹⁾.

Sample Group III

The third group of samples was obtained from Dr. T. Weaver, Montana State University, Bozeman, Montana. He was studying Ag accumulation in vegetation and the effect of Ag on vegetation and soil microorganisms in order to look into the ecological consequences of cloud seeding with AgI⁽⁵³⁾. Samples of vegetation grown in soils enriched with AgI or AgNO₃ were analyzed utilizing the furnace atomic absorption instrumentation available at Montana State University.

Procedure

The different plants, wheat, maize (corn), or soybeans, were first washed to remove as much soil and dust as possible. They were then dried and delivered for analysis.

The dried plant was weighed, then ashed in a muffle furnace at incremental temperatures until a maximum between 500-600°C was reached and essentially all carbon was oxidized. The total ashing time ranged from 6-8 hours. Following the ashing steps, weights were again recorded. Five ml of distilled, concentrated HNO₃ was added to each ashed sample, to dissolve the metal oxides and residue. After slight heating to aid the dissolution, the resultant solution was diluted to 100 ml with doubly-distilled water. Ten- to 50-μl portions of the final solution were placed on sample cups, dried, and

inserted into the furnace.

Sample Group IV

A final group of samples was obtained in connection with a Chem 470 problem undertaken by C. Moell of the Geology Department on the MSU campus. He was interested in studying the geology of certain areas in southwestern Montana and seeing if correlations could be made between known history and trace element concentrations in water courses. Determinations of Ag, Au, Cd, Cu, Hg, Mn, and Pb were performed for him. For comparison, samples were also analyzed from a spring near Big Springs, Idaho, and from a lab in Gaines Hall on the MSU campus.

Procedure

Representative water samples were collected in polyethylene bottles and immediately acidified with nitric acid to ca. pH 2. The samples were analyzed as soon as possible after delivery. In all cases the waters were analyzed directly, without preconcentration or other sample preparation. Appropriate amounts of each sample (generally 100-500 μ l) were placed on cups, dried, and determined for the element of interest.

Calibration curves for all of the above sample types were prepared in the same manner as described in the earlier sections, with the exception of the Ag calibration curve for the solvent extraction procedure and the Zn

calibration curve for the snow-core samples. The calibration curve in the first case was made by running standard silver solutions through the extraction procedure and plotting grams of Ag/ml of aqueous solution versus absorbance. In the second case, Zn standard solutions in the range from 0.05-1 ppm were nebulized into the Beckman burner and absorbances recorded.

RESULTS AND DISCUSSION

Applications of Furnace Atomic Absorption

Several different elements have been determined in the various types of samples. It was necessary to optimize, as much as possible, the instrumental parameters used for each element. It was found that the slit width used for a particular element had little or no effect on the sensitivity obtained. This is born out by hollow cathode lamp data available from Varian Techtron. In order to keep furnace emission entering the monochromator at a minimum and reduce the possibility of spectral interference, slit widths were kept as narrow as possible without causing increased noise or making necessary the use of excessive current and voltage to the hollow cathode lamp and photomultiplier tube, respectively.

Likewise, gas flow through the furnace was found to have no effect on the sensitivities until larger volumes (on the order of .25 l/min) were used. All samples and curves were run using a gas flow of approximately 40 ml/min.

The one parameter which greatly affects the sensitivity obtained for an element is the furnace temperature. Temperature versus absorbance curves were run to determine the optimum temperature for a particular element. Representative curves of this type are shown on page 100 of the Appendix.

Calibration curves were established for each element to be determined.

A representative sample of these calibration curves is shown in the Appendix, page 101. The measured sensitivities for the various elements are given in Table VII.

Table VII: Representative Sensitivities

Element	Wavelength (nm)	Sensitivity (grams)
Ag	328.1	1.5×10^{-12}
Ag	338.3	4.0×10^{-12}
Pb	217.0	4.0×10^{-12}
Pb	283.3	7.0×10^{-12}
Au	242.8	1.0×10^{-11}
Cd	228.8	1.0×10^{-14}
Cu	324.8	1.2×10^{-11}
Hg	253.7	1.0×10^{-10}
Mn	279.5	1.1×10^{-11}
Zn*	213.9	4.5×10^{-9}

*Determined on a Beckman DB flame AA spectrophotometer.

A solvent extraction procedure was used with some of the samples in which Ag was determined. The apparent low values obtained for samples containing larger amounts of Ag having been noted⁽³¹⁾, it was concluded that the extraction efficiency should be checked. Figure 21 shows the data obtained.

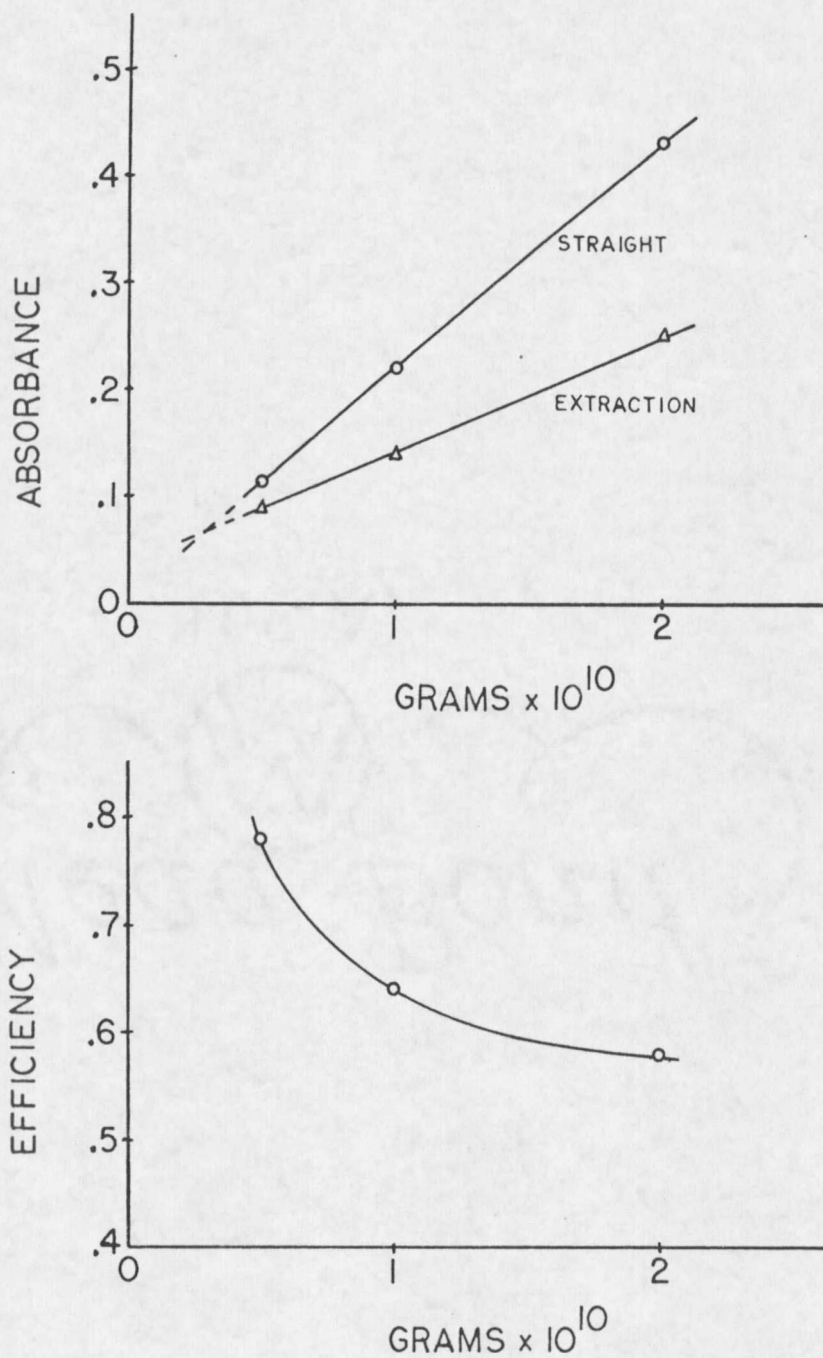


Figure 21. Extraction Efficiency Curves for Ag.

The extraction efficiency is not constant and decreases as the Ag concentration increases. Thus, for samples which gave results off scale in the following results, a smaller portion of the sample was taken (generally 10 ml), diluted to 100 ml with doubly-distilled water, and run through the extraction procedure. This permits the determination of Ag concentrations which fall in the range of the calibration curve and thus compensates for decreasing extraction efficiency as the concentration increases.

It should be noted that in the application section large numbers of samples were analyzed on a routine basis. In most cases two and occasionally three replicates of the same sample were run. The formula used to figure standard deviations in these cases is:

$$S = \left[\frac{\sum (x - \bar{x})^2}{N-1} \right]^{\frac{1}{2}}$$

Thus, relative standard deviations are not as small as they would be if more than five replicates of each sample were run.

Sample Group I

A total of 118 surface water samples collected from the target area of the National Hail Research Experiment in NE Colorado were analyzed for Ag. Initially water samples were sent to the Desert Research Institute, Reno, Nevada, for Ag analysis by the neutron activation method. However, they were

found to contain excessive amounts of interfering substances, and could not be analyzed by neutron activation⁽⁵⁰⁾. Subsequently, they were sent to MSU for the determination of Ag.

It was found that some of the surface water samples contained much suspended sediment of both inorganic and organic nature. This interfered with the solvent extraction procedure, producing an emulsion in the solvent extraction step and reducing the efficiency of extraction, as well as producing non-reproducible results. This problem was partially overcome by including a filtration step prior to the solvent extraction. On samples where there were still problems, a nitric acid digestion was included prior to the dithizone- CCl_4 extraction. One hundred ml of sample was evaporated to a volume of about 5 ml and digested with 4 ml of concentrated HNO_3 . The resultant solution was then diluted to 100 ml with doubly-distilled water and extracted as usual. This produced results which were reproducible, and as was discussed in the previous section, gave results which agreed very well with the direct determination of Ag in the same sample utilizing a background correction technique.

The results obtained for the surface water samples are shown in Tables VIII and IX. They are given in terms of sampling location and sampling time. The sampling times were taken from references 50 and 51. Sample locations

Table VIII: Surface Water Results (Teller)

Date (1971)	Location										Mean
	W403	W106	W219	W207	W304	W371	W405	W081	W041	W409	
June 16-21	-----No data collection-----										
July 28-29	0.1	0.1	---	1.4	1.7	---	---	1.2	4.3	0.9	1.4
Sept. 11-12	0.2	2.1	2.0	1.8	1.0	---	---	---	0.6	2.7	1.5
Oct. 9-23	0.6	2.4	---	2.0	1.1	---	---	0.6	1.5	1.3	1.4
Mean	0.3	1.5	2.0	1.7	1.3	---	---	0.9	2.1	1.6	1.4

Values are given as (g) x 10⁻¹¹/ml.

Table IX: Surface Water Results (Teller)

Date (1972)	Location										Mean
	W403	W106	W219	W207	W304	W371	W405	W081	W041	W409	
April 20 -	---	0.41	0.11	0.13	0.09	---	0.10	0.13	0.28	0.07	0.17
May 4	---	0.32	0.15	0.22	0.22	---	---	0.27	0.26	0.10	0.22
May 22-23	---	0.10	0.22	0.18	0.48	0.67	0.27	0.91	0.21	0.08	0.35
May 27 -	---	0.24	0.13	0.11	---	---	---	---	0.11	0.02	0.12
June 2	---	0.18	0.27	0.18	0.37	5.19	0.12	5.28	0.32	0.36	1.36
June 4-5	---	3.60	0.13	0.51	0.11	0.54	1.45	1.39	0.10	0.25	0.90
June 11-14	---	0.34	3.53	0.12	---	---	---	---	---	---	1.33
June 16-18	No data collection										
June 20	---	---	0.80	0.32	0.50	---	0.21	0.26	0.45	0.20	0.39
June 23	---	0.11	---	0.32	0.22	---	0.29	---	0.22	0.19	0.23
June 24	---	---	0.10	0.11	0.30	3.67	0.19	0.15	0.12	0.18	0.60
June 27	---	---	---	---	---	0.28	0.34	---	12.9	0.10	3.40
July 8-10	---	---	7.27	0.46	0.23	1.17	0.11	---	0.23	0.39	1.41
July 11	---	---	---	---	0.27	0.50	0.43	2.30	0.32	0.18	0.67
July 25	---	0.30	0.24	0.13	0.19	0.18	0.17	0.60	0.31	0.14	0.25
July 27	---	---	---	---	---	---	---	---	---	---	---
July 31 -	---	---	---	---	---	---	---	---	---	---	---
Aug. 5	---	---	---	---	---	---	---	---	---	---	---
Mean	---	0.62	1.18	0.23	0.27	1.53	0.34	1.25	1.22	0.17	0.72

Values are given as $(g) \times 10^{-11}/ml$

shown on maps of the target area are available in the same references. The average relative standard deviation for the surface waters was 11.5%. It is felt that this is quite good considering the concentration range involved which was of the order of 10^{-11} g/ml. For comparison, reproducibility on standards of 10^{-7} , 10^{-8} , and 10^{-9} gram masses of Ag by neutron activation analysis has been reported as $\pm 4\%$, $\pm 7\%$, and $\pm 25\%$, respectively⁽⁵⁴⁾.

Briefly, a few conclusions can be made from the results. The silver concentrations reported for major North American rivers is 0 to 94×10^{-11} g/ml, with a mean of 9×10^{-11} g/ml⁽⁵⁵⁾. The values determined from the target area fall in the reported range, toward the lower end. The silver concentrations indicate a positive correlation with seeding intensity; however, this may be caused by total precipitation during the period rather than total seeded silver⁽⁵¹⁾. The apparent differences in mean Ag concentration between 1971 and 1972 may be a natural phenomenon based on total precipitation and time of sample collection.

Fifteen leachate samples were analyzed for Ag. Ag solutions were infiltrated through different types of soil cores at CSU to determine the movement of surface-applied Ag through soil⁽⁵⁰⁾. The results obtained for the samples are shown in Table X. The average relative standard deviation of the results was 15.4%. The soil types and % of added silver were obtained

Table X: Leachate Water Results

	Soil type					
	Ascalon		Platner		Mitchell	
	Ag (g) x 10 ⁻¹¹ /ml	% of* added Ag	Ag (g) x 10 ⁻¹¹ /ml	% of* added Ag	Ag (g) x 10 ⁻¹¹ /ml	% of* added Ag
Control	1.3	-----	2.6	-----	1.0	-----
Initial conc. = 0.5 ppm						
1	5.1	0.01	2.0	0.004	0.7	0.001
2	0.2	0.0004	1.9	0.004	1.7	0.003
Initial conc. = 5.0 ppm						
1	4.8	0.001	1.7	0.0003	0.9	0.0002
2	6.5	0.001	2.1	0.0004	1.8	0.0004

*Only 1/6 of the total water added was able to be collected. Thus, these percentages should be a factor of 6 high.

from CSU.

The results show that virtually all of the added silver is retained on the 25-cm length cores used, which is born out by determinations made on the cores themselves⁽⁵⁰⁾. Also it can be seen that the leachate concentrations are of the same order of magnitude as was determined for surface waters in the target area.

Four burner condensate samples were analyzed. Originally, the determination was approached by merely diluting portions of the sample by factors of 10^3 or 10^4 and placing portions of the resultant solutions on cups for analysis. This produced results which were very irreproducible, with values varying by factors of 1/5 to 25. This was determined to be due to particulate AgI present in the solution. The use of NaCN to completely dissolve the AgI remedied the problem. The results obtained are shown in Table XI. The values for duplicate samples compare very well and the relative standard deviations are excellent.

Table XI: Burner Condensate Results

Sample	Ag found (ppm)	RSD (%)
1-71-A	40	2.9
1-71-B	38	5.5
2-71-A	260	2.5
2-71-B	270	1.3
	Average	3.1

Sample Group II

Twenty-five snow-core samples gathered during the 1971 snow season were analyzed for Pb, Cd, Zn, and Ag. Since the concentrations of Pb, Cd, and Zn were sufficiently high to be run directly, Ag was attempted in the same manner. However, only eleven gave results which were enough greater than the detection limit to give one confidence in the values. Ag was determined in the remaining samples utilizing a dithizone- CCl_4 extraction procedure.

The Pb results are shown in Table XII. Cd, Zn, and Ag results are shown in Table XIII. Comparison data obtained during the 1972 season by the EPA at Denver, Colorado, are shown for Pb and Ag. A copy of the EPA data was provided by the Bozeman SCS office. A map of sampling sites is shown in the USDA SCS bulletin previously cited (reference 52). The drainages shown in the tables were obtained from this bulletin.

The average relative standard deviation obtained for Pb was 5.1%. Those for Cd and Ag were 9.6% and 8.6%, respectively. Relative standard deviations were calculated for both determining Ag directly and by the solvent extraction technique. They were 11.0% and 6.7%, respectively. The reason for the directly determined samples having a larger RSD is that in this case, very low absorbances, close to the detection limit, were involved.

The Weasel Divide, Desert Mountain, and Carrot Basin snow courses

Table XII: Results of Determinations for Pb (Farnes)

Drainage	Snow course	Pb (g) x 10 ⁻⁸ /ml	Pb* (g) x 10 ⁻⁸ /ml
Kootenai R.	Poorman Crk.	0.47	<2
	Weasel Divide	5.30	
	Weasel Divide	2.02	<2
Flathead R.	Big Crk.	1.40	<2
	Camp Misery	1.42	<2
	Desert Mt.	3.88	6
	N. Fork Jocko	1.45	11
Clark Fork R.	Black Pine	1.38	<2
	Copper Camp	1.01	5
	Hoodoo Basin	0.50	--
	N. Fork Elk Crk.	0.43	6
Bitterrott R.	Saddle Mt.	1.08	<2
	Twin Lakes	0.55	--
Jefferson R.	Rocker Peak	2.30	<2
Madison R.	Madison Plateau	0.27	<2
Gallatin R.	Bear Basin	0.32	<2
	Bridger Bowl	1.90	<2
	Carrot Basin	0.57	
	Carrot Basin	0.59	10
	Shower Falls	0.68	6
Teton R.	Mt. Lockhart	0.81	<2
Judith R.	Big Snowy	0.64	<2
	Spur Park	0.70	
	Spur Park	1.19	<2
Yellowstone R.	Grizzly Peak	0.55	<2

*1972 results from EPA, Denver, Colorado.

Table XIII: Results of Determinations for Zn, Cd, and Ag (Farnes)

Drainage	Snow course	Zn	Cd	Ag	Ag*
		(g) x 10 ⁻⁷ /ml	(g) x 10 ⁻¹¹ /ml	(g) x 10 ⁻¹¹ /ml	(g) x 10 ⁻¹¹ /ml
Kootenai R.	Poorman Crk.	0.40	0.44	0.90	<5000
	Weasel Divide	0.76	1.90	4.40	<5000
	Weasel Divide	1.20	1.45	21.6	<5000
Flathead R.	Big Crk.	1.23	12.9	7.00	<5000
	Camp Misery	0.82	11.9	12.0	<5000
	Desert Mt.	0.57	1.20	0.30	<5000
	N. Fork Jocko	0.99	6.60	2.17	<5000
Clark Fork R.	Black Pine	0.78	2.56	2.02	<5000
	Copper Camp	1.44	6.80	0.20	<5000
	Hoodoo Basin	0.54	2.90	1.73	---
	N. Fork Elk Crk.	0.44	0.65	3.38	<5000
	Saddle Mt.	0.45	0.55	0.87	<5000
Bitterroot R.	Twin Lakes	0.54	3.30	0.72	---
Jefferson R.	Rocker Peak	0.94	5.20	---	<5000
Madison R.	Madison Plateau	0.56	2.65	1.23	<5000
Gallatin R.	Bear Basin	0.94	3.20	3.20	<5000
	Bridger Bowl	1.86	10.5	8.00	<5000
	Carrot Basin	0.97	0.90	4.50	<5000
	Carrot Basin	0.40	1.45	---	<5000
	Shower Falls	0.42	1.75	0.50	<5000
	Mt. Lockhart	0.60	2.75	1.67	<5000
Judith R.	Big Snowy	0.45	1.05	0.95	<5000
	Spur Park	0.63	1.95	1.55	<5000
	Spur Park	0.27	1.55	---	<5000
Yellowstone R.	Grizzly Peak	0.90	1.05	---	<5000

*1972 results from EPA, Denver, Colorado.

are near snowmobiling trails. Big Creek, N. Fork Jocko, Bear Basin, Shower Falls, and Big Snowy snow courses are in remote, roadless, or wilderness areas. Bridger Bowl and Grizzly Peak snow courses are near skiing areas. The remaining snow courses were near little used roadways⁽⁵²⁾.

One can see that for Weasel Divide, Desert Mountain, and Bridger Bowl, higher Pb levels are determined, presumably caused by exhaust from internal combustion engines. Except for Big Creek and N. Fork Jocko, the locations in remote areas show low Pb concentrations. The majority of Ag concentrations fall well within the range of concentrations reported for spring snow pack in the western United States⁽⁵⁶⁾. In general, the higher results in each case are obtained from the same samples.

With respect to correlation with the 1972 EPA values, it can be seen that in most cases the levels observed were lower than the detection limit of the technique used by the EPA. Due to the facts that the reported values are very close to the detection limit and that a high result is given for a remote area such as Shower Falls, the values reported by EPA may be due to contamination rather than the sample.

Sample Group III

A total of 74 plant samples grown in sand or loam enriched with 0, 100, or 1000 ppm Ag as AgI or AgNO₃ were analyzed for Ag. Average results of 62 of

the samples are shown in Table XIV. The enrichment concentration and plant type information were obtained from Dr. T. Weaver. The procedure used produced solutions which were relatively free of suspended matter. The average relative standard deviation for the 74 samples was 5.2%.

There was some variation between values determined for similar plants grown under the same conditions. This could be due to several things. The washing procedure used before drying probably did not leave exactly the same amount of soil or dust on each sample. These particles, especially if from enriched soils, would cause some variation. Also, it was found that the moisture content of the dried plants was not the same for all samples. The ratio ash weight/plant weight covered a range of approximately 8-14%. This could cause almost a factor of 2 in the results based on the dried plant weight. Finally, the three anomalous values reported would seem to indicate the possibility of large variations caused either by the washing and drying technique or chance contamination of a sample by the muffle furnace used for ashing.

There appears to be no significant difference in the concentrations determined for plants grown in soil enriched in 0, 100, or 1000 ppm Ag, either in the AgI or AgNO₃ form. This is supported by the fact that there are no known accumulators of Ag⁽⁵⁷⁾. However, some plants might exist which could accumulate Ag in particular forms.

Table XIV: Results of Plant Samples (Weaver)

Plant	No. of samples	Soil enriched with AgI					
		Sand			Loam		
		0 ppm	100 ppm	1000 ppm	0 ppm	100 ppm	1000 ppm
Wheat ^a	8 (2 each)	1.07	----	5.91* (2.04)	0.54	----	0.59
Soybean ^a	8 (2 each)	0.88	----	0.61	0.69	----	0.88
Maize ^a	8 (2 each)	0.79	----	0.80	1.09	----	0.83
	20 (5 each)	1.79	----	0.73	4.44* (1.95)	----	2.02
Maize average		1.50	----	0.75	3.48 (1.70)	----	1.68
Soil enriched with AgNO ₃							
Maize ^a	18 (3 each)	0.75	2.55* (1.42)	1.36	0.41	0.41	0.45

*One anomalous result. Figures in parentheses are with the high value omitted.

^aResults given in ppm dried plant.

Sample Group IV

Samples taken from eight locations were analyzed. The results obtained are shown in Table XV. Also included in the table are values reported in references 58 and 59, in order to put the determined concentrations in perspective. The values given for streams are values collected from various parts of the world. The values given for finished water are from public water supplies in 100 United States cities.

Table XV: Bozeman Area Surface Water Results*

Location	Ag	Au	Cd	Cu	Hg	Mn	Pb
Big Creek	.03	---	.038	1.4	.1	.9	.38
Bridger Creek	.02	.08	.053	.52	.09	---	.18
Emmigrant Creek	.03	.04	.039	12	.09	---	1.0
Hodgeman Creek	.016	---	.040	.16	.12	.8	.65
Hyalite Creek	.015	---	.028	.22	.07	1.5	.16
Rochester Creek	.10	.25	.056	.35	.20	---	1.7
Big Springs, Idaho	.018	---	.092	1.0	---	.07	---
Bozeman (6-7-71)	.014	---	.036	260	.52	---	.42
(6-11-71)				97			
(6-11-71)				56			
Streams (Ref. 58)	0.3	0.002	---	7	.07	7	3
Finished water (Ref. 59)	.23	---	---	8.3 max. 250	---	5.0	3.7

*Concentrations given as (g) x 10⁻⁹/ml.

It can be seen that the water values at Gaines Hall correspond with those obtained from area stream waters, with the exception of Cu. The much higher Cu values would be due to the copper pipe used in the building's water distribution system. The June 7 sample was collected immediately after opening the tap. The June 11 samples were collected after letting the water run for approximately 15 minutes in the first case and approximately 30 minutes in the second.

The values obtained for the surface waters are generally less than or of the same order of magnitude as those in other parts of the world, with the exception of Au. The water supply values fall within the range of those reported for the United States. The Cd value obtained for the Idaho spring is higher than any of the other Cd values.

It should be noted that Ag, Au, Cu, and Pb were mined in the Rochester area in the early 1900's⁽⁶⁰⁾. The Emmigrant area was mined for Au, Cu, and Pb. There are no known ore deposits in the Big Creek or Bridger Creek areas. In general, the above facts are borne out by the concentration data presented.

The results and discussion presented in the application section show that furnace atomic absorption can be used for routine analysis. In many cases small concentrations can be analyzed directly without preconcentration.

The values obtained fall within ranges previously reported, and the standard deviations in most cases are excellent.

CONCLUSIONS

These investigations were undertaken to determine if:

1. The design of the Woodruff furnace could be improved to increase the life of interior graphite parts, increase reproducibility, and simplify construction.
2. An optical system involving polarizing beam splitters could be used as a background absorption correction technique for single-beam instruments in atomic absorption.
3. A dual-wavelength spectrophotometer, much simpler in construction than those commercially available, could be developed, used for background correction and the simultaneous determination of two elements by atomic absorption, and also give accurate and reproducible results.
4. The Woodruff furnace can be used routinely for the determination of trace element concentrations in the nanogram and sub-nanogram region with real samples.

The furnace designs developed have been shown to produce dramatic improvements in the life of interior graphite parts. Reproducibility has been improved and in many instances the construction has been simplified.

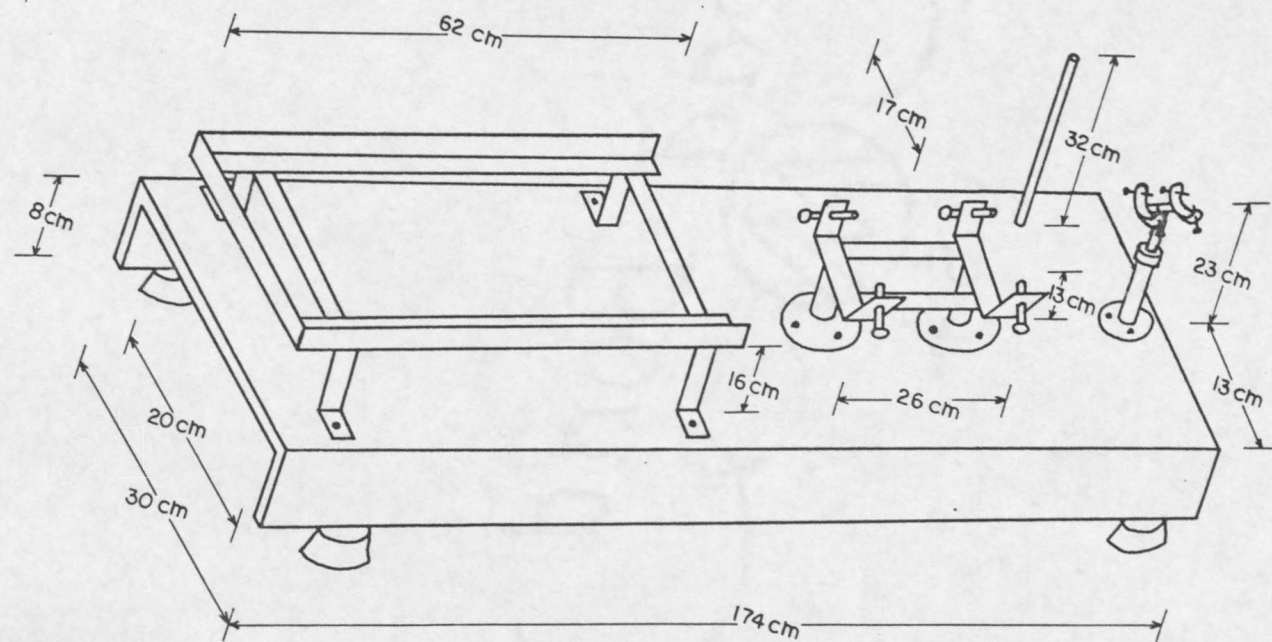
It was shown that a system involving polarized light could be used to

compensate for background absorption associated with some samples in atomic absorption. The system allows a continuous and simultaneous record of both hollow cathode and reference radiation to be obtained and subsequently compared.

A simple and versatile dual-wavelength spectrophotometer was developed. Results obtained for various types of samples prove that it can be used for the correction of background absorption and the simultaneous determination of two elements by atomic absorption. The accuracy and reproducibility of results are excellent, indicating great potential utility for the instrument.

The determination of different elements in various samples has shown that the Woodruff furnace can be used for routine analyses in the nanogram and sub-nanogram concentration region. Values obtained for different elements fall within ranges previously reported, reproducibility in most cases is excellent (in all cases much better than neutron activation techniques), and conclusions regarding problems of current interest can be made from the results.

APPENDIX



-06-

Figure 22. Optical Bench and Accessories.

NOT TO SCALE

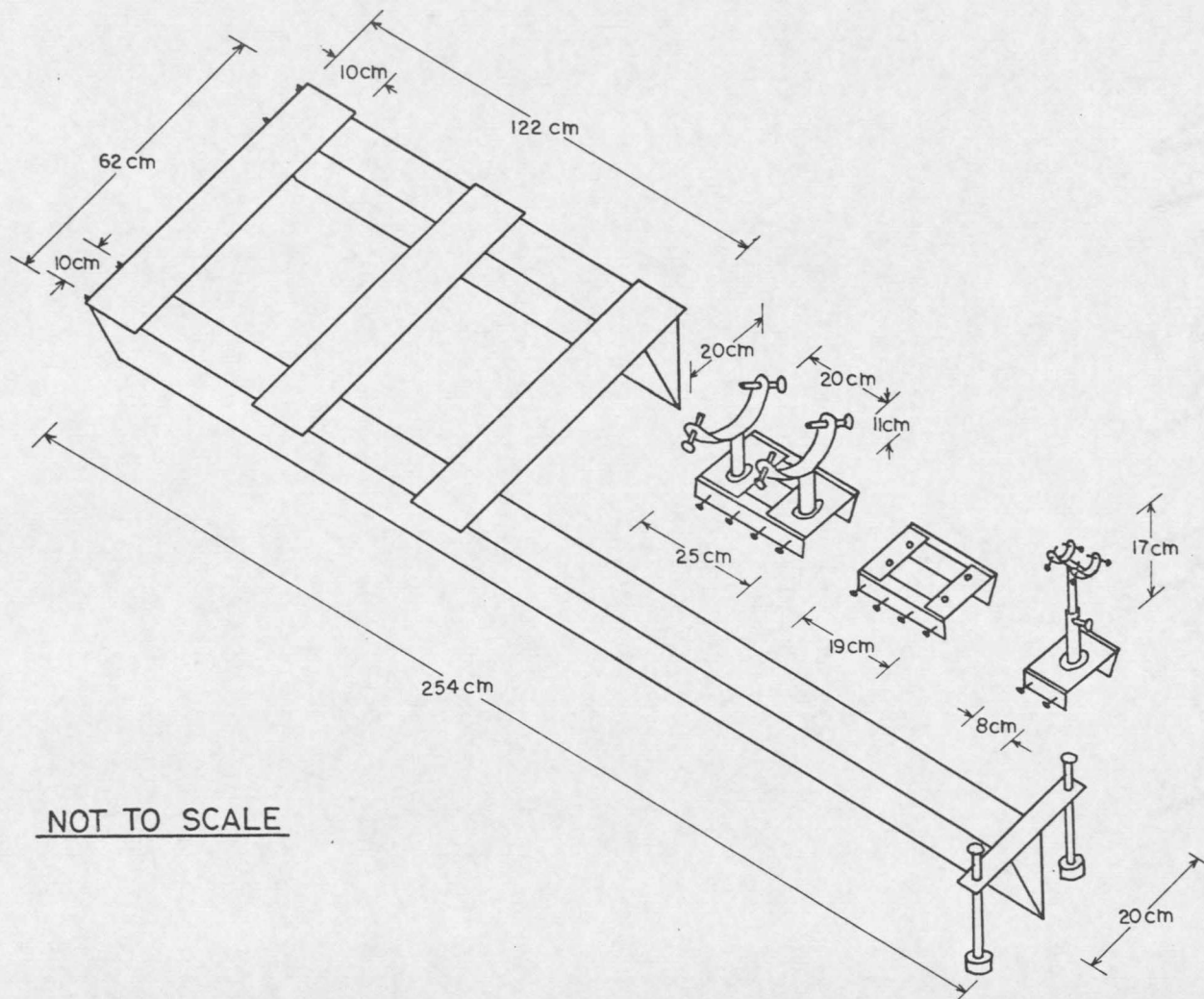
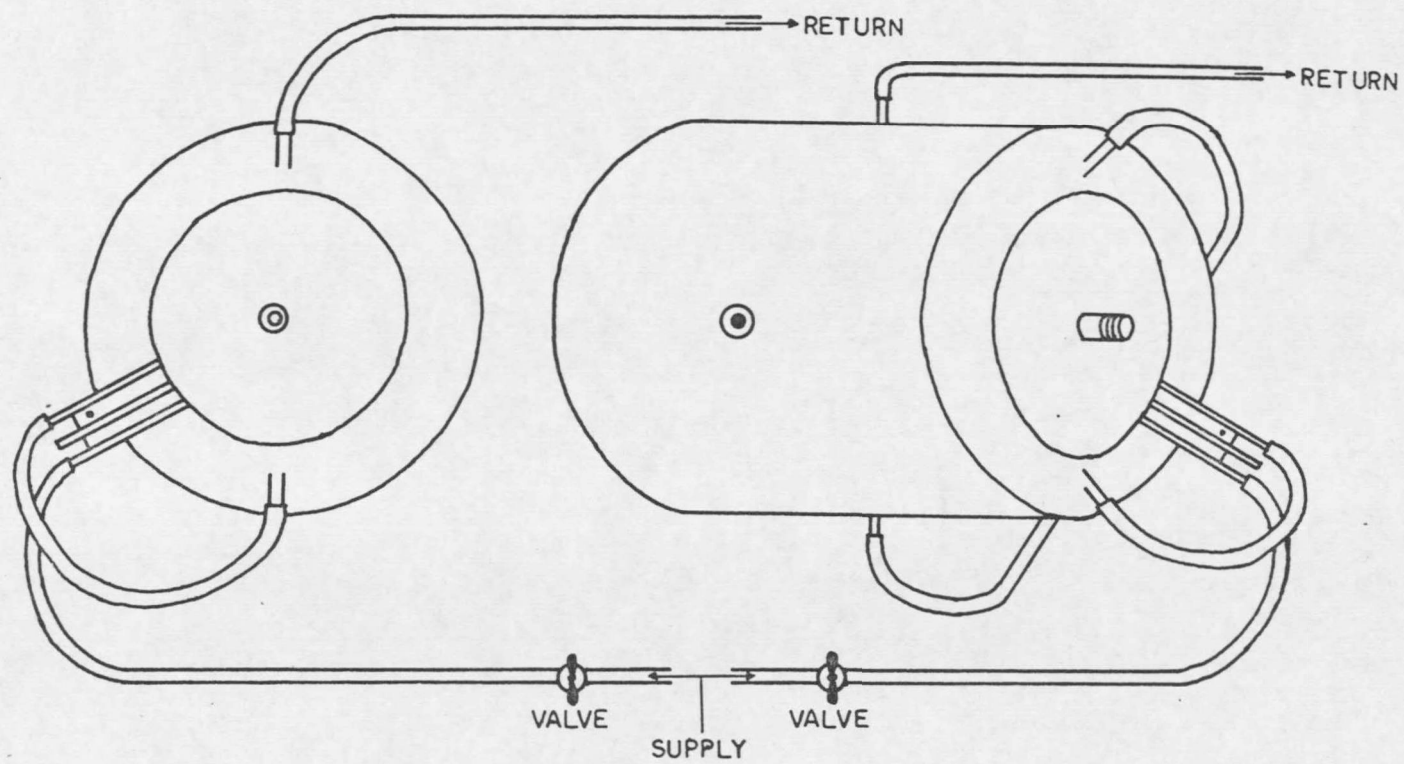


Figure 23. Optical Bench and Accessories.



-92-

Figure 24. Water Flow System.

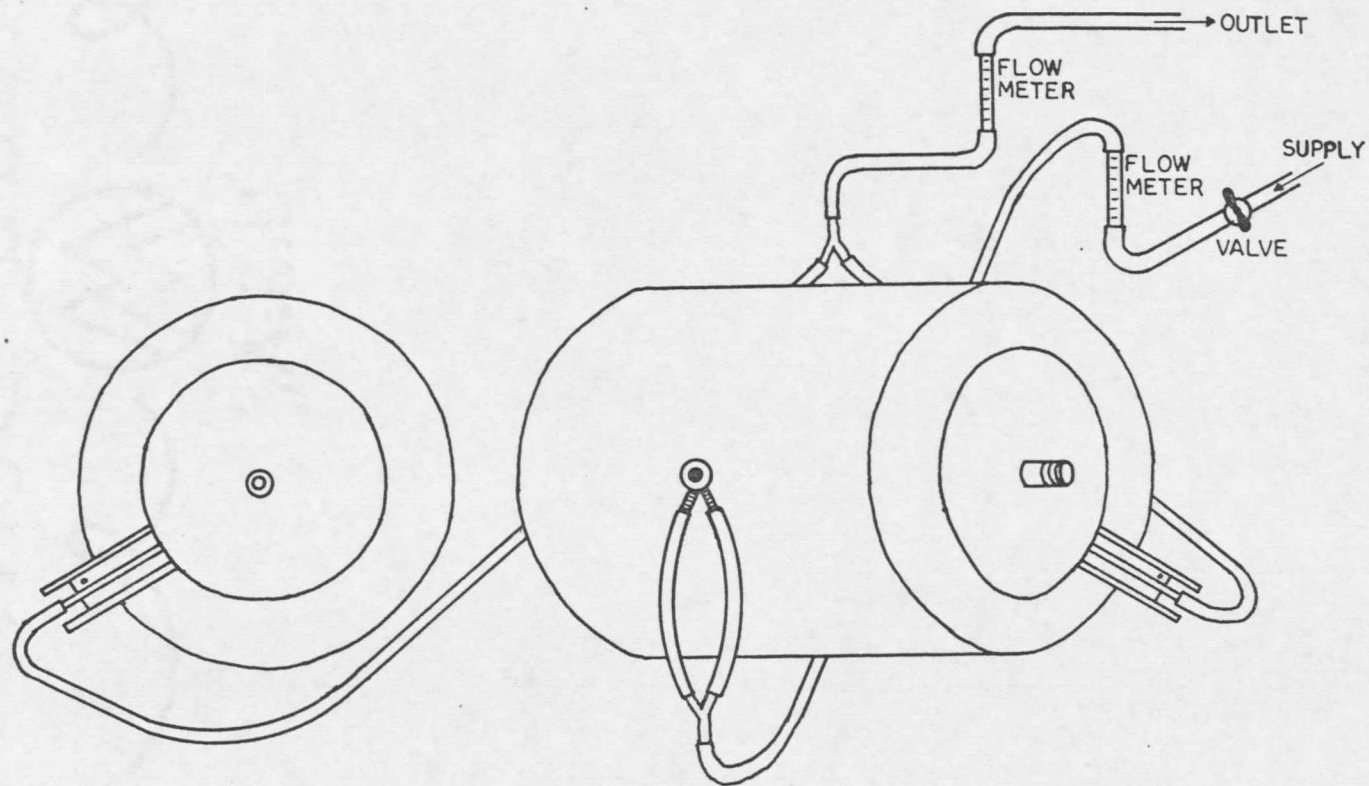


Figure 25. Gas Flow System.

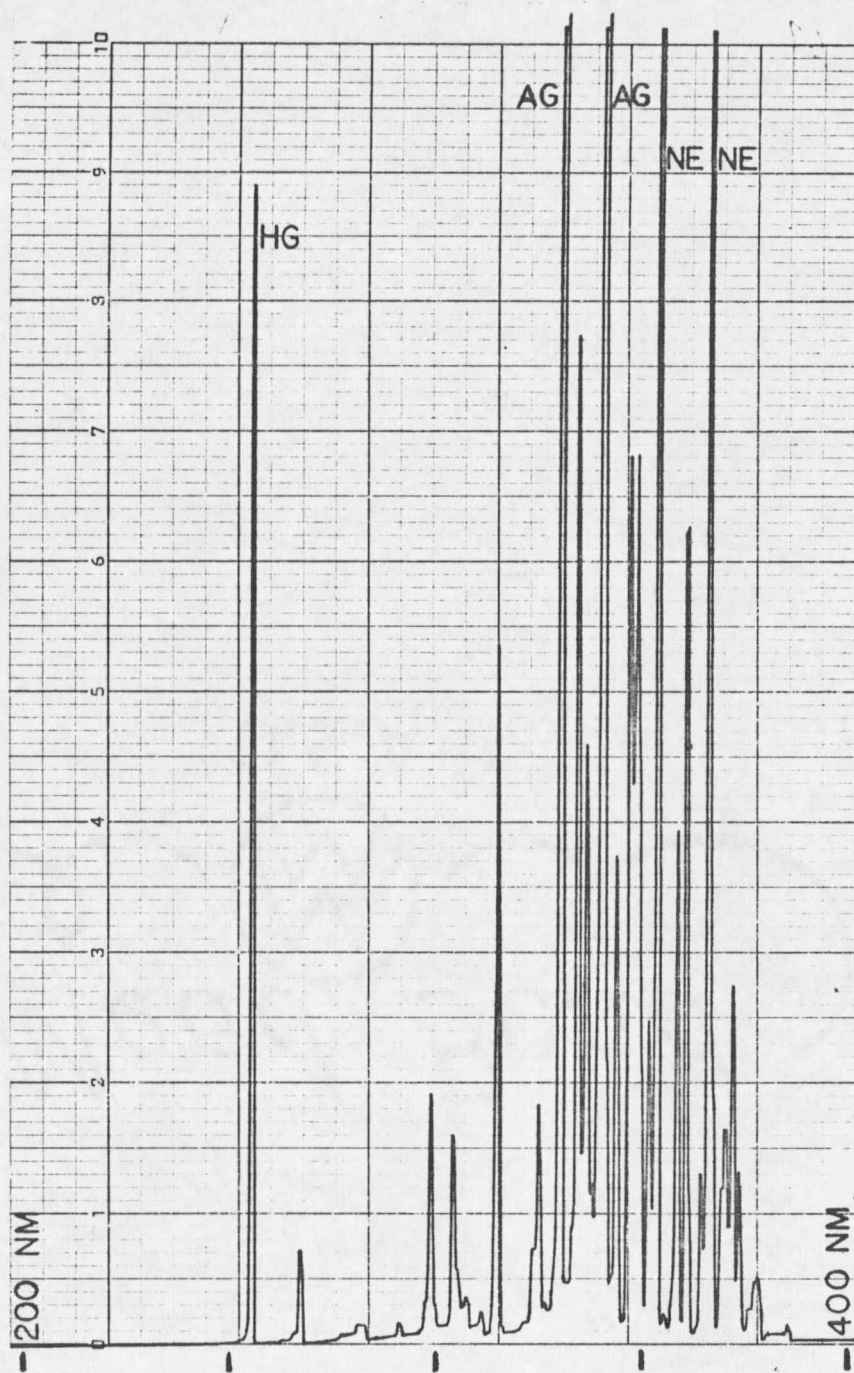


Figure 26. Hg Hollow Cathode Spectra.

Table XVI: Hg Hollow Cathode Emission Lines.

250 nm - 375 nm Wavelength (nm)	(49 lines ^a) Element
253.7	Hg*
328.1	Ag*
332.0	---
332.4	---
334.6	---
337.0	Ne
337.8	---
338.3	Ag*
339.3	---
341.8	Ne
344.8	---
345.4	---
346.7	---
347.2	Ne
352.1	Ne
356.8	---
359.3	Ne

*Resonance lines.

^a Only the stronger lines are tabulated.

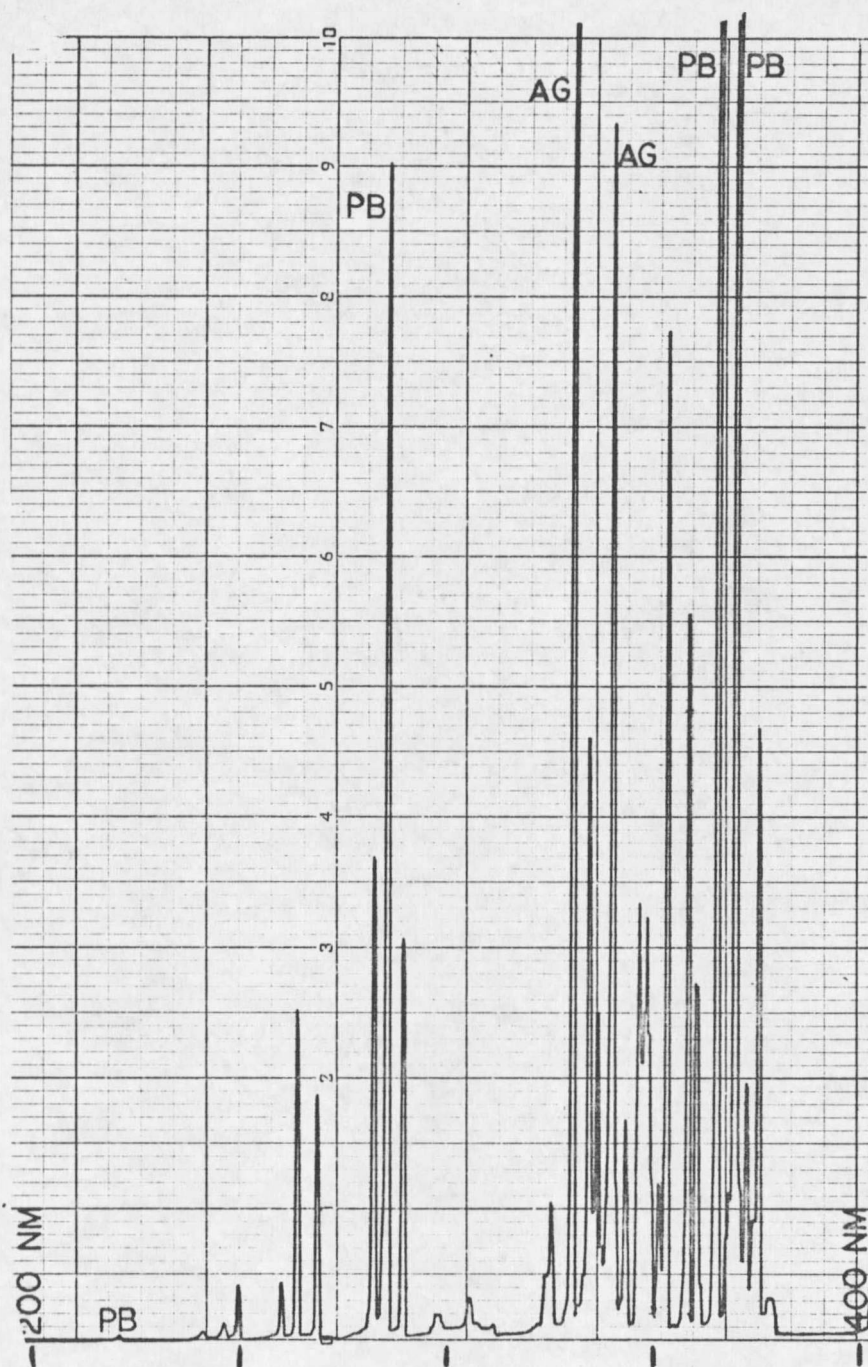


Figure 27. Pb Hollow Cathode Spectra.

Table XVII: Pb Hollow Cathode Emission Lines.

250 nm - 375 nm Wavelength (nm)	(94 lines ^a) Element
266.3	Pb
280.3	Pb
283.3	Pb*
287.3	Pb
328.1	Ag*
332.0	--
332.4	--
337.0	Ne
337.8	--
338.3	Ag*
341.8	Ne
344.8	--
345.4	--
346.7	--
347.2	Ne
352.1	Ne
356.8	--
357.3	Pb
359.3	Ne
364.0	Pb
368.3	Pb
374.1	Pb

*Resonance lines.

^a Only the stronger lines are tabulated.

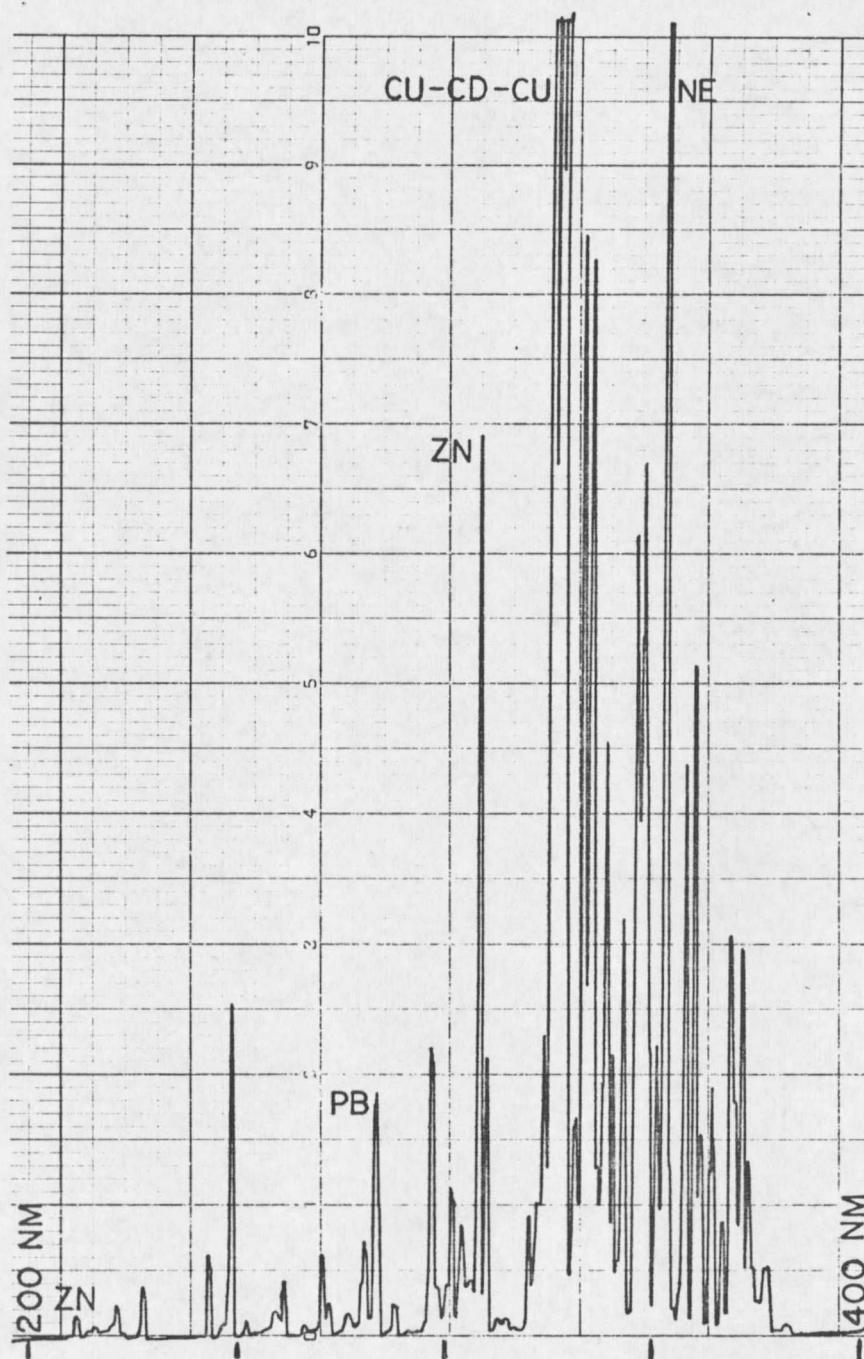


Figure 28. Cu-Zn-Pb-Cd Hollow Cathode Spectra.

Table XVIII: Cu-Zn-Pb-Cd Hollow Cathode Emission Lines.

250 nm - 375 nm Wavelength nm	(62 lines ^a) Element
283.3	Pb*
307.6	Zn*
309.4	---
324.8	Cu*
326.1	Cd*
327.4	Cu*
332.0	--
332.4	--
337.0	Ne
337.8	--
341.8	Ne
344.8	--
345.4	--
346.6	Cd
347.2	Ne
352.1	Ne
359.3	Ne
361.1	Cd
364.0	Pb
368.3	Pb

*Resonance lines.

^a Only the stronger lines are tabulated.

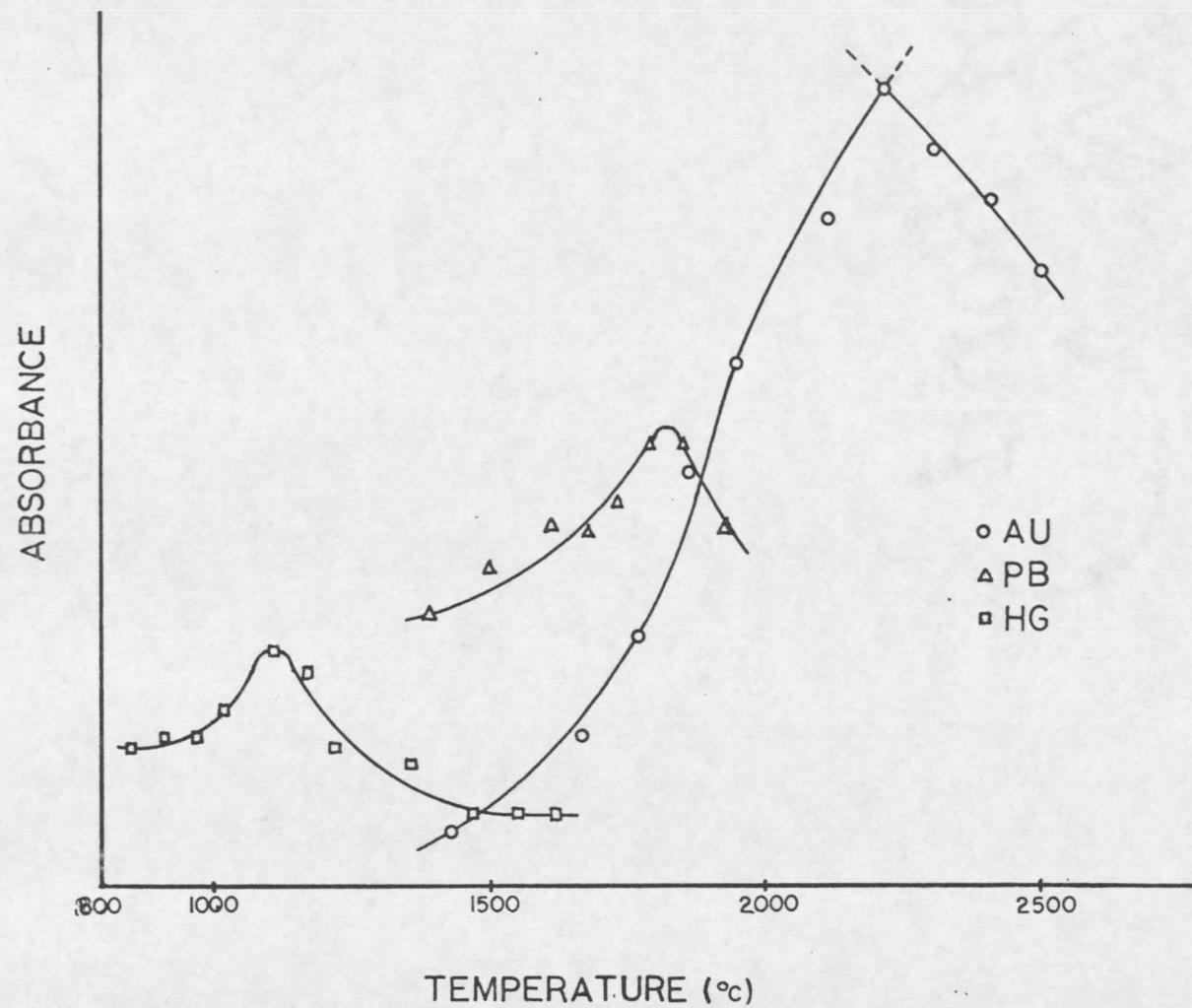


Figure 29. Temperature versus Absorbance Curves.

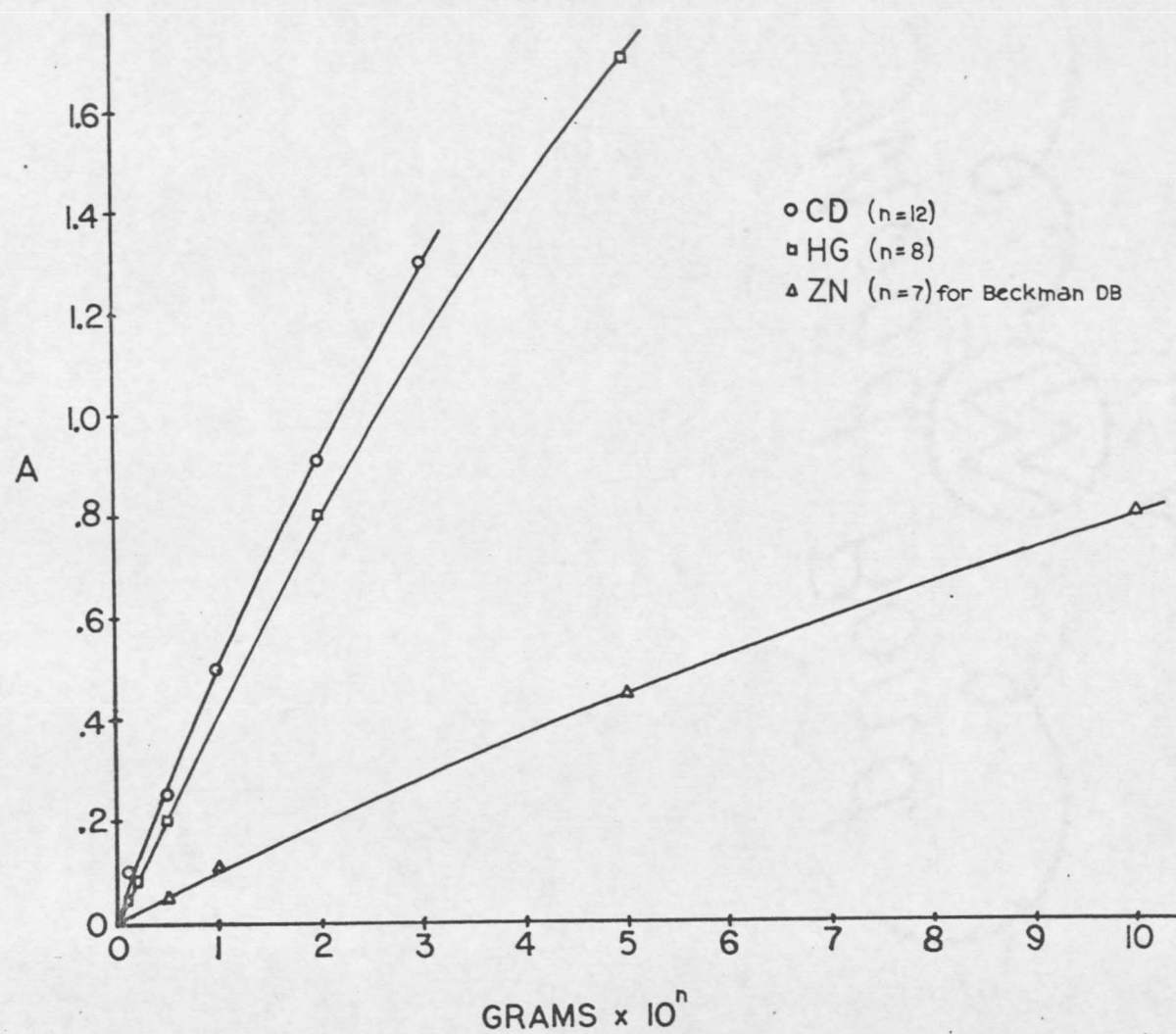


Figure 30. Representative Calibration Curves.

BIBLIOGRAPHY

1. A. Walsh, Spectrochim. Acta, 7, 108 (1955).
2. B. V. L'vov, Spectrochim. Acta, 17, 761 (1961).
3. H. Massmann, Spectrochim. Acta, 23B, 215 (1968).
4. R. Woodruff and G. Ramelow, Spectrochim. Acta, 23B, 665 (1968).
5. T. S. West and X. K. Williams, Anal. Chim. Acta, 45, 27 (1969).
6. D. Manning, "Graphite Tube Furnace for Atomic Absorption." Paper, Society for Applied Spectroscopy, New Orleans, La., Oct. 1970.
7. P. W. Lung, J. P. Matousek, and G. P. Thomas, "Carbon Rod Atomizer in Atomic Absorption and Fluorescence." Paper, Society for Applied Spectroscopy, New Orleans, La., Oct. 1970.
8. J. Y. Hwang, S. B. Smith, and A. L. Malenfant, "A Critical Evaluation of a Non-Flame Atomic Absorption Technique." Paper, Society for Applied Spectroscopy, St. Louis, Mo., Oct. 1971.
9. M. D. Amos, Amer. Lab., 4(8), 57 (1972).
10. J. B. Willis, "Methods of Biochemical Analysis" Vol. XI, edited by D. Flick, Interscience, New York (1963).
11. S. R. Koirtyohann and E. E. Pickett, Anal. Chem., 38, 1087 (1966).
12. S. R. Koirtyohann and E. E. Pickett, Anal. Chem., 37, 601 (1965); 38, 585 (1966).

13. B. V. L'vov, Spectrochim. Acta, 24B, 53 (1968).
14. R. Woodruff, B. R. Culver, and K. W. Olsen, Appl. Spectrosc., 24, 530 (1970).
15. D. P. Sandoz and D. L. Murray, Resonance Lines, 2(1), 7 (1970).
16. H. L. Kahn and D. C. Manning, Amer. Lab., 4(8), 51 (1972).
17. A. C. Menzies, Anal. Chem., 32, 898 (1960).
18. J. D. Kerber, Appl. Spectrosc., 20, 212 (1966).
19. H. Massmann, Zeitschrift für analyt. Chemie, 225, 203 (1967).
20. P. B. Zeeman and J. A. Brink, Analyst, 93, 388 (1968).
21. L. R. P. Butler and A. Strasheim, Spectrochim. Acta, 21, 1207 (1965).
22. J. V. Sullivan and A. Walsh, Appl. Opt., 7, 1271 (1968).
23. R. Mavrodineau and R. C. Hughes, Appl. Opt., 7, 1281 (1968).
24. R. Woodruff and G. Ramelow, "Graphite Tube Furnace for Atomic Absorption Spectroscopy." Paper, Society for Applied Spectroscopy, Chicago, Ill., June 1966.
25. R. Woodruff, R. W. Stone, and A. M. Held, Appl. Spectrosc., 22, 408 (1968).
26. J. P. Matousek and B. J. Stevens, Clin. Chem., 17, 363 (1971).
27. K. G. Brodie and J. P. Matousek, Anal. Chem., 43, 1557 (1971).

28. F. J. Fernandez and D. C. Manning, Atomic Absorp. Newsletter, 10, 65 (1971).
29. J. Y. Hwang, P. A. Ullucci, S. B. Smith, Jr., and A. L. Malenfant, Anal. Chem., 43, 1319 (1971).
30. P. A. Ullucci, C. J. Mokeler, and J. Y. Hwang, Amer. Lab., 4(8), 63 (1972).
31. R. Woodruff, B. R. Culver, D. Shrader, and A. B. Super, Anal. Chem., 45, 230 (1973).
32. R. Woodruff and J. F. Lech, Anal. Chem., 44, 1323 (1972).
33. F. K. West, P. W. West, and T. V. Ramakrishna, Environ. Sci. Technol., 1, 717 (1967).
34. F. K. West, P. W. West, and F. A. Iddings, Anal. Chem., 38, 1566 (1966).
35. R. V. Coyne and J. A. Collins, Anal. Chem., 44, 1093 (1972).
36. W. A. Shurcliff, "Polarized Light," Harvard University Press, Cambridge, Mass. (1962).
37. H. L. Hyde, J. Opt. Soc. Amer., 38, 663 (1948).
38. J. W. Ellis and L. Glatt, J. Opt. Soc. Amer., 40, 141 (1950).
39. L. Baxter, A. S. Makas, and W. A. Shurcliff, J. Opt. Soc. Amer., 46, 229 (1956).

40. R. Woodruff and R. Stone, Appl. Opt., 7, 1337 (1968).
41. R. J. Jaworowski and R. P. Weberling, Atomic Absorp. Newsletter, 5(6), 125 (1966).
42. Certificate of Analysis, Standard Reference Material 1571, Orchard Leaves, National Bureau of Standards.
43. J. C. Sheridan, Hoffmann-LaRoche Inc., Personal Communication.
44. G. D. Christian and F. J. Feldman, "Atomic Absorption Spectroscopy," John Wiley and Sons, Inc., New York (1970).
45. G. R. Webber, Geochim. et Cosmochim. Acta, 29, 229 (1965).
46. E. E. Angino and G. K. Billings, "Atomic Absorption Spectrometry in Geology," Elsevier Publishing Company, New York (1967).
47. D. J. Trent and W. Slavin, Atomic Absorp. Newsletter, 3, 118 (1964).
48. C. B. Belt, Jr., Econ. Geol., 59, 240 (1964).
49. I. Rubeska, Z. Sulcek, and B. Moldan, Anal. Chim. Acta, 37, 27 (1967).
50. H. L. Teller and D. A. Klein, "Disposition and Environmental Impact of Silver Iodide in the National Hail Research Experiment." Operations Report No. 1, Contract No. 198-71, Colorado State University, Fort Collins, Colo. (1972).

51. H. L. Teller and D. A. Klein, "Disposition and Environmental Impact of Silver Iodide in the National Hail Research Experiment." Operations Report No. 2, Contract No. 198-71, Colorado State University, Fort Collins, Colo. (1973).
52. P. E. Farnes and B. A. Shafer, "Analysis of Snow Samples — 1971 Snow Season." Report, USDA Soil Conservation Service, Bozeman, Mt. (1972).
53. T. Weaver and A. Super, "Some Ecological Consequences of Cloud Seeding with Silver Iodide in the Bridger Range, Montana." Paper, American Society of Civil Engineering, Spokane, Wash., Sept. 1972.
54. J. A. Warburton and L. G. Young, Anal. Chem., 44, 2043 (1972).
55. W. H. Durum and J. Haferty, Geochim. Cosmochim. Acta, 27, 1 (1963).
56. E. Bollay Associates, Final Report, Bureau of Reclamation Contract No. 14-06-D-5573 (1965).
57. C. Cooper and W. Jolly, Water Resources Research, 6, 88 (1970).
58. "Handbook of Geochemistry" Vol. I, Springer-Verlag, New York (1969).
59. "Environmental Geochemistry in Health and Disease," Memoir 123, The Geological Society of America (1971).
60. C. Moell, Chem 470 Report (1971).

61. R. Woodriff and D. Shrader, Anal. Chem., 43, 1918 (1971).
62. D. Shrader and R. Woodriff, "The Analysis of Silver in Precipitation and Aquatic Samples by Furnace Atomic Absorption." Paper, Intermountain Section, Society for Applied Spectroscopy, Bozeman, Mt., May, 1972.
63. R. Woodriff and D. Shrader, Appl. Spectrosc., 27, 181 (1973).
64. D. Shrader, "Instruction Manual for the Woodriff Furnace — Series 8020," 34 pages (1971).



3 1762 10011209 1

D378

Sh83

cop.2

Shrader, Douglas E
Improvement and
application of non-
flame atomic
absorption

NAME AND ADDRESS

Glenn Hansen
Rt 2 Box 52

D378
Sh83
Cop.2