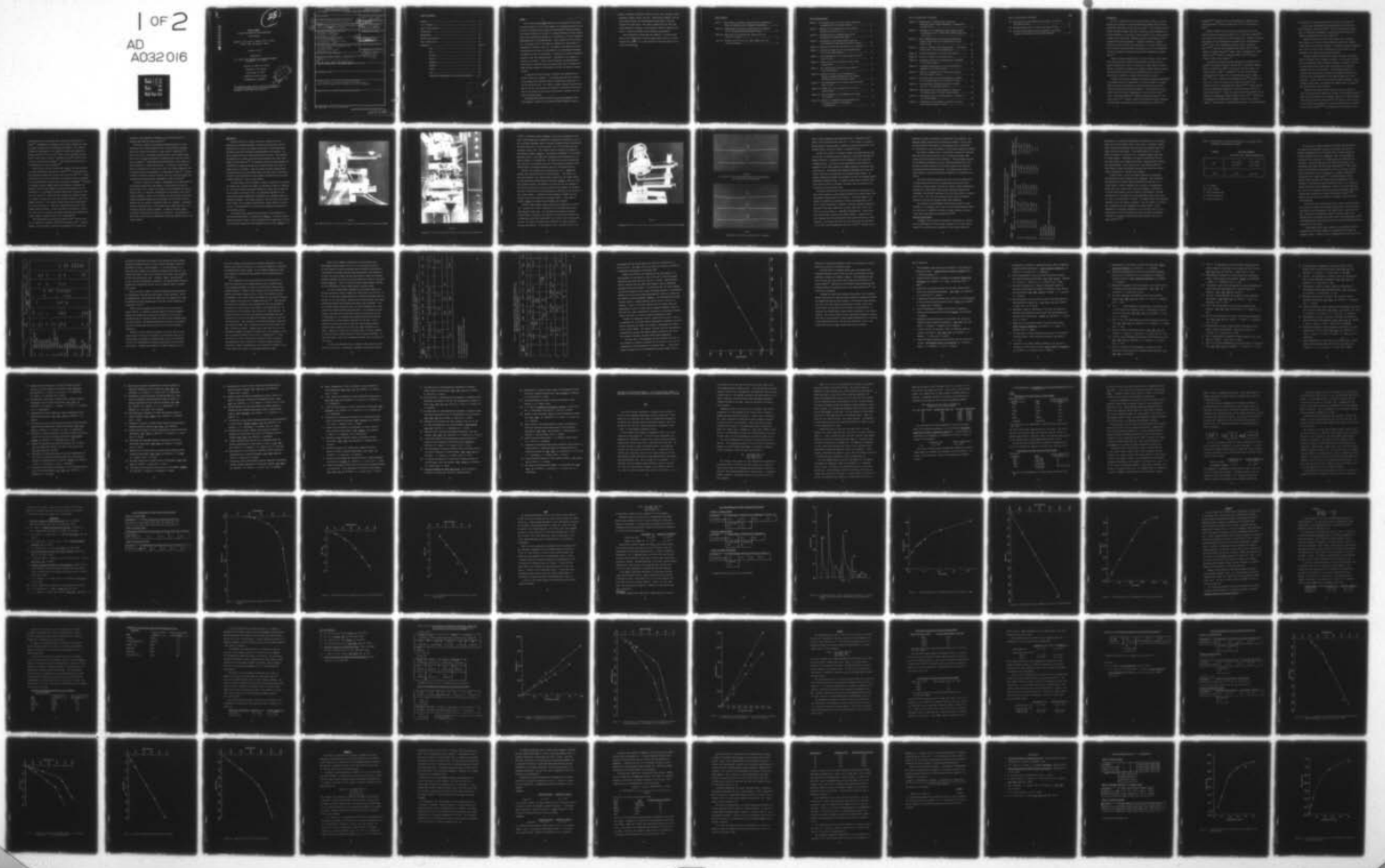
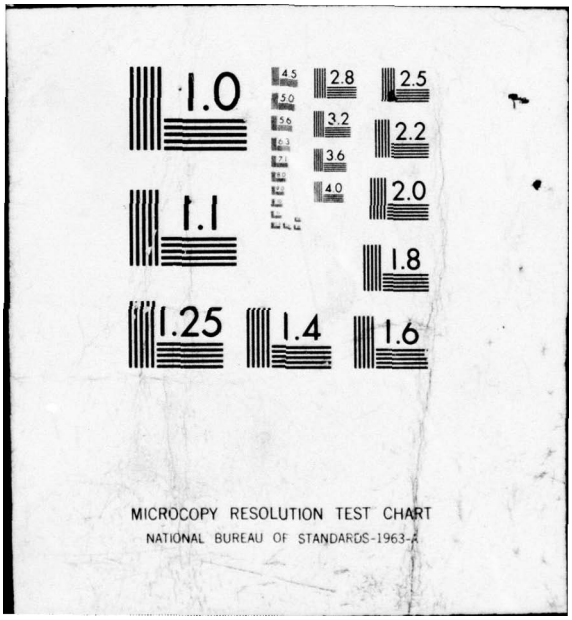
AD-A032 016 NEW ORLEANS UNIV LA DEPT OF CHEMISTRY F/G 7/4
ANALYSIS BY FLAMELESS ATOMIC ABSORPTION.(U)
OCT 76 C L YUAN, J V CHAUVIN, J F MOLINA DAMD17-75-C-5048
UNCLASSIFIED 357-30-5105 NL

1 OF 2
AD
A032016




1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD A032016

25
B.S.

REPORT NUMBER 1

Analysis by Flameless Atomic Absorption

Annual Report

Charles L. Yuan, Judy V. Chauvin, John F. Molina,
Mike H. West, and Donald G. Davis

October 20, 1976

Supported by

U. S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Washington, D. C. 20315

Contract No. DAMD 17-75-C-5048

University of New Orleans

New Orleans, La. 70122

Approved for Public Release

DISTRIBUTION - UNLIMITED



The findings in this report are not to be construed as an official Department of the Army position unless so designed by other authorized documents

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO	3. RECIPIENT'S CATALOG NUMBER
1		

4. TITLE (and Subtitle)

(6) Analysis by Flameless Atomic Absorption.

5. TYPE OF REPORT & PERIOD COVERED

Annual - June 1, 1975 -- May 31, 1976

(14) **6. PERFORMING ORG. REPORT NUMBER**

357-30-5105

7. AUTHOR(s)

(10) Charles L. Yuan, Judy V. Chauvin, John F. Molina, Mike H. West and Donald G. Davis

8. CONTRACT OR GRANT NUMBER(s)

(15) DAMD 17-75-C-5048

9. PERFORMING ORGANIZATION NAME AND ADDRESS

Department of Chemistry
University of New Orleans
New Orleans, LA 70122

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS

(11) M. D. Woodin, President
Louisiana State University System
Baton Rouge, LA 70803

12. REPORT DATE

(12) October 20, 1976

13. NUMBER OF PAGES

121 p.

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

Mr. George D'Aquin, Vice Chancellor for Business Affairs
University of New Orleans
New Orleans, LA 70122

15. SECURITY CLASS. (of this report)

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release - Distribution Unlimited

(9) Annual rept. no. 1,
1 Jun 75 - 31 May 76,

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Atomic Absorption, Flameless Atomization, Drinking Waters, Lead, Cadmium, Copper, Zinc, Chromium, Iron, Silver, Manganese

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

409091 LB

Table of Contents

Summary..... 2

List of Tables..... 4

List of Illustrations..... 5

Introduction..... 8

Experimental..... 13

Results and Discussion..... 20

List of References..... 34

Appendices..... 45-117

Zinc..... 45

Iron..... 58

Chromium..... 65

Silver..... 75

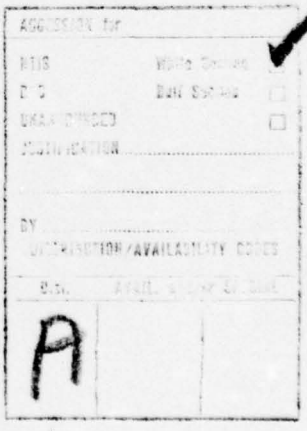
Manganese..... 84

Cadmium..... 96

Copper..... 99

Lead..... 109

Temperature Measurements of the Wire Loop Atomizer..... 118



Summary

We have been developing techniques for the analysis of trace metals in natural waters as well as other samples of biological and environmental interest by flameless atomic absorption spectrometry. Aqueous standard and unknown solutions are applied to a tungsten-rhenium wire loop atomizer, which can be electrically heated, in 5 μℓ aliquots by a Varian "Autopette" dispensing pipet (the aliquot method). After evaporation of the solvent at a low voltage setting, the sample is atomized upon application of a predetermined voltage to the loop. In addition, the analyte can be preconcentrated on the wire loop (presumably by an ion-exchange mechanism) by soaking the loop in the solution of interest for carefully controlled periods of time (the soaking method). Atomization of the analyte is carried out as before. Where it may be employed, the soaking method offers greater sensitivity than the aliquot method and the former technique has been applied to the analysis of silver and copper in aqueous solution.

A template has been developed to expedite the reproducible production of wire loop atomizers. The atomizer head can now be mounted on the commercially available Varian or Perkin-Elmer burner base replacing the burner head. As a result, a greatly improved optical alignment of the wire loop atomizer with respect to the hollow cathode lamp beam can be attained by employing the horizontal, vertical, and rotational adjustment dials.

Employing pure aqueous standards, we have utilized peak height absorbance as a measure of the transient atomic absorption signal in

order to establish calibration curves for zinc, iron, chromium, silver, manganese, cadmium, copper, and lead. Natural water samples, provided by the United States Army Environmental Hygiene Agency, have been analyzed for these metals. The results obtained from the wire loop aliquot method are compared to those found by "referee" analysis techniques -- flame and nonflame atomic absorption spectrometry.

Any interferences arising from the presence of transition metal salts or the sodium salts of various common anions, each at a concentration of ca. 10^{-3} M, in 1.0 ppm solutions of the above metals are reported and evaluated.

List of Tables

Table I. Sensitivities and Absolute Sensitivities for Analysis by Flame and Nonflame Atomic Absorption Spectrometry..... 21

Table II. Sensitivities and Absolute Sensitivities for Analysis by the Spontaneous Preconcentration Method..... 23

Table III. Evaluation of Interferents for Analysis with the Wire Loop Atomizer..... 25

Table IV. Analysis of the U.S.A.E.H.A. Water Samples with the Wire Loop Atomizer..... 29

List of Illustrations

Figure 1. The Atomizer Head for the Wire Loop Atomizer and Configuration for the Aliquot Method..... 14

Figure 2. Alignment of the Atomizer Head on the Optical Railing of the Varian AA-5..... 15

Figure 3. Configuration of the Atomizer Head for the Spontaneous Preconcentration Method..... 17

Figure 4. Loop Design for the Aliquot Method (top) and the Spontaneous Preconcentration Method (bottom)..... 18

Figure 5. Comparison of Wire Loop Construction by a Template..... 18

Figure 6. Standard Additions Plot for the Determination of Iron by the Aliquot Method..... 32

Figure 7. Zinc Determination by the Aliquot Method Over The Range 0-6 ppm..... 55

Figure 8. Working Curve for the Analysis of Zinc by the Aliquot Method..... 56

Figure 9. Zinc Determination Using the Varian Model 63 Carbon Rod Atomizer..... 57

Figure 10. Absorbance Profile at 248.3nm Produced by Heating a Tungsten-Rhenium Wire Loop Atomizer (Atomization Variac Settings Are Given)..... 61

Figure 11. Iron Determination by the Aliquot Method Over The Range 0-5 ppm..... 62

Figure 12. Working Curve for the Analysis of Iron by the Aliquot Method..... 63

Figure 13. The Determination of Iron Employing the Carbon Tube Atomizer..... 64

Figure 14. Analysis of Chromium(VI) and Chromium(III) by the Aliquot Method. Δ Chromium(VI), O Chromium(III)..... 72

List of Illustrations (continued)

Figure 15. Determination of Chromium Using the Aliquot Method and Linear Voltage Programming. Δ Chromium(VI), O Chromium(III)..... 73

Figure 16. Enhancement of the Chromium Atomic Absorption Signal by Hydrogen Gas with a Carbon Tube Atomizer. □ H_z gas, O no H_z gas..... 74

Figure 17. Silver Determination by the Spontaneous Preconcentration Method (100 second soaking time) Over the Range 0-1 ppm..... 80

Figure 18. Analysis of Silver by the Soaking Method. O 200 second soaking time, □100 second soaking time..... 81

Figure 19. Silver Determination by the Carbon Tube Method..... 82

Figure 20. Analysis of Silver by the Aliquot Method..... 83

Figure 21. Calibration Curve for the Determination of Manganese by the Aliquot Method..... 93

Figure 22. An Expanded Working Curve for the Determination of Manganese by the Aliquot Method..... 94

Figure 23. Analysis of Manganese by the Carbon Tube Atomizer Over the Range 0-0.5 ppm. 95

Figure 24. Calibration Curve for the Determination of Cadmium by the Aliquot Method Over the Range 0-0.2 ppm..... 98

Figure 25. The Relationship between Absorbance and Soaking Time for a 0.1 ppm Copper Solution..... 106

Figure 26. Working Curve for the Determination of Copper by the Soaking Method (20 second soaking times)..... 107

Figure 27. Calibration Curve for the Determination of Copper by the Aliquot Method..... 108

Figure 28. Calibration for the Analysis of Lead by the Aliquot Method Over the Range 0-15 ppm..... 115

List of Illustrations (continued)

29. Working Curve for Lead Analysis in the Range 0-70 ppb with the Aliquot Method..... 116

30. Expanded Working Curve for Lead in the Range 0-18 ppb..... 117

31. The Relationship Between Atomizer Temperature and Variac Setting as Determined with an Optical Pyrometer..... 119

Introduction

The use of graphite or various metals and their alloys as nonflame atomizers for analysis by atomic absorption spectrometry (AAS) has been extensively investigated in the past two decades.[1] The nonflame atomizers require far smaller sample sizes than conventional flame techniques and are more efficient at converting a large proportion of the analyte species to atoms in the vapor phase. However, precision and accuracy are often problems with nonflame atomizers.[2] Nonatomic absorption, caused by molecular absorption and/or light scattering, is a classic obstacle common to nonflame atomic absorption spectrometry and must be surmounted by the use of background correction systems and/or minimization of matrix effects.[3]

Numerous graphite atomizers such as corbon filaments, rods, braids, tubes and furnaces have enjoyed varying degrees of success in trace analysis applications by AAS. At present, the carbon tube and graphite furnace are employed in commercially available nonflame atomizer systems, the Varian Techtron CRA-90 and the Perkin-Elmer HGA-74, and 2100 respectively (in addition to several earlier versions of each).

Lundgren and co-workers employed a photodiode (radiation programming) to accurately control the temperature of a heated graphite tube within $\pm 10^{o}C$ and applied the system to the analysis of metals in biological tissue[4] and cadmium in blood[5] and seawater.[6] Other applications of the carbon tube have been the determination of trace metals in water,[7-9] zinc in sea-bottom sediments,[10] cadmium in biological matrices,[11] and lead in blood.[12,13] Various versions of the graphite furnace, developed by Perkin-Elmer Corporation, have found application to saline[14] and

freshwater[15-17] analyses and to the determination of cadmium in biological materials,[18] copper in edible oils,[19] and to the analysis of zinc.[20]

Graphite filaments were extensively characterized for AAS and atomic fluorescence spectrometry (AFS) by T. S. West and co-workers[21-24] and applied to the analysis of numerous elements in a variety of matrices. Among these were the determination of cadmium, gold, and manganese by AFS,[25-27] gold, zinc, molybdenum, manganese, nickel, and iron by AAS,[25,28-31] sodium by atomic emission spectrometry (AES),[32] several elements in organic matrices,[33] copper, silver, and manganese in lubrication oils,[34,35] nickel in crude and residual oils,[36] and lead in "instant" coffee and tea powders.[37]

The carbon rod atomizer has been applied to the analysis of biological[38] and clinical samples by AAS and AFS[39] including the determination of copper[40] and iron[41] in blood serum, and gold, cobalt, and lithium in blood plasma.[42] Winefordner's as well as Chakrabarti's groups employed the carbon rod for analyzing wear metals in engine oils,[43,44] lead in petroleum and petroleum products,[45,46] vanadium in crude oil,[47] silver and copper in jet engine oil by AFS,[48] and a variety of metals in lubricating and crude oils.[49,50] Silver and copper may be determined sequentially by taking advantage of their different volatilities.[51] Silver and gold have also been analyzed in geological and metallurgical samples using the carbon rod.[52] Fairless and Bard employed electrodeposition on graphite rods for the analysis of copper.[53] The importance of rapid detection systems for transient signals

was pointed out by Maessen and Posma for the carbon rod atomizer.[54]

Crouch et al. investigated the characteristics of the graphite braid atomizer in both AAS and AFS.[55] They also examined the possible modes of temperature programming for graphite braids concluding that radiation programming was the most efficient.[56]

Graphite atomizers on the other hand require large, elaborate power supply units in order to electrothermally produce the requisite atomic vapors in or above the atomizer. The electrode holders (terminals) must be water-cooled in order to dissipate the large amounts of heat generated by the ashing and atomization processes.

Nonflame atomizers constructed from metals and their alloys offer several advantages over the graphite atomizers. Since metals and alloys have an intrinsically lower resistivity compared to graphite, the need for sophisticated power supply units is obviated and the electrode terminals need not be water-cooled. Electrothermal atomizers constructed from elements having suitable electrochemical properties may be utilized for preconcentration of the analyte species by electrodeposition. Platinum wire coils and loops, tungsten filaments, tantalum filaments, silver wires, and tantalum and tungsten boats are among the most widely employed metal atomizers.

Tantalum strip atomizers were adapted for use on a commercial basis by Instrumentation Laboratories in their IL 355 Flameless Sampler.[57] Agget and Sprott compared the atomization properties of various analytes using tantalum strips and carbon rods.[58] The effect of salts and acids on the analyte signal generated by vaporizing samples from the tantalum strip has been studied.[59,60] Tantalum tends to become brittle after

repeated heating and its surface reacts with nickel and cobalt compounds.[61] Molybdenum strip atomizers can be used to analyze for cobalt and nickel although nitric acid damages the atomizers. The tantalum filament has been applied to the analysis of barium and antimony in gunshot residues,[62] lead in blood,[63] lead, silver, and indium in rainwater,[64] trace metals in water,[65] chromium in steel,[66] and for the introduction of analyte into plasmas.[67] The tantalum boat was used for the determination of zinc in seawater.[68]

Bratzel et al. used both platinum and tungsten wire loop atomizers for atomic fluorescence spectrometric studies.[69,70] Crouch's group has also evaluated platinum wire loops for use in AAS and AFS.[56,71] A platinum-rhodium alloy has been developed by the National Bureau of Standards for the determination of lead in paint using flame techniques.[72] Williams and Piepmeier adapted tungsten light bulb filaments to flameless AAS analyses,[73] and Reid and Peipmeier constructed an integrator for the measurement of the transient absorbance signals from a horizontal tungsten coil atomizer.[74] Cantle and West evaluated the tungsten filament and compared its properties as an electrothermal atomizer to the carbon filament atomizer.[75] The tungsten filament gives better sensitivities and is less susceptible to vapor phase interferences than the corresponding graphite filament. Cresser and Mullins calculated the temperature time curves for tungsten and graphite filaments and concluded that current filament designs are open to much improvement.[76]

Electrodeposition on platinum and tungsten wires[77] has been used for the analysis of cadmium in urine[78] and seawater by AAS.[74] Mercury, cadmium, lead, and nickel, deposited electrochemically on silver wire

electrodes, were analyzed by exploding the wire electrode and subsequently measuring the atomic emission.[80]

Davis and co-workers have developed tungsten-rhenium wire loops, constructed from a tungsten-rhenium alloy, as electrothermal atomizers and the wire loops have exhibited a great amount of versatility.[81] A loop can be used for spontaneous preconcentration of the analyte (probably by an ion-exchange mechanism) by soaking the wire loop in the solution of interest.[82] Electrochemical preconcentration of the analyte can also be employed to reduce matrix effects. In addition, several microliters of solution can be placed on the loop, the solvent evaporated, and the analyte atomized upon passage of a predetermined current.[83] A number of metals, dissolved in aqueous solution, have been directly analyzed and zirconium and hafnium have been determined by indirect methods.[84]

We wish to report here a number of improvements in the application of the tungsten-rhenium wire loop atomizer to the analysis of metals in natural waters and in samples of biological and environmental interest by flameless AAS. An exhaustive investigation of the elements lead, copper, cadmium, manganese, silver, zinc, chromium, and iron has been carried out using the tungsten-rhenium wire loop atomizer and the effects of interferences upon the analyte's absorbance signal are evaluated. Furthermore, important alterations made in the atomizer head design allow for a significantly improved optical alignment. An analysis of water samples provided by the United States Army is also reported. The appendices to this report contain further experimental details pertaining to each of the metals studied.

Experimental

A Varian Techtron AA-5 single beam atomic absorption spectrophotometer was utilized throughout the research reported here with the exception of the copper and cadmium studies where a Perkin-Elmer Model 306 double beam atomic absorption spectrophotometer was employed. All hollow cathode lamps were purchased from Varian Techtron. Lamp currents, monochromator slit widths, and analytical wavelengths were those recommended by Varian Techtron.[85] The transient atomic absorption signals were recorded with a single pen Varian A-25 recorder having a full scale response time of 0.5 seconds. Since the atomic absorption signals have a very sharp profile, the peak height rather than peak area was employed as a measure of the absorbance for each solution concentration and in establishing calibration curves for each element.

The power supply, used to provide a current sufficient to 1) evaporate the solvent and 2) atomize the sample, is described in detail in reference 81. The manual Sargent polarograph referred to therein was not employed in any aspect of the present work. The appropriate settings for the drying and atomization Variacs are discussed in the appendices under the respective elements. The voltage, applied to the wire loop by the atomization Variac, may be ramped by substituting a Variac driven at 4 rpm by a motor. The advantages of the voltage ramp technique are discussed in the following section.

The atomizer head, designed and constructed in the University of New Orleans machine shop, is illustrated in Figure 1. The brass atomizer head was machined so that it could be mounted on the commercially available Varian Techtron burner base thus replacing the burner head, Figure 2. As

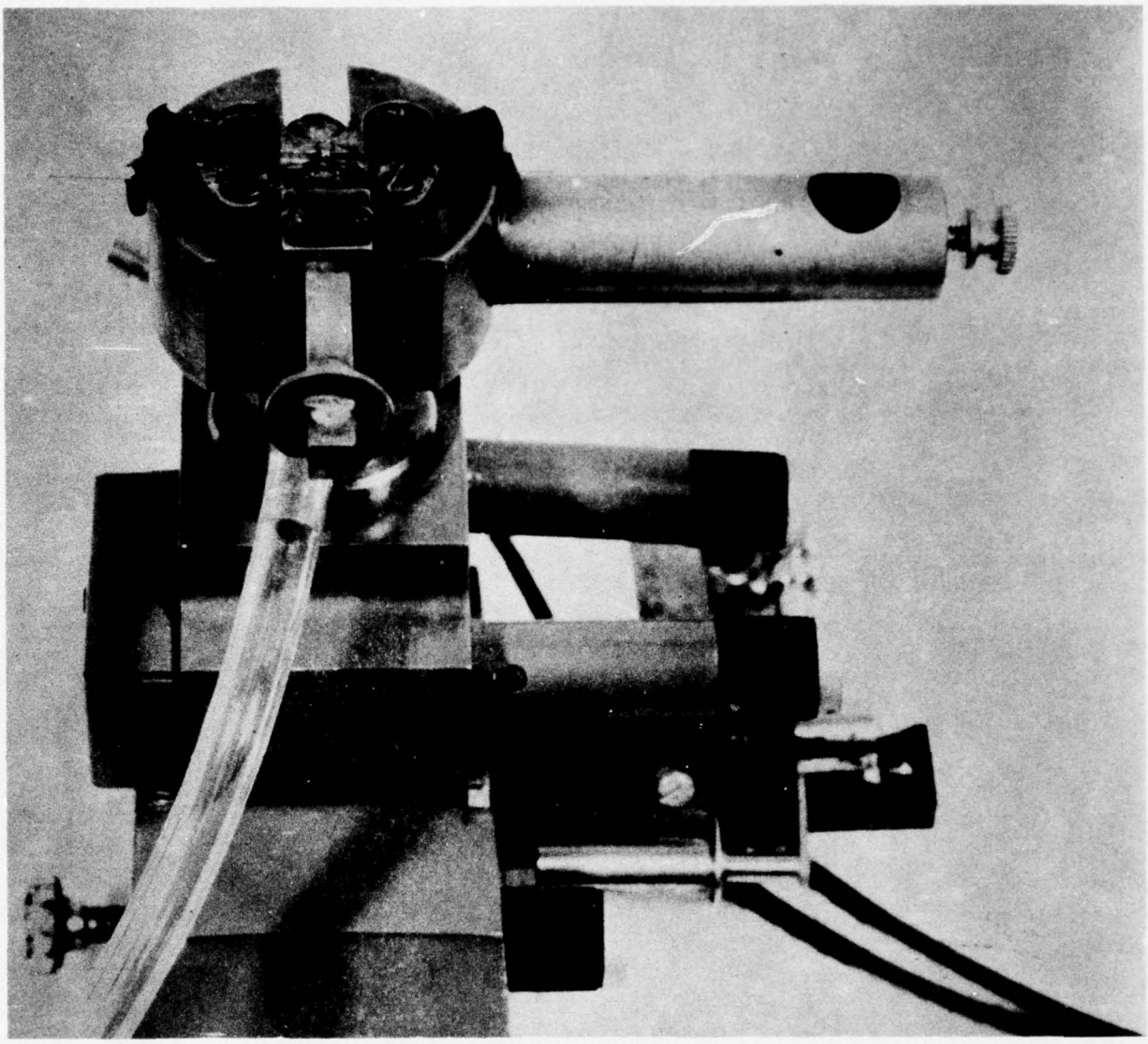


Figure 1

The Atomizer Head For The Wire Loop Atomizer And Configuration For The Aliquot Method

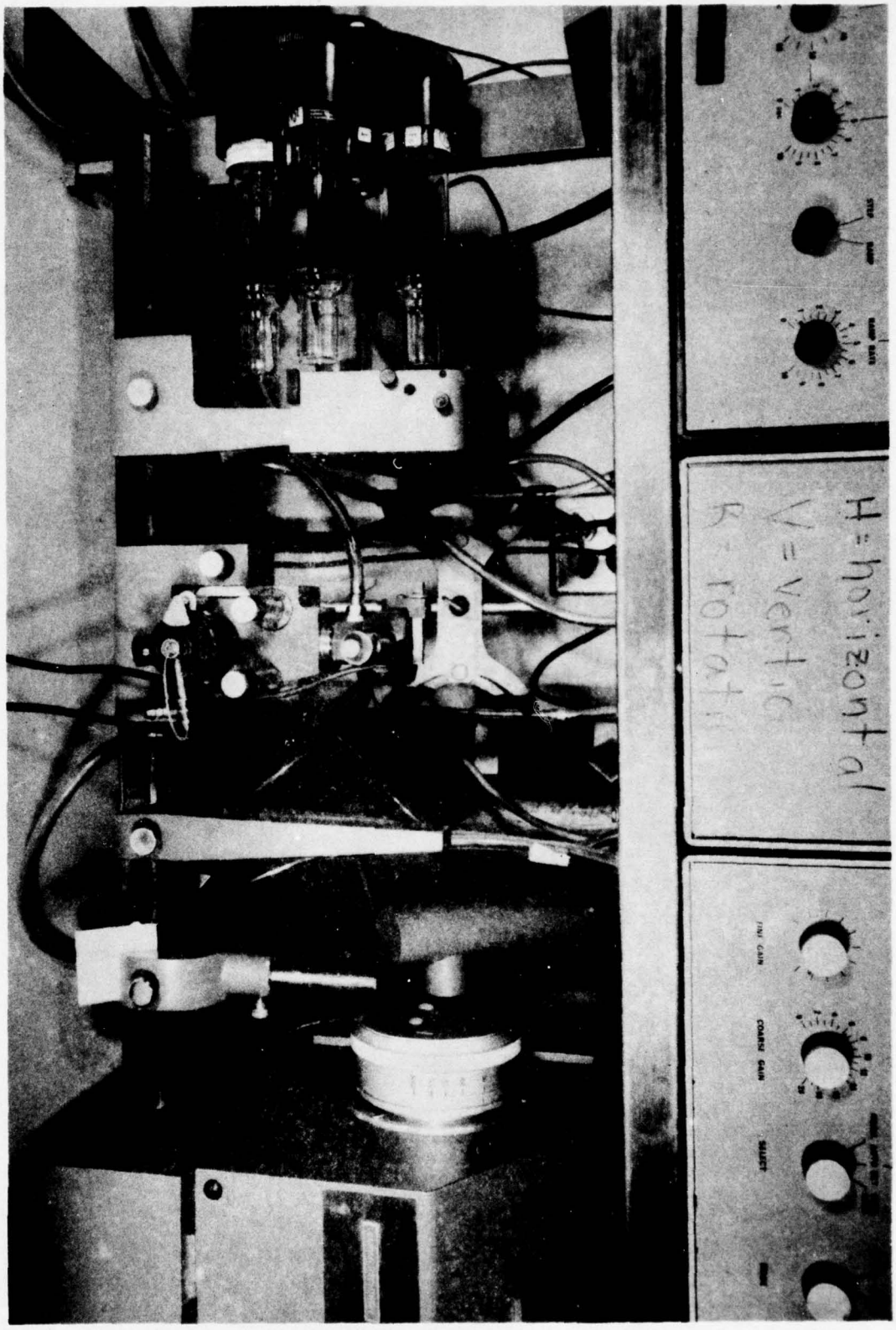


Figure 2

Alignment Of The Atomizer Head On The Optical Railing Of The Varian AA-5

a result, an improved optical alignment of the wire loop atomizer in the hollow cathode lamp beam is possible by adjusting the horizontal, vertical, and rotational adjustment dials to achieve a maximum percent transmittance. The burner base was placed on the optical rail at 19.9 cm from the monochromator entrance slit. The atomizer head was inverted for adaption to the soaking technique, Figure 3. The previous arrangement of the atomizer head with respect to the light path, employing the fluorescence rail, is shown in Figure 1 of reference 86. The leads from the power supply unit were attached to the atomizer head with screws mounted in phenolic blocks which replaced the asbestos formerly used as an insulating material.

The wire loop atomizer was constructed from a 97%. tungsten-3% rhenium alloy (General Electric 3D 218-CS process). The shape of the wire loop employed in the aliquot method differs from the design adapted for the spontaneous preconcentration technique, Figure 4. When the loops were produced manually, the height of the wire loop and the diameter of the circular portion of the loop were particularly difficult to reproduce. This led to differences in loop performance as indicated by the sensitivity for a given element. A template has been designed to improve the uniformity of loop construction for the aliquot method. Three loops are shown in Figure 5 to indicate the uniformity thus achieved.

For the aliquot method, aqueous samples were applied to the loop in 5-µℓ aliquots with a Varian "Autopette" 5-µℓ dispensing pipet fitted with disposable pipet tips. For the soaking (spontaneous preconcentration) method, aliquots of the solution of interest were pipetted into a minibeaker and the wire loop soaked in the solution for a known period of time. The time was measured with a Standard S-10 timer, Standard Electric Time Company. It was important that a constant portion of the

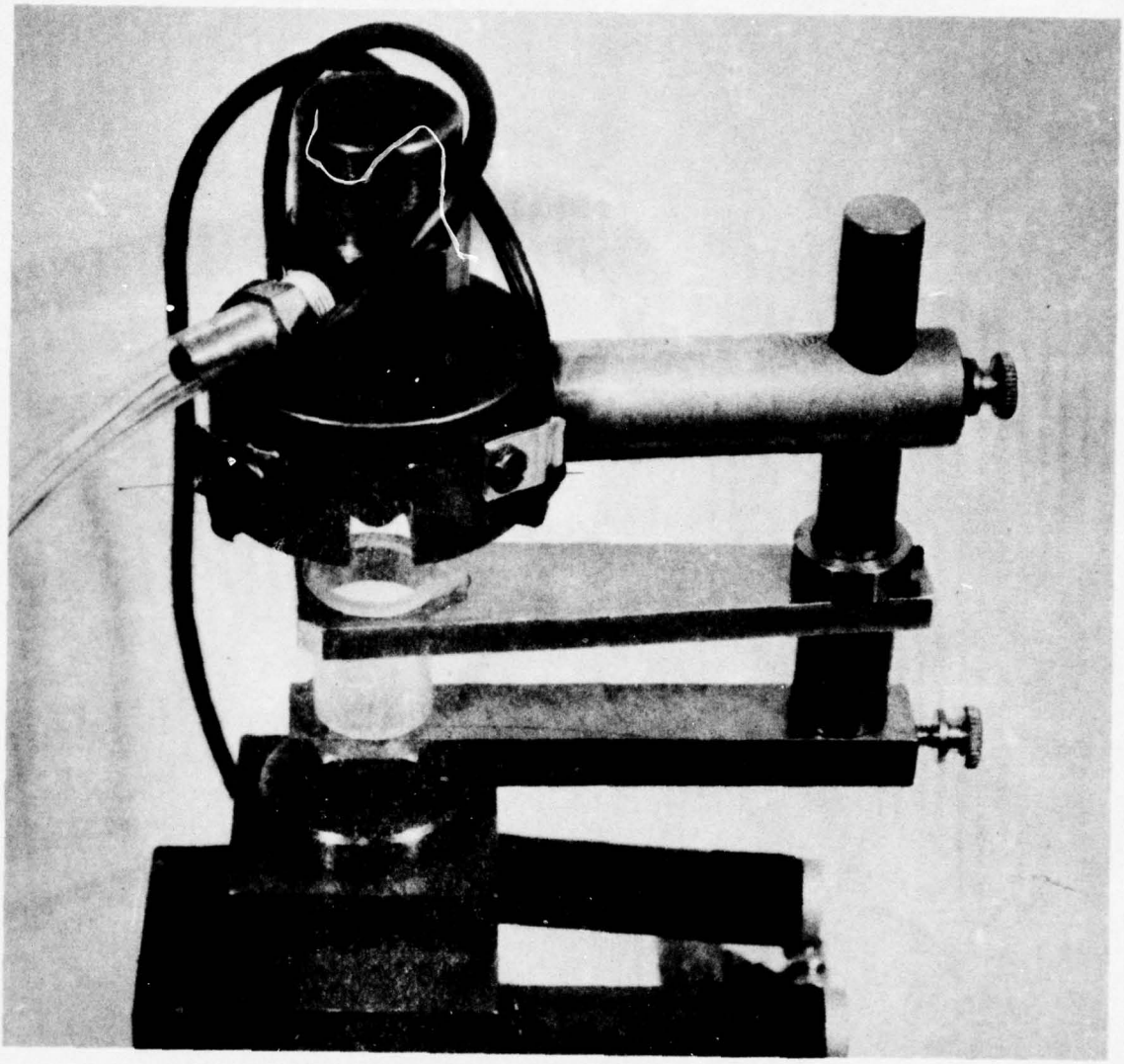


Figure 3

Configuration Of The Atomizer Head For The Spontaneous Preconcentration Method

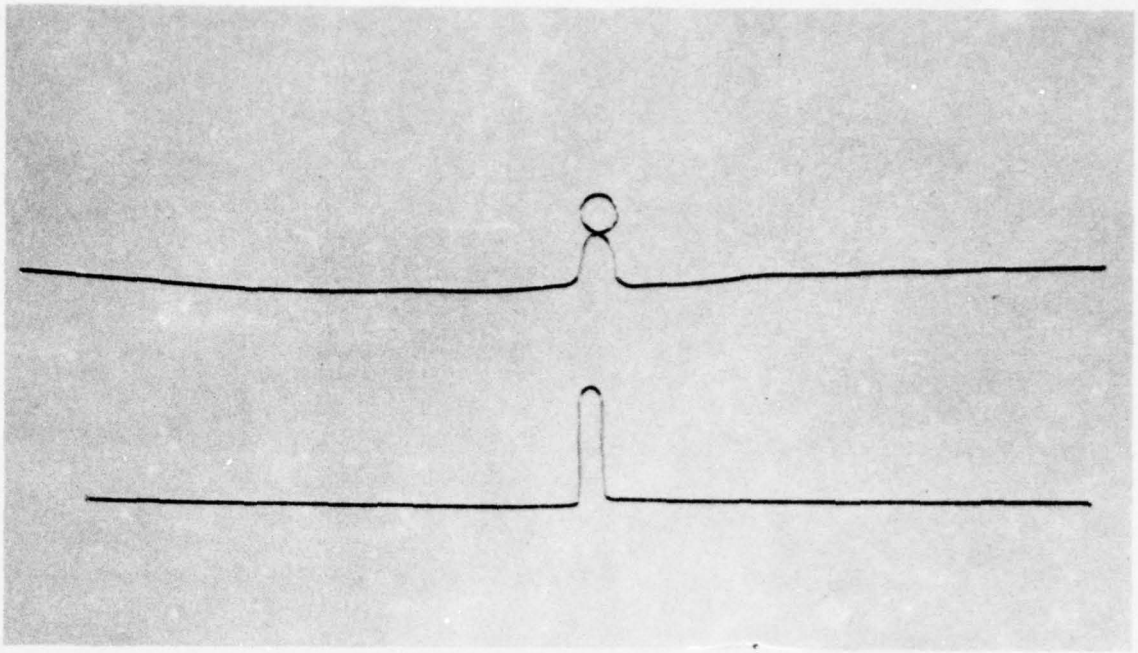


Figure 4

Loop Design For The Aliquot Method (top) And The Spontaneous Preconcentration Method (bottom)

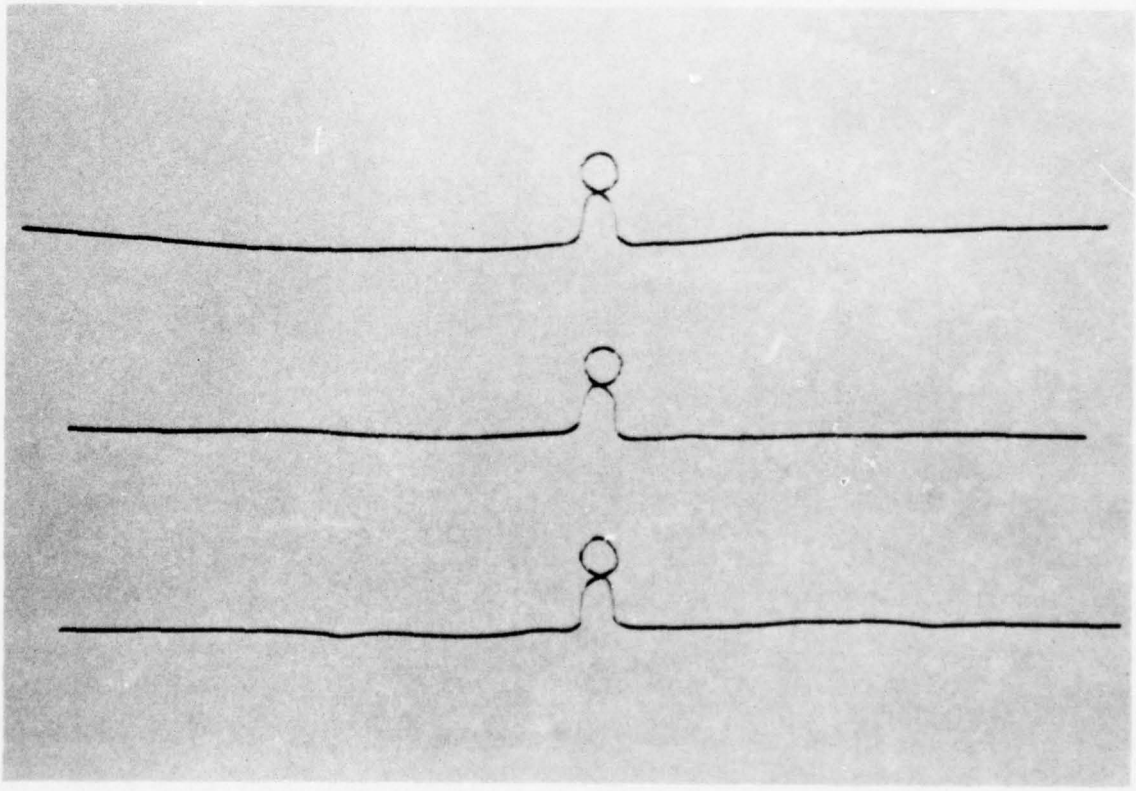


Figure 5

Comparison of Wire Loop Construction By A Template

loop be soaked during each preconcentration step. Otherwise, the precision of the analysis became quite poor. A short rinse (~5 seconds) in doubly-distilled deionized water, followed by drying of the loop at a low voltage setting, insured the absence of adsorbed solution.

An inert gas, either dry nitrogen or argon, was passed over the loop at 1.95 and 1.63 ℓ/min for nitrogen and argon, respectively (Gilmont #13 Compact Flowmeter) to maintain an inert atmosphere in the region surrounding the loop. The inert gas was supplemented by the presence of hydrogen at 0.225 ℓ/min (Gilmont #12 Compact Flowmeter) during the atomization process. The hydrogen gas extended considerably the useful lifetime of each loop by reacting with any entrained oxygen present. At elevated temperatures during the atomization process, the hydrogen ignited producing an invisible flame. To assist in maintaining a reducing atmosphere about the wire loop atomizer, the metal cover was moved over the loop prior to the atomization step.

The Varian Techtron Model 63 Carbon Rod Atomizer was employed to obtain referee analyses of water samples provided by the United States Army Environmental Hygiene Agency (U.S.A.E.H.A.). The power supply to the carbon rod workhead was constructed from the transformer(115V to 12V, 150 A, A and R Transformers, Melbourne, Australia) normally required for the Model 63-CRA power supply and a rheostat (Type V20, 0-135V, 20 A, 50-60 cps, General Radio Co., Cambridge, Massachusetts). Carbon tubes and electrodes were purchased from Varian Techtron. Aliquots of 5 μℓ were dispensed into the pyrolitically-coated carbon tubes with a Varian Autopette. The nitrogen gas flow over the carbon tube was maintained at 4.0 ℓ/min, and the hydrogen gas flow was 1 ℓ/min.[87] Hydrogen gas was

employed only where it improved the sensitivity of the analysis. The hydrogen normally ignited when the sample was atomized. Cooling water was passed through the workhead at the suggested rate of 600 ml/min. It is necessary to allow the workhead to cool between consecutive analyses.

The specific inorganic salts or pure metals, selected for preparing 1000 ppm standard stock solutions, were of analytical reagent grade quality and are delineated in the appendices. Dilute standard solutions for establishing calibration curves or standard additions plots, were prepared by serial dilution of the 1000 ppm standard stock solutions with doubly-distilled deionized water. All solutions were made up in glass volumetric flasks and immediately transferred to polythylene containers.

The doubly-distilled deionized water was produced by distillation of singly-distilled water with a Corning Mega-Pure One Liter still followed by passage through a Corning LD-3 General Purpose Demineralizer equipped with Corning 3508-B high capacity disposable demineralizer cartridges. The specific resistance of the water was found to be greater than 1×10^6 Ω -cm. The water utilized for the copper and cadmium analyses was purified as described under those appendices.

All glassware and polyethylene containers were soaked in either 50% HNO_3 or 1:1 HNO_3/H_2SO_4 for at least two days before thorough rinsing with tap water to eliminate all traces of acids, followed by several rinses with doubly-distilled deionized water.[88,89]

Results and Discussion

In Table I, the sensitivity and absolute sensitivity are reported for the determination of each of eight elements by the aliquot method. Similarly, sensitivities are tabulated for flame atomic absorption

Table I. Sensitivities And Absolute Sensitivities For Analysis By Flame And Nonflame Atomic Absorption Spectrometry

element	flame[e]	wire loop(aliquot), 5µℓ		tantalum ribbon[c]	carbon tube, 5µℓ[d]
	sensitivity, ppm	sensitivity, ppm	absolute sensitivity, g	absolute sensitivity, g	absolute sensitivity, g
Zn	9×10^{-3}	0.17×10^{-3}	8.5×10^{-13}	4×10^{-12}	1.85×10^{-13}
Fe	62×10^{-3}	1.9×10^{-3}	9.4×10^{-12}	2×10^{-10}	3.6×10^{-12}
Cr	55×10^{-3}	2.45×10^{-3} [a]	3.26×10^{-11}[a]	4×10^{-11}	6.25×10^{-12}[f]
Ag	36×10^{-3}	1.72×10^{-3}	8.59×10^{-12}	2×10^{-11}	1.35×10^{-12}
Mn	24×10^{-3}	1.9×10^{-3}	9.6×10^{-12}	2×10^{-11}	1.4×10^{-12}
Cd	11×10^{-3}	0.88×10^{-3}	4.4×10^{-12}	7×10^{-12}	------
Cu	40×10^{-3}	13×10^{-3}[b]	3.1×10^{-11}[b]	2×10^{-11}	------
Pb	110×10^{-3}	5.4×10^{-3}	2.7×10^{-11}	3×10^{-11}	------

a) for Cr(VI)

b) 2.5µℓ sample

c) reference 57

d) Varian Model 63-CRA and determined in this study

e) reference 85

f) with H_2 gas

spectrometry, and absolute sensitivities are delineated for the tantalum ribbon and the Varian Model 63-CRA (carbon tube). In general, nonflame atomic absorption spectrometry provides better sensitivities than flame atomic absorption spectrometry. The sensitivities for the aliquot method are generally at least an order of magnitude higher than those for flame analysis. Furthermore, the absolute sensitivities for the wire loop atomizer are somewhat better than a comparable metal atomizer, the tantalum ribbon. Work carried out in this laboratory with the Varian Model 63 Carbon Rod Atomizer indicated the carbon tube provides greater sensitivity than the wire loop atomizer.

A limited amount of data is provided regarding the spontaneous preconcentration method (soaking method), Table II. Where applicable, the soaking method provides improved sensitivities compared to the aliquot method. However, manganese did not appear to preconcentrate during 1500 second soaking times, and the iron signals, resulting for 50 second soaking times, were not related to concentration. Chromium preconcentrated on the loop but the peak absorbance values leveled off at a very low concentration (~ 50 ppb). The exchange sites were apparently saturated at very low levels of chromium. More work needs to be carried out to determine the exact mechanism of preconcentration. By the application of appropriate potentials to the wire loop, metals can be preconcentrated and then determined by atomic absorption spectrometry. Isolation of the anlyte from the matrix may circumvent some serious matrix effects.[81,82]

Table II. Sensitivities and Absolute Sensitivities For Analysis By The Spontaneous Preconcentration Method

element	wire loop (soaking)	
	sensitivity, ppm	absolute sensitivity, g
Ag[a]	0.52×10^{-3}[c] 0.3×10^{-3}[d]	2.62×10^{-9}[c] 1.55×10^{-9}[d]
Cu[b,e]	5×10^{-3}	3.4×10^{-7}

a) 5 µl samples

b.) 6.8 µl samples

c) 100 sec soaking time

d) 200 sec soaking time

e) 20 sec soaking time

For most of the elements examined some limited study was made of the change in peak absorbance signal in the presence and absence of possible interferents such as the sodium salts of various anions and several transition metal salts, Table III. Most of the interferent evaluations were carried out at a single analyte and interferent concentration. Smeyers-Verbeke et al. have shown that the sign of the interference may change with interferent concentration.[90] Thus, variation of the interferent concentration as well as the analyte to interferent concentration ratio is necessary for a complete evaluation of interferences for a given element.[23] For sodium sulfate, calcium nitrate, sodium chloride, and sodium nitrate concentrations of one millimolar, increasing the copper concentration from 0.1 to 0.75 ppm increased the percent signal suppression. Based on the work of Alger et al., this could conceivably indicate gas phase interferences rather than interferences originating on the wire loop atomizer surface.[23,26]. However, the data is much too limited, at present, to make any definitive conclusions.

Iron as the ferric chloride salt caused a rather severe depression in the zinc and chromium peak absorbance signals while the ferric nitrate salt caused a large suppression of the copper signal. Since iron salts have a relatively low volatility compared to zinc and copper salts (chromium salts are somewhat more volative than the corresponding salts)[58], the interference may have occurred on the wire loop by preventing effective volatization of the analyte.

Interestingly enough, cupric sulfate at one millimolar levels enhanced the zinc and silver signals, but suppressed the chromium and manganese signals. Perhaps the rate of evaporation from the loop of zinc

Table III. Evaluation of Interferents For Analysis With The Wire Loop Atomizer

Interferent, 10^{-3}M Salt		Cr[b] 1.0 ppm	Zn 1.1 ppm	Cu 0.1ppm LVP Yes	Cu 0.1ppm LVP No	Cu 0.75 ppm LVP Yes	Cu 0.75 ppm LVP No	Mn[b] 0.2 ppm	Ag[c] 1 ppm	Pb[b] 1.0 ppm
Fe	$FeCl_3$ (HCl matrix)	-58.7	-30.0[a]							
	$Fe(NO_3)\cdot 9H_2O$			-75						
Cu	$CuSO_4\cdot 5H_2O$	-19.2	31					-54	40.7	
Mn	$MnSO_4\cdot H_2O$	0.0	15						0.0	
	$MnCl_2\cdot 4H_2O$					-48	-58			
Cd	$3CdSO_4\cdot 8H_2O$	0.0	12					-19	0.0	
	$CdCl_2\cdot 2\frac{1}{2} H_2O$						-62			
Pb	$Pb(NO_3)_2$	0.0					-76			
Zn	$Zn(NO_3)_2$ (HNO_3 matrix)	0.0								
Ca	$Ca(NO_3)_2\cdot 4H_2O$			12		-5	-19			
NO_3^-	$NaNO_3$	-10.6	-28.2	-48			-83	-16	-6.1	-16.3
Cl^-	NaCl	0.0	-31.6	-15			-34	- 1		
SO_4^-	Na_2SO_4	-13.0	-16.2	6		-61	-88	-30	0.0	-78.2
Phosphate	Na_2HPO_4			-100		-61	-89			-28.8
	$NaH_2PO_4\cdot H_2O$					-67	-85			
	$Na_3PO_4\cdot 12H_2O$									-27.9
^-OAC	$NaOAc\cdot 3H_2O$									-36.3
F^-	NaF									-30.5
I^-	NaI									-94.7
Carbonate	$Na_2CO_3\cdot H_2O$	0.0	-22.7						-14.6	-65.9
	$NaHCO_3$		-18.6						0.0	
Br^-	NaBr	0.0	-40.2							

a) 2.2ppm Zinc b) LVP employed c) soaking method

and silver or their salts was reduced in the presence of cupric sulfate allowing the detection system to follow the peak absorbance signal more efficiently for these volative elements. It is more difficult to explain the reduced signals for chromium and manganese since they are less volative than copper. More work is needed to shed light on the mechanism by which the interferences occur. Sensmeier, Wagner, and Christian[65] as well as Maruta and Takeuchi[61] commented on the complex pattern generally observed for interferences and the lack of a coherent theory to explain their origin.

Since lead forms a number of insoluble compounds with common anions, the interferences observed were quite severe in many instances. The use of ethylenediamine tetraacetic acid (EDTA) has been suggested as a means of eliminating several interferences in the flame atomic absorption determination of lead.[91]

Linear voltage programming (LVP) was used in some of the interference studies. By ramping to voltages higher than those ordinarily employed for atomization, the analyte in addition to less volatile interferents may be routinely cleaned from the loop thus reducing memory and matrix effects. The ramping technique may also lead to the separation of the analyte peak from any peak due to the matrix (nonatomic absorption).

Obviously, the most important inference to be made from the interference study is that since a multitude of interferences exist in employing either the aliquot or soaking methods, the use of calibration curves for the determination of unknown concentrations must be viewed with caution. Assuming the existence of a linear working curve for a

particular element, both the method of standard additions and a calibration curve should be carried out for any matrix suspected of enhancing or suppressing the analyte signal. If the standard additions plot and the calibration curve parallel one another, then no observable matrix effect exists.

Since calibration curves were utilized for the determination of metal ion concentrations in variable matrices such as natural waters, it was generally desirable to check for possible matrix effects using standard additions. However, linear working curves were observed over limited concentration ranges for zinc, silver, lead, cadmium, copper, and manganese. Zinc, silver, lead, and cadmium are very volatile elements while manganese and copper are of moderate volatility.[58] The inert gas flow through the absorption cell containing the wire loop undoubtedly decreases the residence time of the analyte in the absorption cell in combination with the relatively high volatility of these elements. The decreased residence time makes peak absorbance measurements less than satisfactory in terms of obtaining linear working curves over large concentration ranges. The utilization of integrated absorbance rather than peak absorbance might lead to calibration curves which are linear over wider concentration ranges. Sturgeon et al. found that the use of the integrated absorbance increased the linear range of the working curve for zinc and cadmium by factors of 16.7 and 4.0, respectively.[92] In the near future, we plan to interface the Varian AA-5 atomic absorption spectrophotometer with a Digital Lab 11 computer (Digital Equipment Corporation, Maynard, Massachusetts) and to program the computer to calculate, among other values, the integrated absorbance signal.

Finished water samples, provided by the United States Army Environmental Hygiene Agency (U.S.A.E.H.A.) and previously analyzed for ten elements by flame and nonflame atomic absorption spectrometry on a Perkin-Elmer 503 atomic absorption spectrophotometer, were analyzed by the wire loop aliquot method and the Varian Model 63 Carbon Rod Atomizer. Excellent agreement was found for the determination of silver by the three methods, Table IV. Thus, the wire loop aliquot method appears adequate for the measurement of silver concentrations in natural waters.

The zinc concentrations, determined by the aliquot method, were neither consistently lower or higher than those found by the A.E.H.A. In the case of four water samples having zinc concentrations between 100 and 200 ppb, two of these samples, analyzed by the aliquot method, gave values intermediate between those obtained with flame atomic absorption. Zinc was the only element examined to give a non zero absorbance for a blank consisting of doubly-distilled deionized water. All glassware and polyethylene containers were scrupulously cleaned with 50% nitric acid or 1:1 HNO_3/H_2SO_4 and all solutions were prepared using doubly-distilled deionized water to help minimize correction for the blank. The remaining two samples were found to have zinc concentrations slightly lower than those predicted by the other two atomic absorption techniques. Because of curvature in the working curve it was not possible to check for matrix effects using the method of standard additions. In one water sample, A 358, zinc was detected although none was reported by the A.E.H.A.

The lead concentrations were, in general, higher than the values given by the A.E.H.A. Considering the numerous interferences possible

Table IV. Analysis of the U.S.A.E.H.A. Water Samples with the Wire Loop Atomizer (values on the left provided by A.E.H.A. and Those on the Right by the Aliquot Method). (Cont'd)

Metal \ Sample Number	A278	A360	D390	A358	A365	B259	B279	B275	C210	C199	C219	A390
Pb		19 36.5	64 258		19 18.3	8 11.4	19 26.2	6 14.6	5		19 6.8	2.9
Cr		17.5 38[b]			23 17.5 35[b]		17.5 35				16.1 39[b]	
Ba					280		330		300			
Hg		1900			1900		1600				3200	

a) Flame (air-acetylene) determination

b) determined on Varian Model 63-CRA

c) standard additions value for aliquot method

ND-not detectable

Table IV. Analysis of the U.S.A.E.H.A. Water Samples with the Wire Loop Atomizer (values on the left provided by A.E.H.A. and Those on the Right by the Aliquot Method).

Metal \ Sample Number	A278	A360	D390	A358	A365	B259	B279	B275	C210	C199	C219	A390
Cu		187			191		192	850			195	
Fe	106	167	2051 900 1800[c] 2200[a]	285 49.5	183	3925 1800[c] 3900 4900[a]	163	277 49.5			200 31.5	
Mn	15 28[b]		14	181 132[b] 132	11 20[b]	38 20[b] 22			750 1835[b] 1820			
Zn		141 177 196[a]	ND < 2.5		136 173 184[a]	505	183 169 196[a]	202 157 216[a]	28 13.7	ND < 2.5	177	
Ag		28 27.5 29[b]			31 23.5 31[b]		30 25 30[b]				32 22.5 31[b]	
Cd		15			8		14			100	14	

Continued

lead analyses by the aliquot method, one would have expected the results to be low. The large discrepancy noted for D 390 can be attributed to background contribution to the analyte peak.

Severe matrix effects were observed for the iron analyses. The concentrations of iron found in A 358, B 275, and C 219 by the aliquot method were much lower than the U.S.A.E.H.A. results. Our preliminary results, obtained with the carbon tube atomizer, were in substantial agreement with the Army values. For D 390 and B 259, the iron concentrations were determined by flame atomic absorption analysis of the undiluted samples and by the aliquot method employing both calibration curves and the method of standard additions, Figure 6. The concentrations obtained by flame analysis, standard additons, and the A.E.H.A. were in good agreement. However, the results derived from the working curve were approximately one-half of those found by standard additions, Table IV. The reason for signal suppression by the matrix is not known and further study is necessary to evaluate possible interferents for iron.

Wherever the manganese analyses, provided by the A.E.H.A., were not in agreement with the aliquot method determinations, analyses in our laboratory, employing the carbon tube atomizer, corroborated the results from the latter method. For samples A 278 and A 365 the lower manganese concentrations obtained with aliquot sampling relative to the carbon tube atomizer indicated a possible matrix signal suppression.

For both chromium and manganese the data presently available are not sufficient to warrant conclusions on the accuracy of metal ion determinations in natural waters by the aliquot method. Standard water samples, obtained from the Environmental Protection Agency, will be

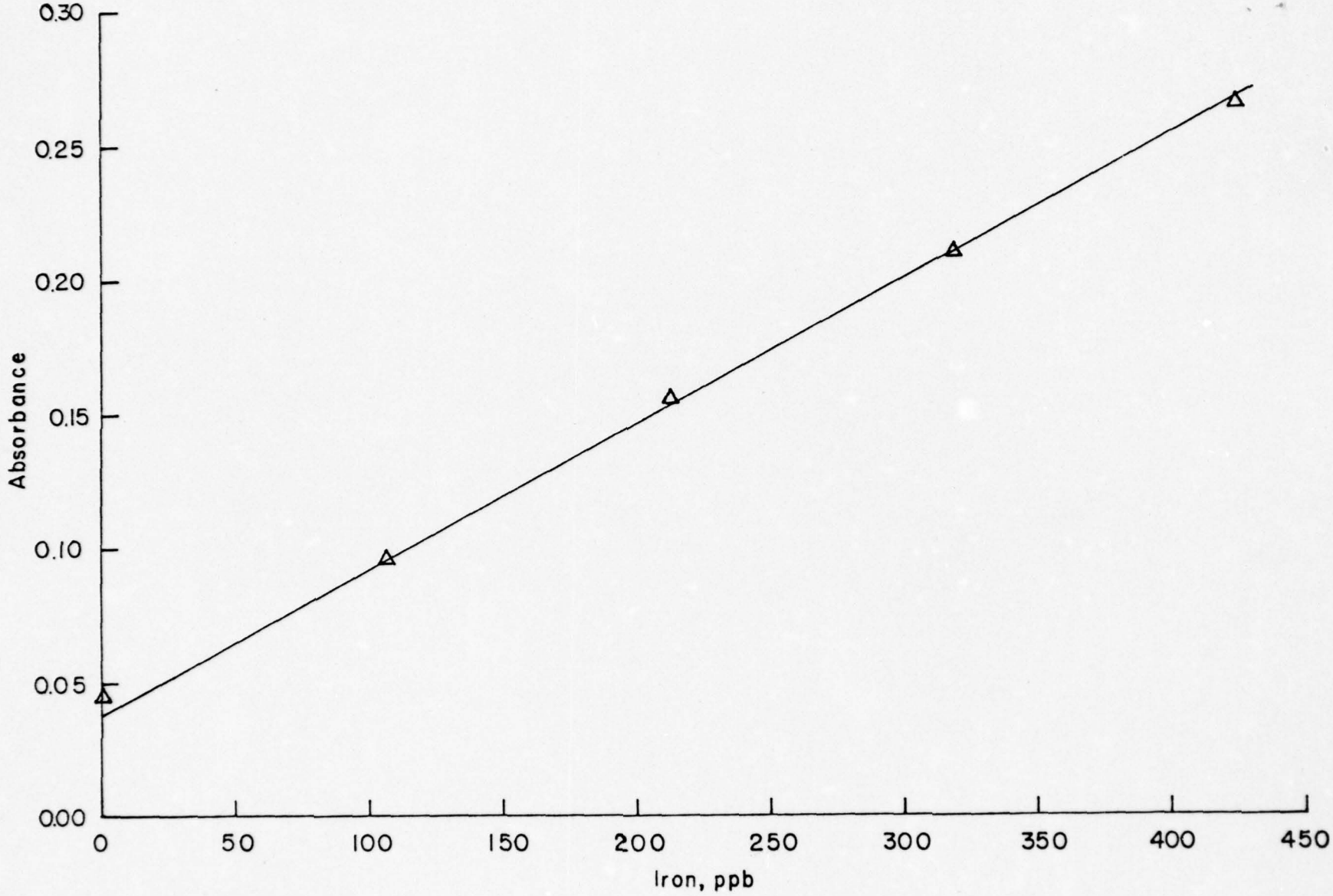


Figure 6

Standard Additions Plot for the Determination of Iron by the Aliquot Method

analyzed for chromium and manganese as well as other metals in order to assess the accuracy of the aliquot method.

National Bureau of Standards bovine liver and orchard leaves (Standard Reference Materials 1577, and 1581, respectively) are being analyzed at present for a number of metals. Zinc and manganese have been extracted from bovine liver with 1% HNO_3 and determined by the aliquot method.[93] Digestion of both standard reference materials with oxidizing agents in a microwave oven is also being carried out.[94] The results are forthcoming.

Although the carbon tube atomizer (Varian Model 63 CRA) provides greater sensitivity for flameless atomic absorption analysis than either the tungsten-rhenium wire loop atomizer or the tantalum ribbon atomizer, the cost of the power supply and accessories ($4,500), carbon tubes (50 per $130), and electrodes (50 per $205) is relatively high. In addition, the workhead must be water-cooled and allowed to cool between analyses. On the other hand, the wire loop atomizer requires no cooling water and no waiting period to reach thermal equilibrium after completion of the atomization process. The cost per atomizer is at most a few pennies and the power supply construction costs are minimal.

List of References

1. "Electrothermal Atomic Absorption Spectrometry of Trace Metals in Biological Fluids." Current Topics in Clinical Chemistry (1975). F. William Sunderman, Jr.
2. Solving Precision Problems in Flameless AA Sampling Research and Development, 27, 30(1976). H. L. Kahn, M. Bancroft, and R. H. Emmel.
3. Interference of Molecular Spectra Due to Alkali Halides in Non-flame Atomic Absorption Spectrometry. Anal. Chem., 47, 920(1975). B. R. Culver and T. R. Surles.
4. A Temperature-Controlled Graphite Tube Furnace for the Determination of Trace Metals in Solid Biological Tissue. Talanta, 21, 257(1974). G. Lundgren and G. Johansson.
5. Direct Determination of Cadmium in Blood with a Temperature-Controlled Heated Graphite-Tube Atomizer.Talanta, 23, 309(1976). G. Lundgren.
6. Temperature Controlled Heating of the Graphite Tube Atomizer in Flameless Atomic Absorption Spectrometry. Anal. Chem., 46, 1028 (1974). G. Lundgren, L. Lundmark, and G. Johannson.
7. A Carbon Tube for the Analysis of Water by flameless atomic absorption spectrometry. Anal. Chim. Acta, 69, 207(1974). J. F. Chapman, L. S. Dale, and J. W. Kelley.
8. Comparative Atomic Absorption Spectroscopic Study of Trace Metals in Water. Environmental Science and Technology, 9, 1073(1975). T. Surles, J. R. Tuschall, Jr., and T. T. Collins.

9. Determination of Chromium in Industrial Effluent Water by Flameless Atomic Absorption Spectroscopy. Atomic Absorption Newsletter, 13, 45(1974). R. W. Morrow and R. J. McElhaney.

10. Direct Determination of Zinc in Sea-bottom Sediments by Carbon Tube Atomic Absorption Spectrometry. Anal. Chim. Acta,70, 448(1974). D. V. Brady, J. G. Montalvo, Jr., G. Glowacki, and A. Pisci.

11. The Direct Determination of Cadmium in Biological Samples by Selective Volatilization and Graphite Tube Resevoir Atomic Absorption Spectrometry. Anal. Chim. Acta,70, 443(1970). R. T. Ross and J. G. Gonzalez.

12. The Determination of Lead in Blood by Atomic Absorption with the High-Temperature Graphite Tube. Anal. Chim. Acta, 58, 47(1972). E. Norval and L. R. P. Butler.

13. Fundamental Studies on Improvement of Precision and Accuracy in Flameless Atomic-Absorption Spectroscopy Using the Graphite-tube Atomizer.Lead in Whole Blood. Talanta, 22, 881(1975). V. P. Garnys and L. E. Smythe.

14. Application of the Graphite Furnace to Saline Water Analysis. Atomic Absorption Newsletter, 13, 61(1974). R. D. Ediger, G. E. Peterson, and J. D. Kerber.

15. The Application of Atomic Absorption Spectroscopy to the Analysis of Natural Waters. Atomic Absorption Newsletter, 10, 69(1971). P. E. Paus.

16. Evaluation of the Heated Graphite Atomizer for the Routine Determination of Trace Metals in Water. Atomic Absorption Newsletter, 12, 118(1973). W. M. Barnard and M. J. Fishman.

17. Determination of Trace Metals in Power Plant Effluents. Atomic Absorption Newsletter, 13, 135(1974). J. C. Guillaumin.

18. Heavy Metal Determination in Sea Water and In Marine Organisms with the Aid of Flameless AAS. II: Determination of Cadmium in Biological Material. Atomic Absorption Newsletter, 14, 60(1975). K. R. Sperling.

19. Oxygen-Rich Atmosphere for Direct Determination of Copper in Oils by Nonflame Atomic Absorption Spectrometry. Anal. Chem., 46, 1591(1974). M. K, Kundu and A. Prevot.

20. The Atomic Absorption Determination of Zinc with A Graphite Furnace. Anal. Chim. Acta, 63, 11(1973). D. Clark, R. M. Dagnall, and T. S. West.

21. Part I. Atomic Absorption and Fluorescence Spectroscopy with a Caron Filament Atom Reservoir. Part I. Construction and Operation of Atom Resevoir. Anal. Chim. Acta, 45, 27(1969). T. S. West and X. K. Williams.

22. Part II. Use of the Atom Reservior in Atomic Fluorescence Spectroscopy. Anal. Chim. Acta, 51, 355(1970). R. G. Anderson, I. S. Maines, and T. S. West.

23. Part VI. A Study of Some Matrix Effects. Anal. Chim. Acta, 57, 271(1971). D. Alger, R. G. Anderson, I. S. Maines, and T. S. West.

24. Part VII. Atomic Absorption Under Limited Field Viewing Conditions. Anal. Chim. Acta, 57, 281(1971). R. G. Anderson, H. N. Johnson, and T. S. West.

25. Part III. A Study of the Determination of Cadmium by Atomic Fluorescence Spectroscopy with an Unenclosed Atom Reservoir. Anal. Chim. Acta, 51, 365(1970).

26. Part IV. The Determination of Gold by Atomic Fluorescence and Atomic Absorption Spectroscopy with an Unenclosed Atom Reservoir. Anal. Chim. Acta, 55, 349(1971). J. Aggett and T. S. West.

27. Determination of Manganese by Atomic-Fluorescence Spectroscopy using a Carbon-filament Atom-reservoir. Talanta, 19, 1301(1972). L. Ebdon, G. F. Kirkbright, and T. S. West.

28. A Comparative Study of the Determination of Zinc and Molybdenum by Atomic Absorption Spectrometry with a Carbon Filament Atom Reservoir. Anal. Chim. Acta, 66, 171(1973).

29. Part VIII. The Determination of Manganese by Atomic Absorption Spectroscopy. Anal. Chim. Acta, 58, 39(1972). L. Ebdon, G. F. Kirkbright, and T. S. West.

30. Part X. The Determination of Nickel with an Unenclosed Atom Reservoir. Anal. Chim. Acta, 59, 187(1972). K. W. Jackson and T. S. West.

31. Part XI. The Determination of Iron by Atomic Absorption Spectroscopy. Anal. Chim. Acta, 61, 15(1972). L. Ebdon, G. F. Kirkbright, and T. S. West.

32. Determination of Sodium by Atomic Emission Spectrometer Using a Carbon Filament Atom Reservoir. Spectroscopy Letters, 6, 767(1973). G. L. Everett and T. S. West.

33. Part V. Determination of Elements in Organic Solvents. Anal. Chim. Acta, 57, 15(1971). J. Agett and T. S. West.

34. Part IX. The Direct Determination of Silver and Copper in Lubricating Oils. Anal. Chim. Acta, 58, 331(1972). J. F. Alder and T. S. West.

35. The Determination of Manganese in Lubricating Oils by Carbon Filament Atomic Absorption Spectrometry. Anal. Chim. Acta, 70, 204(1974). G. L. Everett, T. S. West, and R. W. Williams.

36. Part XII. The Determination of Nickel in Crude and Residual Fuel Oils by Atomic Absorption Spectrometry. Anal. Chim. Acta, 61, 132(1972). J. F. Alder and T. S. West.

37. Determination of Lead in "Instant" Coffee and Tea Powders by Carbon Filament Atomic Absorption Spectrometry. Anal. Chim. Acta, 73, 180(1974). J. K. Kapur and T. S. West.

38. Biological Applications of the Carbon Rod Atomizer in Atomic Absorption Spectroscopy. Clin. Chem., 17, 363(1971) J. P. Matousek and B. J. Stevens.

39. Carbon Rod Atomizer in Atomic Absorption and Fluorescence Spectrometry and Its Clinical Application. Anal. Chem., 43, 211(1971). M. D. Amos, P. A. Bennett, K. G. Brodie, P. W. Y. Lung, and J. P. Matousek.

40. Determination of Copper in Serum with a Graphite Rod Atomizer for Atomic Absorption Spectrophotometry. Anal. Chim. Acta, 57, 263(1971). M. Glenn, J. Savory, L. Hart, T. Glenn, and J. Winefordner.

41. Graphite Rod Atomizer in Atomic Absorption Spectrometry for Direct Determination of Iron in Serum. Anal. Chem., 45, 203(1973). M. T. Glenn, J. Savory, S. A. Fein, R. D. Reeves, C. J. Molnar, and J. D. Winefordner.

42. Direct Determination of Gold, Cobalt, and Lithium in Blood Plasma Using the Mini-Massmann Carbon Rod Atomizer, Anal. Chem., 46, 1445(1974). F. J. M. J. Maessen, F. D. Posma, and J. Balke.

43. Construction and Evaluation of a Versatile Graphite Filament Atomizer for Atomic Absorption Spectrometry. Appl. Spectrosc., 26, 606(1972). C. J. Molnar, R. D. Reeves, J. D. Winefordner, M.T. Glenn, J. R. Ahlstrom, and J. Savory.

44. Determination of Wear Metals in Engine Oils by Atomic Absorption Spectrometry with a Graphite Rod Atomizer, Anal. Chem., 44, 2205(1972). R. D. Reeves, C. J. Molnar, M. T. Glenn, J. R. Ahlstrom, and J. D. Winefordner.

45. Determination of Lead in Gasoline by Heated Vaporization Atomic-Absorption Spectrometry. Anal. Chim. Acta, 65, 285(1973). W. K. Robbins.

46. Determination of Lead in Petroleum and Petroleum Products by Atomic Absorption Spectrometry with a Carbon Rod Atomizer. Anal. Chim. Acta, 61, 25(1972). M. P. Bratzel, Jr. and C. L. Chakrabarti.

47. Evaluation of Carbon Rod Atomizers for Routine Analysis of Vanadium in Crude Oil by Atomic Absorption Spectrometry. Spectroscopy Letters, 6, 385(1973). C. L. Chakrabarti and G. Hall.

48. Graphite Rod Atomization and Atomic Fluorescence for the Simultaneous Determination of Silver and Copper in Jet Engine Oils. Anal. Chim. Acta, 64, 135(1973).

49. Evaluation of a Carbon-Rod Atomizer for Routine Determination of Trace Metals by Atomic-Absorption Spectroscopy: Applications to Analysis of Lubricating Oil and Crude Oil. Talanta, 20, 755(1973). G. Hall, M. P. Bratzel, Jr., and C. L. Chakrabati.

50. Application of the Carbon Rod Atomizer to Atomic Absorption Spectrometry of Petroleum Products, Anal. Chem., 43, 1557(1971), K. G. Brodie and J. P. Matousek.

51. Rapid Atomic Absroption Determination of Silver and Copper by Sequential Atomization from a Graphite Rod. Anal. Chem., 44, 1913(1972). R. D. Reeves, C. J. Molnar, and J. D. Winefordner.

52. Determination of Gold and Silver in Parts-per-Billion or lower Levels in Geological and Metallurgical Samples by Atomic Absorption Spectrometry with a Carbon Rod Atomizer. Anal. Chem., 44, 372(1972). M. P. Bratzel, Jr., C. L. Chakrabarti, R. E. Sturgeon, M. W. Mc Intyre, and H. Agemian.

53. Electrodepositon Techniques for Carbon Rod Flameless Atomic Absorption Analysis. Anal. Letters, 5(7), 433(1972). C. Fairless and A. J. Bard.

54. Fundamental & Aspects of Flamess Atomic Absorption Using the Mini-Massmann Carbon Rod Atomizer. Anal. Chem., 46, 1439(1974).

55. Graphite Braid Atomizer for Atomic Absorption and Atomic Fluorescence Spectrometry. Anal. Chem. 46, 599(1974). A. Montaser, S. R. Goode, and S. R. Crouch.

56. New Methods for Programmed Heating of Electrically Heated Non-Flame Atomic Vapor Cells. Anal. Chem. 47, 38(1975). A. Montaser and S. R. Crouch.

57. Maximization of Sensitivities in Tantalum Ribbon Flameless Atomic Absorption Spectrometry. Anal. Chem. 44, 2018(1972). J. Y. Hwang, C. J. Mokeler, and P. A. Ullucci.

58. Non-Flame Atomization in Atomic Absorption Spectrometry. Anal. Chim. Acta, 72, 49(1974). J. Agget and A. J. Sprott.

59. Trace Analysis by Flameless Atomic-Absorption Spectrometry. Talanta, 19, 465(1972). T. Takeuchi, M. Yanagisawa, M. Suzuki.

60. Interferences of Acids in Atomic Absorption Spectrometry with a Tantalum Filament Atomizer. Anal. Chim. Acta, 62, 253(1972). T. Maruta and T. Takeuchi.

61. Flameless Atomic Absorption Determination of Cobalt, Nickel, and Copper--A Comparison of Tantalum and Molybdenum Surfaces. Anal. Chem., 46, 1983(1974). N. S. Mc Intyre, M. G. Cook, and D. G. Boase.

62. The Determination of Barium and Antimony in Gunshot Residue by Flameless Atomic Absorption Spectroscopy Using a Tantalum Strip Atomizer. Appl. Spectrosc., 29, 44(1975). T. A. Goleb and C. R. Midkiff, Jr.

63. An Evaluation of Some Atomic Absorption Systems for the Determination of Lead in Blood. Clinica, Chimica. Acta, 50, 129(1974). W. N. Anderson, P. M. G. Broughton, J. B. Dawson, and G. W. Fisher.

64. Determination of Soluble Cadmium, Lead, Silver and Indium in Rainwater and Stream Water with the use of Flameless Atomic Absorption. Anal. Chem., 46, 739(1974). A. Rattonetti.

65. A Simple Tantalum Strip Atomizer for the Flameless Atomic Absorption Determination of Trace Metals in Water. Z. Anal. Chem., 277, 19(1975). M. R. Sensmeir, W. F. Wagner, and G. D. Christian.

66. Determination of Trace Amounts of Chromium by Atomic Absorption Spectrometry with a Tantalum Filaments. Anal. Chim. Acta, 66, 5(1973). T. Maruta and T. Takeuchi.

67. Inductively Coupled Plasma-Optical Emission Analytical Spectroscopy. Tantalum Filament Vaporization of Microliter Samples. Anal. Chem., 46, 210(1974). D. E. Nixon, V. A. Fassel, and R. N, Kniseley.

68. Direct Determination of Zinc in Seawater by Atomic Absorption Spectrophotometry. Anal. Chim. Acta, 48, 45(1969). D. C. Burrell and G. G. Wood.

69. A New, Simple Atom Reservoir for Atomic Fluorescence Spectrometry. Anal. Chim. Acta, 48, 197(1969). M. P. Bratzel, R. M. Dagnell, and J. D. Winefordner.

70. A Hot Wire Loop Atomizer for Atomic Fluorescence Spectrometry, Appl. Spectrosc., 24, 518(1970). M. P. Bratzel, Jr., R. M. Dagnell, and J. D. Winefordner.

71. Optimization of Instrumental Parameters in an Automated Nonflame Atomic Fluorescence Spectrometer. Appl. Spectros., 27, 355(1973). S. R. Goode, A. Montaser, and S. R. Crouch.

72. A Rapid Wire-loop Method for Determination of Lead in Paint by Atomic Absorption Spectrometry. Appl. Spectros., 30, 56(1976). M. Kubota, D. W. Golightly, and R. Mavrodineanu.

73. Commercial Tungsten Filament Atomizer for Analytical Atomic Spectrometry. Anal. Chem., 44, 1342(1972). M. Williams and E. H. Piepmeier.

74. Horizontal Tungsten Coil Atomizer and Integrated Absorbance Readout for Atomic Absorption Spectrometry. Anal. Chem., 48, 338(1976). R. D. Reid and E. H. Piepmeier.

75. Ultramicro Atomic-Absorption Spectroscopy with a Tungsten-Filament Atom-Reservoir. Talanta, 20, 459(1973). J. E. Cantle and T. S. West.

76. Theoretical Temperature-Time Curves for Electrically Heated Filament Atom Reservoirs. Their Significance in Analytical Spectrometry. Anal. Chim. Acta, 68, 377(1974). M. S. Cresser and C. E. Mullins.

77. The Application of Electrodeposition Techniques to Flameless Atomic Absorption Spectrometry. Anal. Chim. Acta, 70, 299(1974), W. Lund and B. V. Larsen.

78. The Application of Electrodeposition Techniques to Flameless Atomic Absorption Spectrometry. Part III. The Determination of Cadmium in Urine. Anal. Chim. Acta, 81, 319(1976). W. Lund, B. V. Larsen, and N. Gundersen.

79. The Application of Electrodeposition Techniques to Flameless Atomic Absorption Spectrometry. Part II. Determination of Cd in Seawater. Anal. Chim. Acta, 72, 57(1974). W. Lund and B. V. Larsen.

80. Exploding Wire excitation for trace Analysis of Hg, Cd, Pb, and Ni using electrodepositon for preconcentration. Spectrochimica Acta, 28B, 451(1973). J. A. Holcombe and R. D. Sacks.

81. Flameless Atomic Absorption Spectrometry Employing a Wire Loop Atomizer. Anal. Chem., 47, 2003(1975). M. P. Newton and D. G. Davis.

82. A New Highly Sensitive Preconcentrating Sampling Technique for Flameless Atomic Absorption Spectroscopy. Anal. Letters, 6, 89(1973). M. P. Newton, J. V. Chauvin, and D. G. Davis.

83. The Determination of Lead and Nickel by Atomic Absorption Spectrometry with a Flameless Wire Loop Atomizer. Anal. Chim. Acta, 65, 291(1973). J. V. Chauvin, M. P. Newton, and D. G. Davis.

84. An Indirect Determination of Some Ions by Flameless Atomic Absorption Using a Wire Loop Atomizer. Anal. Letters, 6, 923(1973). M. P. Newton and D. G. Davis.

85. Analytical Methods for Flame Spectroscopy, Varian Instrument Division, 611 Hansen Way, Palo Alto, California 94303.

86. Determination of Mercury Using a Copper Wire Atomizer for Flameless Atomic Absorption Spectroscopy. Anal. Letters, 8, 729(1975), M. P. Newton and D. G. Davis.

87. Instruction Manual For Model 63 Carbon Rod Atomizer, Varian Techtron, p. I-9 (April, 1972).

88. R. E. Thiers in Methods for Biochemical Analysis, D. Glick, Ed., Vol. 5, Interscience, New York, N.Y., 1957, pp. 274-309.

89. Removal of Trace Elemental Impurities from Polyethylene by Nitric Acid, Anal. Chem., 47, 2296(1975). R. W. Karin, J. A. Buono, and J. L. Fasching.

90. Matrix Effects in the Determination of Copper and Manganese in Biological Materials Using Carbon Furnace Atomic Absorption Spectrometry. Anal. Chem., 48, 125(1976). J. Smeyers-Verbeke, Y. Michotte, P. Van den Winkel, and D. L. Massart.

91. Atomic Absorption Spectroscopy. J. W. Robinson, Marcel Dekker, Inc., New York, p. 131(1966).

92. Atomization in Graphite-Furnace Atomic Absorption Spectrometry-Peak Height Method vs. Integration Method of Measuring Absorbance: Carbon Rod Atomizer 63, Anal. Chem., 47, 1240(1975). R. E. Sturgeon, C. L. Chakrabarti, I. S. Malnes, and P. C. Bertels.

93. Atomic Absorption Analysis of Liver Without Ashing. Z. Anal. Chem,, 277, 377(1975). T. A. Hinners.

94. Wet Ashing of Some Biological Samples in a Microwave Oven. Anal. Chem., 47, 1475(1975). A. Abu-Samra, J. S. Morris, and S. R. Koirtyohann.

THIS REPORT IS DIVIDED INTO SECTIONS - ONE FOR EACH ELEMENT STUDIED AND CONCLUDES WITH SOME ANALYTIC RESULTS ON REAL SAMPLES SUPPLIED BY THE ARMY.

ZINC

Due to the excellent sensitivities reported for the analysis of zinc by atomic absorption spectrometry (typical sensitivity = 0.009 µg/ml) (1), all materials, used either in transferring (diluting) or in storing zinc solutions, must be meticulously cleaned. The cleaning process will lower the zinc concentration to acceptable levels in order to avoid spurious analytical results.

We have modified the procedure recommended by Thiers (2) to that suggested by Karin et al. (3). All glassware and polyethylene and polypropylene containers are soaked in an Alconox solution and thoroughly rinsed with tap water prior to immersion in an acid bath. The acid bath consists of either an equimolar mixture of concentrated sulfuric and nitric acids or 50% nitric acid. A cylindrical jar, covered with a glass plate and stored in a hood, serves as the acid bath container (Kimax Brand Glass, Serial 32600 available from Curtin Matheson Scientific, Inc., OD 16", height 12", 8.5 gallons). It is preferable that the glassware and polyethylene remain in the acid for 3 days to assure complete leaching of trace metals by the acid (3). Once the acid has drained from each piece of glassware, it must

be thoroughly rinsed with tap water and given several final rinses with doubly-distilled, deionized water. After the glassware and polyethylene containers are reasonably dry, they should be stored in clean, dustfree drawers. The sulfuric acid-nitric acid bath produces noxious fumes in addition to slowly deteriorating polyethylene containers cleaned repeatedly in the bath. Thus, the 50% nitric acid bath is more desirable.

Although zinc has been detected in the disposable tips used for autopipettes (4), this problem was not evident from the flameless atomic absorption method utilized here. However, the 10 ml disposable beakers supplied by Calbiochem and used for sample containers do contain zinc as a trace impurity. Since these beakers cannot withstand acid treatment, 5 ml polypropylene beakers supplied by Bolab, Inc. (Bolab, Inc., 6 Tinkham Ave., Derry, N.H. 03038) are used instead. The polypropylene beakers can withstand repeated acid washing that reduces the zinc contamination to below detectable levels.

All zinc determinations were carried out using the aliquot method (5). The instrumental parameters for the Varian AA5 and Varian Techtron zinc hollow cathode lamp (HCL) were adjusted according to Varian's Analytical Methods for Flame Spectroscopy (1)

Zinc: wavelength, 213.9 nm
slit width, 100μ
lamp current, 5 mA

The standard, stock solution of zinc (1110 μg/ml) was prepared by dissolving 0.5550 g of 20 mesh zinc metal (Baker A.R.) in 20 ml of reagent grade nitric acid (Mallinckrodt) and diluting to 500 ml in a volumetric flask with doubly-distilled, deionized water. Appropriate standard solutions were freshly prepared by serial dilution of the stock solution.

A sample size of 5-μℓ was dispensed from an Autopette 5-μℓ dispensing pipet available from Varina Techtron. The inert gas flow was adjusted to 1.959 liters/min N_2 or 1.635 liters/min Ar and during the atomization process an H_2 flow of 225.9 μℓ/min was employed. The variac for evaporating the solvent was set at 10 and the best setting for the atomization variac was determined to be 22. One may determine the proper atomization setting by atomizing a given standard at various variac settings. The setting corresponding to the most intense signal was used subsequently in this work. In every instance the peak height was measured rather than peak area (in absorbance units). Since the peaks are quite sharp in detail, this appears feasible. Reproducibility of peak height was good as the standard deviation for a number of runs at each concentration was small.

A calibration curve for zinc over the range 0.055 - 5.55 ppm exhibits very little slope until the region below 1.11 ppm is attained, Figure 7. A plot, covering the range between 4.4 and 44.4 ppb exhibits curvature near the low concentration end, Figure 8. The data between 22.2 and 44.4 ppb lie on a straight line. The smooth line connecting the data points also intersects the origin of the calibration curve indicating no background absorbance for the zinc standards. A less sensitive analytical wavelength for zinc at 307.6 nm (typical sensitivity = 76 μg/ml) may prove adaptable to work in the ppm range (1).

The zinc concentrations in the Fort Knox samples were determined by matching the absorbances found for the samples to a calibration curve for zinc. The range of the calibration curve was between 11.1 and 44.4 ppb. The background, measured by utilizing a hydrogen continuum lamp, increased as the number of samples analyzed also increased. In fact, the background for sample 24 was initially 0.035 absorbance

units but increased to 0.095 absorbance units when examined again between analyses for samples 21 and 22. After several of the Fort Knox samples were atomized, the wire loop acquired a grayish, eroded appearance. As mentioned elsewhere in the paper, this problem may be alleviated by utilizing the linear voltage programming technique.

Zinc Content of the Fort Knox Water Samples as Determined by the Aliquot Method

Fort Knox Sample Number	Concentration Zinc, ppb	Absorbance	(Background)
24	20.5	0.457	(0.035)
15	6.8	0.290	(0.050)
23	6.3	0.283	(0.065)
21	9.5	0.324	(0.105)
22	43.2	0.643	(0.109)
13	14.7	0.388	(0.125)

The sensitivities for the determination of zinc by the aliquot method were calculated according to the Varian Techtron Instruction Manual for the Model 63 Carbon Rod Atomizer (6). In this method, the concentration corresponding to an absorbance of 0.100 is utilized to calculate the sensitivity.

	sensitivity, ppm	absolute sensitivity, g
Zn:	1.7×10^{-4}	8.5×10^{-13}

The effect on the zinc signal of adding the sodium salt of various common anions to a standard zinc solution was also investigated. The extent of the interference, if any, is quantitatively described as follows:

$$\% = \frac{10^2 \left| \text{Absorbance, Zn} - \text{Absorbance, Zn + added interferent electrolyte} \right|}{\text{Absorbance, Zn}}$$

signal change

Interferences for Zinc using the Aliquot Method

added electrolyte*, 10^{-3} M	salt	percent signal change, Zn 1.1 ppm
$NaNO_3$	$NaNO_3$	-28.2
NaBr	NaBr	-40.2
Na_2SO_4	Na_2SO_4	-16.2
NaCl	NaCl	-31.6
$NaHCO_3$	$NaHCO_3$	-18.6
$Na_2CO_3H_2O$	$Na_2CO_3 \cdot H_2O$	-22.7

* The electrolyte is in approximately a 100-fold concentration excess over zinc.

All of the salts caused a depression in the zinc signal. The contributions to the observed signal depression by sodium ion and the respective anion cannot be separated. Hence, the reported signal decrease can be attributed only to the combined effect of the two ions.

The interferences resulting from the additon of transition metal salts to a standard zinc solution are listed in the following table.

Interferences for Zinc using the Aliquot Method

added salt*, 10^{-3} M	salt	percent signal change, Zn 1.1 ppm
$MnSO_4$	$MnSO_4 \cdot H_2O$	15
$CuSO_4$	$CuSO_4 \cdot 5H_2O$	31
$CdSO_4$	$3CdSO_4 \cdot 8H_2O$	12
$FeCl_3$	Fe metal in excess HCl	-30 (Zn, 2.2 ppm)

* The salt is in approximately a 100-fold concentration excess over zinc.

All the metal salts except ferric chloride gave an enhancement in the zinc signal. It was necessary to frequently recheck the standard zinc signal. A possible "memory" effect caused the signal of the standard to decrease after several runs containing the interferent.

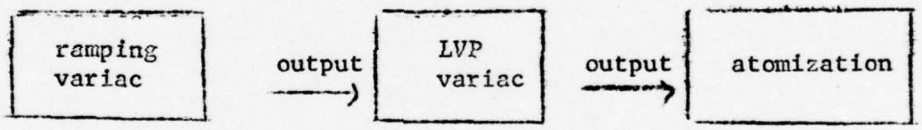
A detailed examination of the effect by salts on flameless atomic absorption signals would necessarily encompass a wide concentration range for the salt. Smeyers-Verbeke et al. have demonstrated in a detailed investigation that the sign of the interference can change over a wide concentration range (7). They reported a 60% increase in the manganese signal (50 ppb) at 50 ppm magnesium as magnesium chloride and an 80% decrease at a magnesium concentration of 1000 ppm.

Sensmeier et al. have noted that many interferences show no general trend in their work with the tantalum strip atomizer, another flameless atomic absorption technique (9). In fact, although 100 ppm of cadmium, manganese, chromium, and iron were found to individually increase the silver signal and 100 ppm copper to decrease the signal, a solution containing 100 ppm of the above metals in addition to 1 ppm silver gave no evidence of signal enhancement or repression.

Although the study of interferences gives a quantitative idea of what signal change to expect under rigidly controlled solution conditions, the matrix in most natural water samples is either unknown or varies from sample to sample. The Environment Protection Agency recommends acidifying all water samples with nitric acid to a pH · 2 (8). In the absence of significant amounts of other matrix components, the matrix is essentially nitric acid. The standard additions technique may be used to circumvent the matrix effects by utilizing one unknown

sample to obtain a standard additions plot. Thus, other samples of similar origin may be analyzed using the standard additions plot as a calibration curve.

The linear voltage programming (LVP) technique developed by Newton and Davis (5) is helpful whenever matrix effects exist. The temperature of the loop can be raised above the normal atomization temperature thus clearing the wire loop of deposits that tend to corrode the surface and create memory effects. This process can be improved by varying the ramping rate of the LATP variac with the output of another variac. The separation of analyte and background peaks is then a possibility.



For use as a reference method, the Varian Techtron Model 63 Carbon Rod was employed for atomization of standard zinc samples. As can be seen from the comparison made below, the carbon tube atomizer provides a greater sensitivity for zinc determinations that is possible with the wire loop aliquot method.

	sensitivity, ppm	absolute sensitivity, g
carbon tube (5μℓ)	3.7×10^{-5}	1.85×10^{-13}
aliquot, wire loop (5μℓ)	1.7×10^{-4}	8.5×10^{-13}

The comparison is particularly relevant since the sample sizes used in the two methods are identical. A calibration curve is shown in Figure 9 for the range 0-11 ppb. It is essentially linear with curvature toward the concentration axis at higher concentration.

A single power supply, built by the electronics and machine shops at the University of New Orleans, was used for drying and atomizing the samples. An atomization setting of 56 volts and a drying setting of 16-17 volts were used for determing zinc. A nitrogen flow rate of 3.5-4 liters/minute was used as recommended by the Varian Techtron Model 63 manual (6). However, hydrogen gas was not employed although the Varian manual recommends its use (10).

Pyrolytically coated carbon tubes and electrodes, obtained from Varian, were used in conjunction with the carbon rod work head. The pyrolytic coating prevents liquid samples from soaking into the surface of the tube (11).

The exterior of the tubes and electrodes exhibit a pitted appearance after repeated use. Since the sample solution tends to soak into the pitted areas, a lowering of the corresponding signal height is observed. By holding the disposable tip of the autopette in the carbon tube aperture for approximately 20 sec, this problem can be alleviated. Clyburn et al. suggest using a gas stream that includes methane in addition to argon (12). With the tube heated at a temperature above 2000°C, the methane deposits a layer of nonporous pyrolytic graphite. The disposable pipet tips become coated with graphite after extended use and this coat is not removed upon acid treatment. However, since the cost per tip is nearly 5 cents, acid cleaning of the tip is recommended after use in the aliquot method.

Varian Techtron sells a power supply for its Model 63 carbon rod atomizer which can be programmed to carry out drying, ashing, and

atomization of the sample. However the cost ($4300) is rather high. Likewise, the graphite tubes and electrodes represent an investment of 130 and 205 dollars per package of 50, respectively.

REFERENCES

1) Analytical Methods for Flame Spectroscopy, Varian instrument Division, 611 Hansen Way, Palo Alto, California 94303

2) R. E. Thiers in Methods for Biochemical Analysis, D. Glick, Ed., Vol. 5, Interscience, New York, N. Y., 1957, pp. 274-309.

3.) R. W. Karin, J. A. Buono, and J. L. Fasching, Anal. Chem., 47, 2296 (1975).

4.) M. R. Sommerfeld, T. D. Love, and R. D. Olsen, Atomic Absorption Newsletter 14, 31 (1975).

5.) M. P. Newton and D. G. Davis, Anal. Chem., 47, 2003 (1975).

6.) Instruction Manual for Model 63 Carbon Rod Atomizer, Varian Techtron, p. 1-9 (April, 1972).

7.) J. Smeyers-Verbeke, Y. Michotte, P. Van der Winkel, and D. L. Massart, Anal. Chem., 48, 124 (1976).

8.) Methods for Chemical Analysis of Water and Wastes, Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, Environmental Protection Agency, Cincinnati, Ohio 45268 (1974).

9.) M. R. Sensmeier, W. F. Wagner, and G. D. Christian, Z. Anal. Chem. 277 19 (1975).

10.) Private communication, John Morrow, Varian applications chemist.

11.) V. P. Garnys and L. E. Smythe, Talanta, 22, 881 (1975).

12.) S. A. Clyburn, T. Kantor, and C. Veillon, Anal. Chem., 46, 2213 (1974).

Zinc Determination by Atomic Absorption Spectrometry[a]

Figure 7, Aliquot Method

absorbance	0.42	0.49	0.71	0.86	0.96	1.03	1.07
concentration, ppm	0.055	0.11	0.55	1.11	2.22	4.44	5.55

Figure 8, Aliquot Method

absorbance	0.125(0.009)	0.230(0.009)	0.36(0.04)	0.44(0.01)	0.53(0.04)
concentration, ppb	4.44	11.1	22.2	33.3	44.4

Figure 9, Carbon Tube Method

absorbance	0.26(0.05)	0.43(0.06)	0.61(0.03)	0.69(0.05)	0.90(0.05)
concentration, ppb	2.22	4.44	6.66	8.88	11.0

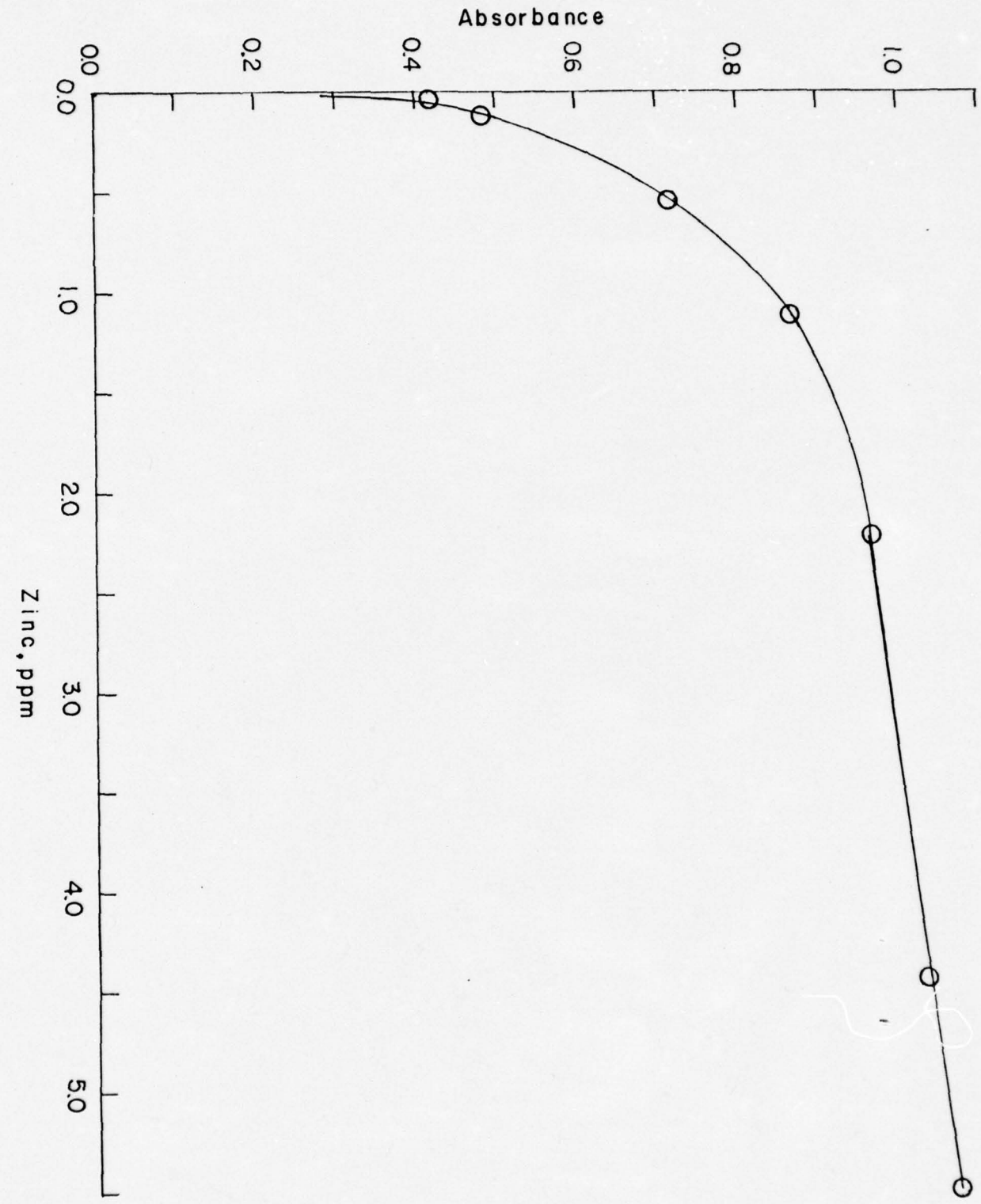


Figure 7. Zinc Determination by the Aliquot Method Over The Range 0-6 ppm.

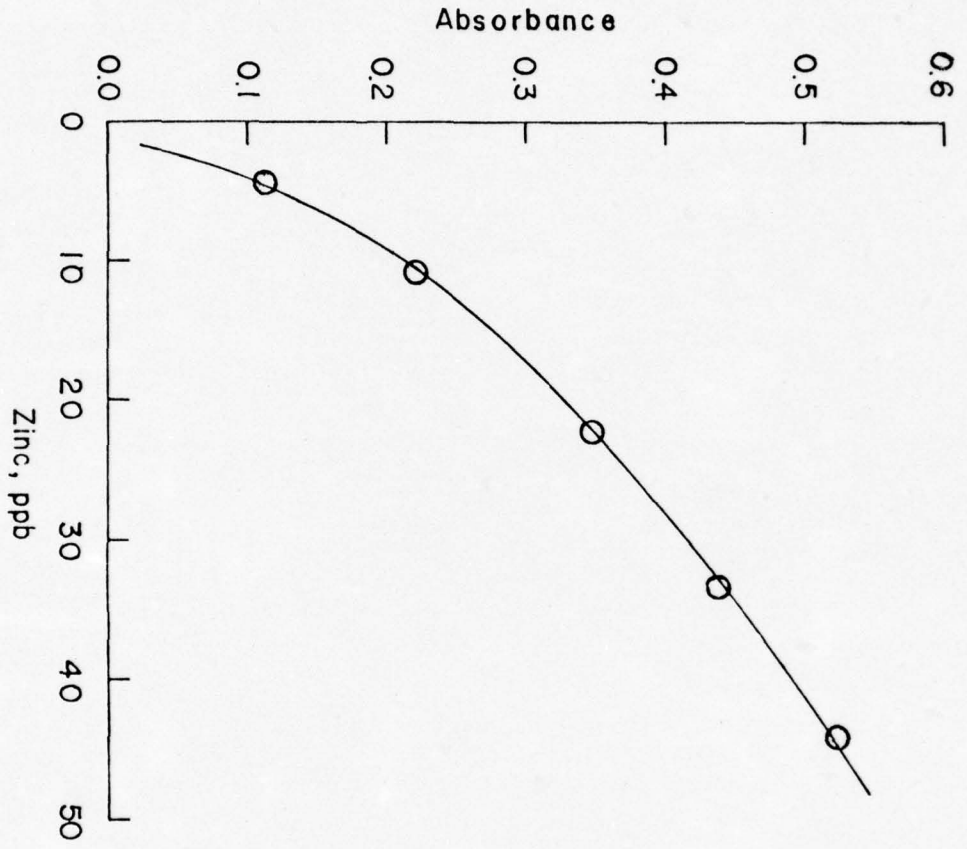


Figure 8. Working Curve for the Analysis of Zinc by the Aliquot Method

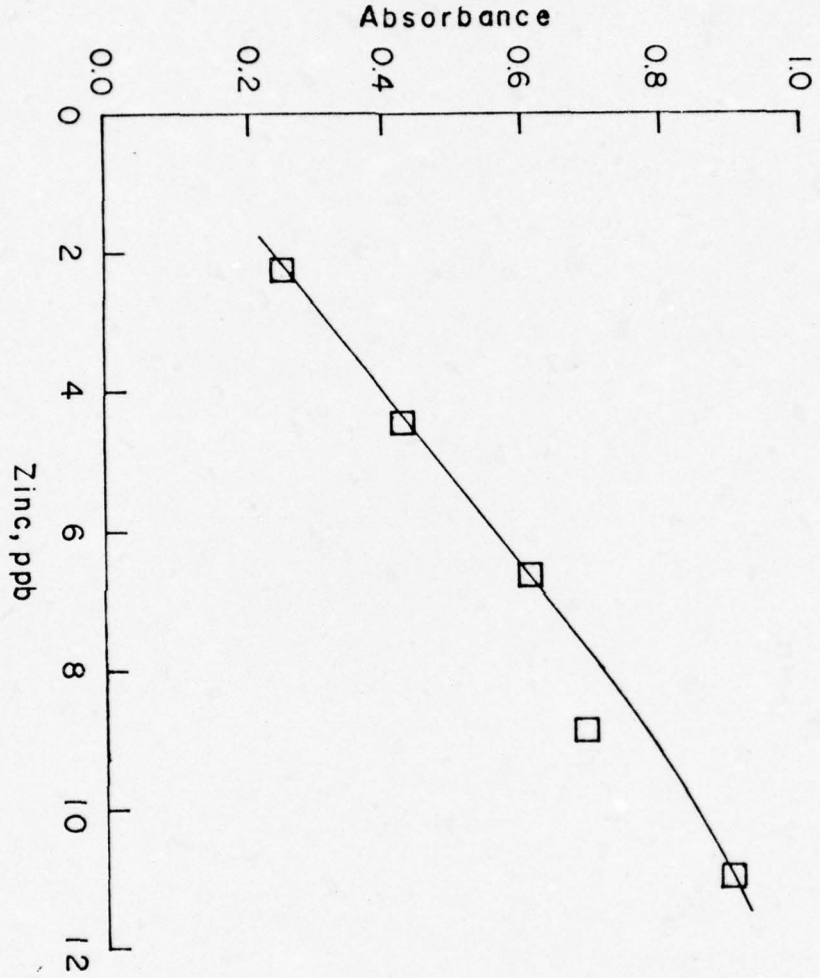


Figure 9. Zinc Determination Using the Varian Model 63 Carbon Rod Atomizer

IRON

The tungsten-rhenium wire loop has been shown to absorb radiation at 248.3 nm from an iron HCL when the loop is heated without any sample on the wire. Upon prolonged heating at a given atomization temperature, the absorbance will gradually decrease, Figure 10. Heating the loop at and above the normal atomization setting for a time will gradually establish a stable baseline near 0.00-0.01 absorbance units. With the assistance of an X-ray fluorescence unit, the presence of iron in the tungsten-rhenium alloy was qualitatively yet unequivocally established.

Since it had been previously established that the soaking method preferentially concentrates the more highly charged positive ions on the wire loop relative to ions of lesser positive charge, this method was also attempted for the determination of iron. However, no obvious correlation between absorbance and concentration of iron was observed for soaking times of 50 seconds. At this point one might surmise that although the iron preconcentrates on the loop there is a problem in the atomization process. On the other hand, preliminary results obtained from the aliquot method indicate a correlation of signal peak height with concentration, Figure 11.

At least for the aliquot method, the atomization process occurs without difficulty.

Iron: wavelength, 248.3 nm
slit width, 50 μ
lamp current, 5 mA

An atomization setting of 35 was employed in the iron analyses.

Calibration curves for iron over the concentration range 0-212 ppb are given in Figures 12 and 13 for the aliquot and carbon tube methods, respectively. The sensitivities and absolute sensitivities, calculated for iron using both the aliquot and carbon tube techniques, are listed in the following table.

	sensitivity, ppm	absolute sensitivity, g
carbon tube (5μℓ)	7.2×10^{-4}	3.6×10^{-12}
aliquot, wire loop(5 μℓ)	1.9×10^{-3}	9.4×10^{-12}

When using the Model 63 carbon rod atomizer, the contact between the electrodes and the tube must be snug at all times to allow for reproducible current-voltage characteristics. At higher atomization temperatures, e.g., a rheostat input of 95 volts, the front and back electrodes do not maintain a snug contact with the tube upon repeated heating and cooling. Although tightening of the front electrode knurled clamping screw with pliers has been suggested (10), the back electrode also needs readjustment to maintain good optical alignment.

At the higher atomization temperature, the electrodes and tubes become pitted rapidly, however, sample introduction occurs without difficulty as long as the autopette tip remains in the aperture for 20 seconds and then is quickly withdrawn. The new, flexible autopette tips from Varian are much more suitable for this purpose than their predecessor.

References:

1) Private communication, John Morrow, Varian applications chemist.

Iron Determination by Atomic Absorption Spectormetry

Figure 11, Aliquot Method

Absorbance	0.291(0.008)	0.410(0.009)	0.450(0.006)	0.515(0.007)
concentration, ppm	0.213	0.532	0.744	1.06
	0.665(0.006)	0.90		
	2.13	5.32		

Figure 12, Aliquot Method

absorbance	0.045(0.006)	0.125(0.009)	0.210(0.004)
concentration, ppb	21.2	53.0	106
	0.270(0.004)	0.310(0.004)	
	159	212	

Figure 13, Carbon Tube Method

absorbance	0.130(0.006)	0.37(0.02)	0.70(0.02)	1.00(0.03)
concentration, ppb	21.2	53.0	106	159
	108(0.02)			
	212			

[a] standard deviations are given in the parenthesis.

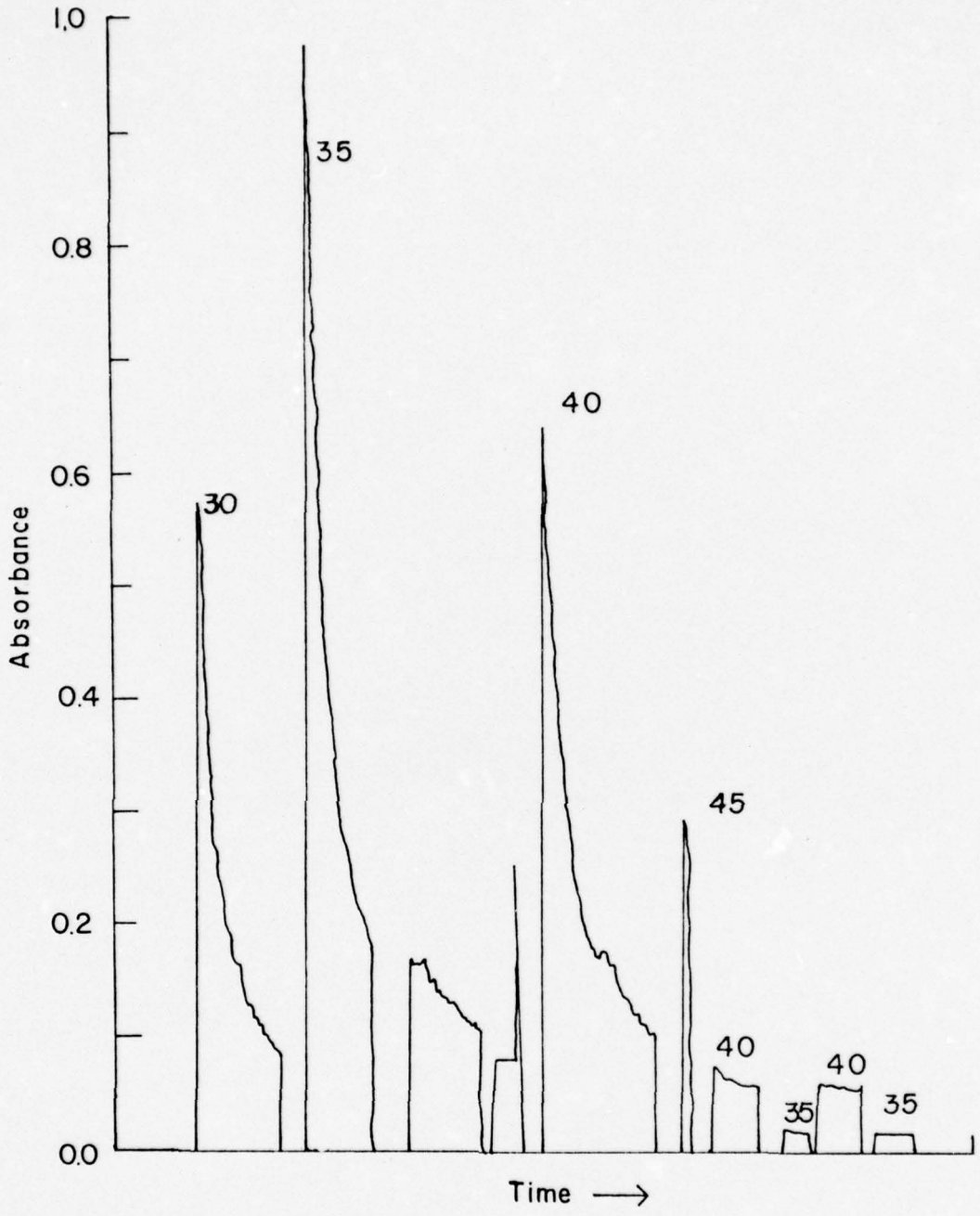


Figure 10. Absorbance Profile at 248.3 nm Produced by Heating a Tungsten-Rhenium Wire Loop Atomizer (Atomization Variac settings are given).

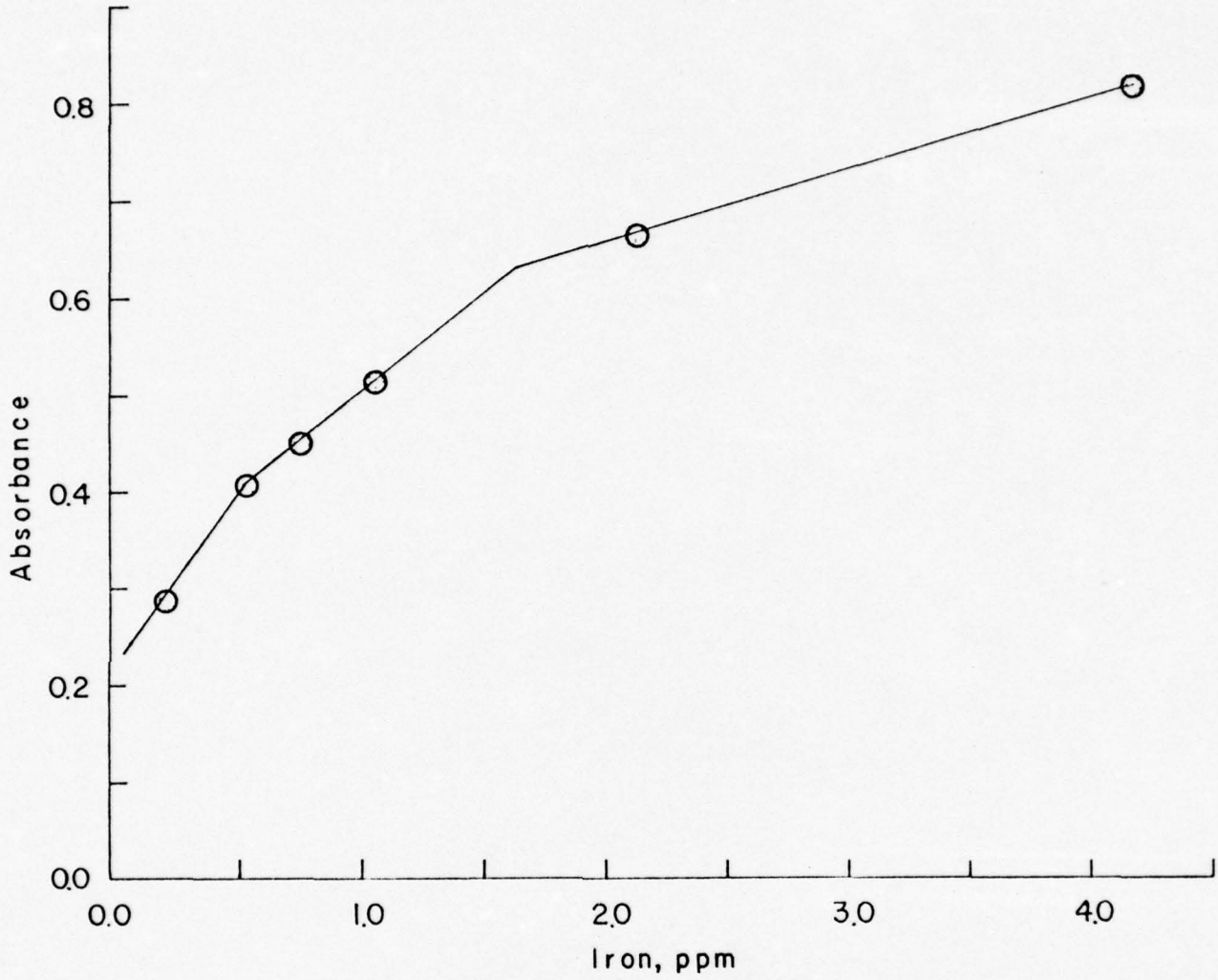


Figure 11. Iron Determination by the Aliquot Method over the Range 0-5 ppm.

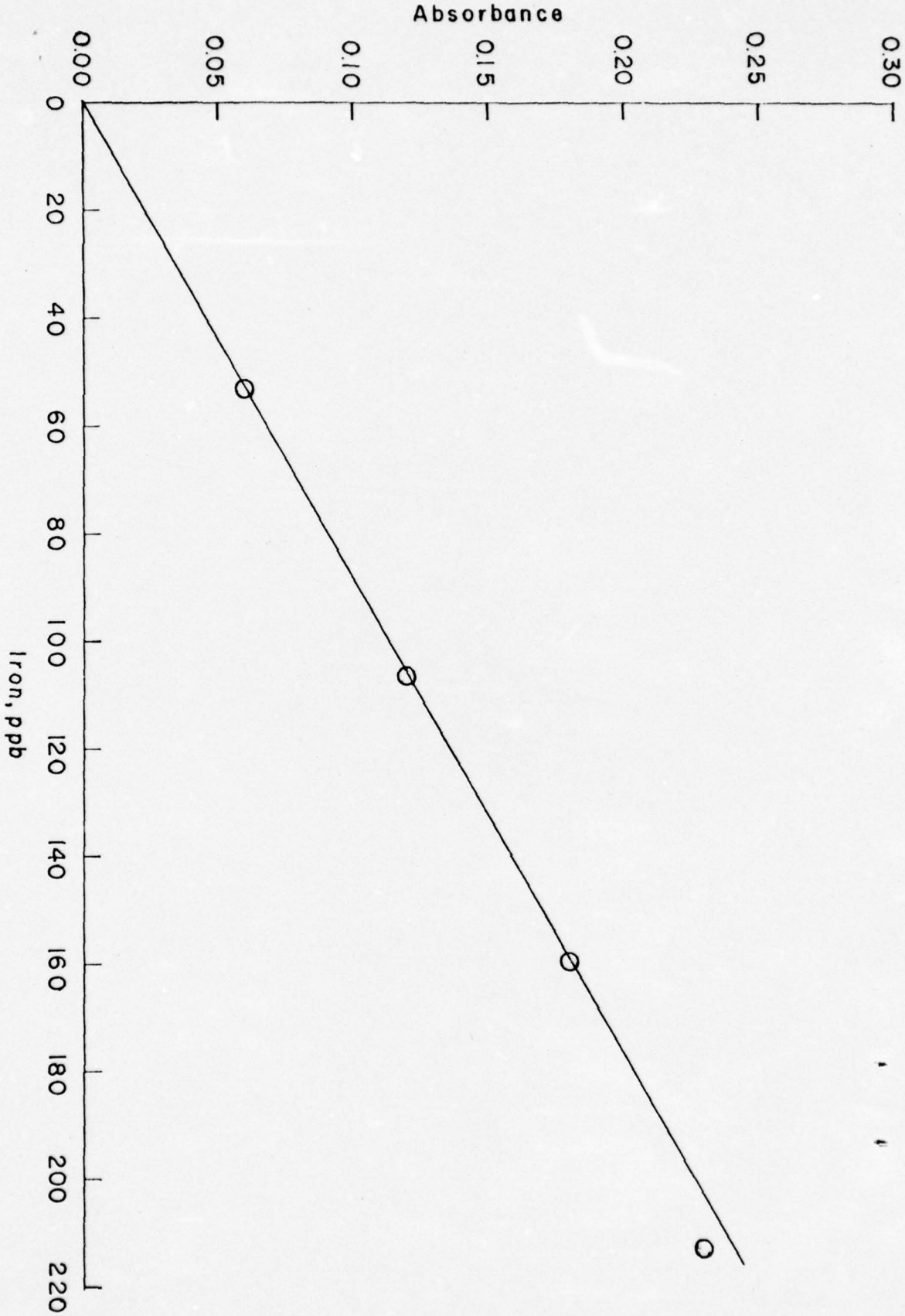


Figure 12. Working Curve for the Analysis of Iron by the Aliquot Method.

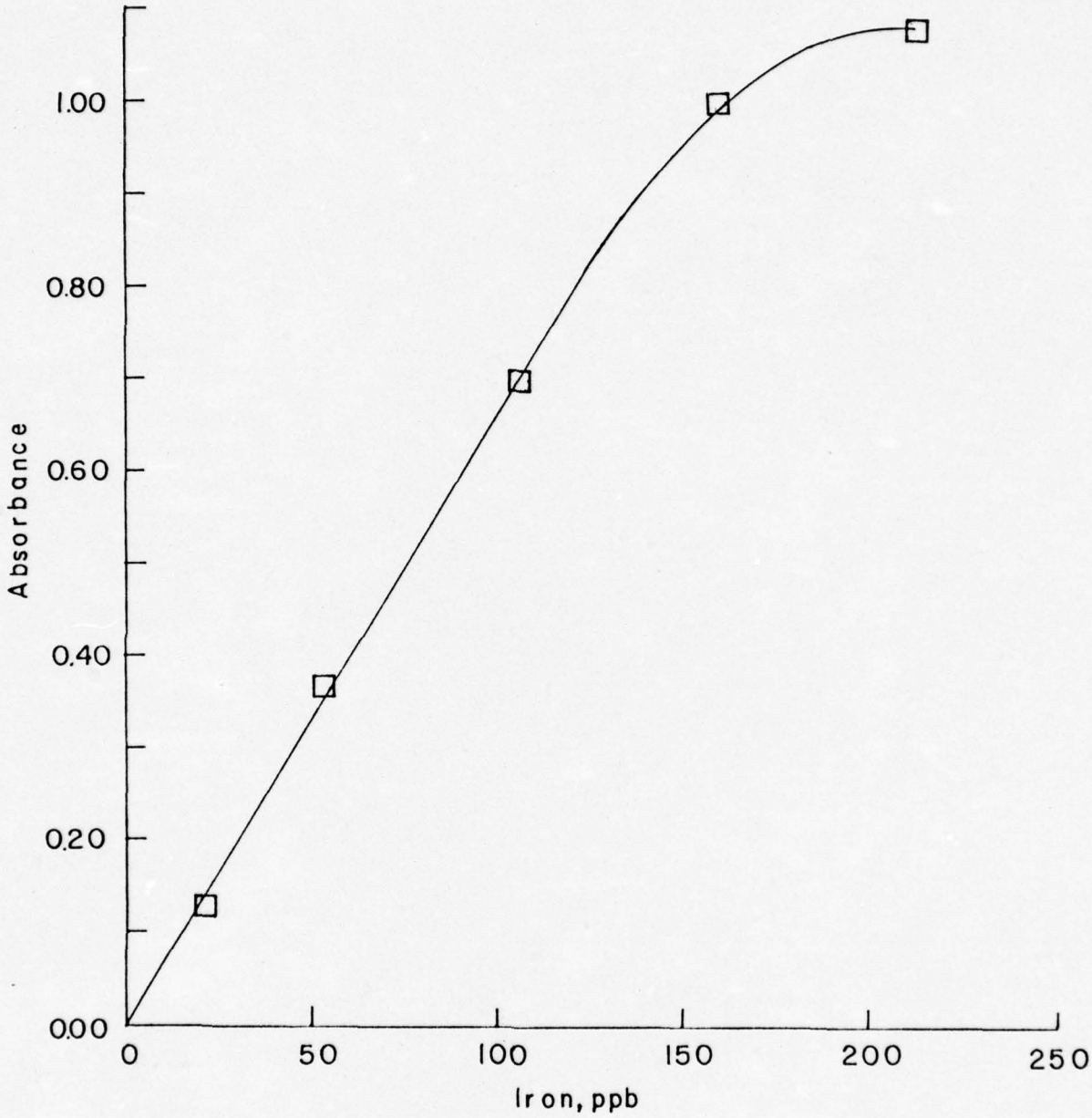


Figure 13. The Determination of Iron Employing the Carbon Tube Atomizer.

CHROMIUM

Several reports have recently appeared indicating the significance of the valence state of chromium in the determination of chromium by flame atomic absorption spectrometry. Green suggests the use of hydrogen peroxide to convert all chromium to the chromium (III) state which may be determined with a greater sensitivity than the chromium (VI) valency state (1). Cresser and Hargitt noted the significance of pH control in analyzing solutions containing chromium (VI) (2). A nitrous oxide-acetylene flame appeared to minimize the variation in the observed signal as the pH was varied between 3 and 9. However, little has appeared to date in the literature regarding the significance of valency in determining metals and nonmetals by flameless atomic absorption. In work with a quartz-tube furnace, Vijan and Wood have shown selenium (VI) to give absorbance signals approximately 66% lower than the corresponding selenium (IV) signals (3). Thus, it was of interest to investigate the effect of valency in the chromium system upon the absorbance signals observed employing the tungsten-rhenium wire loop atomizer of Newton and Davis (4).

Standard stock solutions of 1000 ppm chromium were prepared from potassium dichromate (Baker A.R.) and chromium metal (Sargent chromium metal, carbon free, lump) dissolved in reagent grade hydrochloric acid. The former solution contains chromium (VI) and the latter chromium (III).

The instrument parameters for the Varian Techtron AA-5 atomic absorption spectrophotometer were adjusted according to Varian's Analytical Methods for Flame Spectroscopy (5)

chromium:

Wavelength	357.9 nm
HCL current	5 mA
slit width	50 μ

A sample aliquot of 13.3 μℓ was reproduceably dispensed by a Varian "Autopette". The nitrogen gas flow was maintained at 1.959 liters/minute, and the hydrogen gas flow was maintained at $\leq$ 225 ml/minute during the atomization stage.

The Variac used in vaporizing the solvent, water, was always set on 10 Linear voltage programming (LATP) was utilized throughout the work with chromium. The LVP mode has several advantages in that relatively nonvolatile compounds are routinely cleared from the wire loop after atomization of the analyte, memory and matrix effects being subsequently reduced, and the variation of the optimum variac setting for atomization of a given element with the age of the wire loop is no longer a problem. The physical characteristics of other nonflame atomizers are also altered significantly after repeated use (6).

In Figure 14, calibration curves are given for both chromium (VI) and chromium (III) over the concentration range 0-100 ppb. The calibration curve constructed from the chromium (VI) standards has the larger slope indicative of the greater sensitivity for this valence state with the wire loop atomizer. The sensitivities and absolute sensitivities as calculated in reference (7) are tabulated below for both valence states of chromium studied here.

aliquot method (13.3μℓ)	sensitivity, ppm	absolute sensitivity, g
chromium (VI)	2.45×10^{-3}	3.26×10^{-11}
chromium (III)	3.39×10^{-3}	4.52×10^{-11}

Apparently, the elemental state of chromium is more readily attainable from chromium (VI) than from chromium (III). However, the exact mechanism by which, either oxidation state is reduced to chromium (0) is uncertain at the present time.

In Figure 15, calibration curves are given for both chromium (VI) and chromium (III) up to 1.0 ppm. As expected, the absorbance signal for chromium (VI) is greater than for chromium (III) at a given concentration.

The effect of a variety of 1 mM metal salts and 1 mM sodium salts of common anions on the absorbance signal of a 1.0 ppm chromium solution is delineated in the two following tables. The use of linear atomization temperature programming eliminates or reduces many of the interferences evaluated in this limited study. The interferences noted all lead to a depression of the chromium signal and the effect is particularly serious in the presence of $FeCl_3$, iron salts being considerably less volatile than the other metal salts examined. The low volatility of the iron salt prevents volatilization of the chromium species on the wire loop.

The Effect of Various Sodium Salts on the Absorbance of $CrCl_3$ Solutions.

Salt	added electrolyte, 10^{-3} M	Percent signal changes Cr 1.0 ppm
$NaNO_3$	$NaNO_3$	-10.6
Na_2SO_4	Na_2SO_4	-13.0
$NaCO_3 \cdot H_2O$	Na_2CO_3	0.0
NaCl	NaCl	0.0
NaBr	NaBr	0.0

The Effect of Various Metal Salts on the Absorbance of $CrCl_3$ Solutions:

Salt	added electrolytes, 10^{-3}M	Percent signal changes Cr 1.0 ppm
$Pb(NO_3)_2$	$Pb(NO_3)_2$	0.0
$Zn(NO_3)_2$ (HNO_3 matrix)	$Zn(NO_3)_2$	0.0
$3CdSO_4$ % H_2O	CdSO4	0.0
$MnSO4 \cdot H_2O$	MnSO4	0.0
$CuSO4 \cdot 5H_2O$	CuSO4	19.2
$FeCl_3$ (HCl matrix)	$FeCl_3$	-58.7

It was also desirable for comparative purposes to examine the determination of chromium using a carbon tube atomizer. Standard chromic chloride solutions were atomized in the presence and absence of hydrogen gas (flow rate, 2 liters/minute). In this fashion the effect of the reducing atmosphere, provided by hydrogen gas, on the chromium absorbance signal cound be evaluated.

All instrument operating parameters were identical to the wire loop work. Power supply settings of 17 and 95 volts were utilized for the drying and atomization stages, respectively. The Varian Techtron CRA-63 workhead was used in conjunction with pyrolytically coated carbon tubes and electrodes available from Varian. The recommended flow rate for the nitrogen sheathing gas of ~ 4. liters/minute was also employed.

From Figure 16 one can readily conclude that the presence of hydrogen gas in the gas stream during the atomization process improves the absorbance signal for the chromic chloride solutions. The reducing atmosphere provided by the hydrogen gas during the atomization process prevents formation of refractory oxides to a greater extent than in the presence of nitrogen gas alone. The formation of chromic oxide from chromium metal is thermodynamically quite favorable (ΔG = -460 kJ/mole).

The sensitivities and absolute sensitivities, calculated for the determination of chromium by the carbon tube atomizer technique, are given below:

Carbon tube Method (5μℓ)	Sensitivity, ppm	absolute sensitivity, g
with H_2 gas	1.25×10^{-3}	6.25×10^{-12}
without H_2 gas	1.59×10^{-3}	7.96×10^{-12}

List of References

1.) M.S. Cresser and R. Hargitt Talanta, 23, 153 (1976)

2.) H.C. Green, Analyst, 100, 640 (September, 1975)

3.) P.N. Vijan and G.R. Wood, Talanta, 23, 89 (1975)

4.) M.P. Newton and D.G. Davis, Anal. Chem., 47, 2003 (1975)

5.) Analytical Methods for Flame Spectroscopy, Varian Instrument Division, 611 Hanson Way, Palo Alto, California 94303.

6.) A. Montaser and S.R. Crouch, Anal. Chem., 47, 38 (1975)

7.) Instruction Manual for Model 63 Carbon Rod Atomizer, Varian Techtron, p. 1-9 (April 1972)

Figures 14 and 15 Determination of Chromium by the Aliquot Method with Linear Atomization Temperature Programming (LVP).*

$CrCl_3$, Cr(III)

Cr, ppb	32.4		56.7	81.0
Absorbance	0.045(0.004)	0.050(0.004)	0.070(0.007)	0.105(0.005)
162	202	405	607	810
0.195(0.006)	0.225(0.008)	0.36(0.01)	0.47(0.01)	0.52(0.02)
1010				
0.60(0.03)				

$K_2Cr_2O_7$ (VI)

Cr,ppb	19.9	39.8	49.75
Absorbance	0.030(0.004)	0.075(0.002)	0.80(0.007)
69.6	99.5	149	159
0.12(0.01)	0.156(0.004)	0.235(0.007)	0.24(0.01)
318	556	796	
0.45(0.02)	0.56(0.03)	0.62(0.02)	

* Standard deviation for 13.3 µℓ aliquots given in parentheses.

Figure 16 Determination of Chromium by the Carbon Tube Method *

Cr, ppb[1]	9.95	19.9	39.8	49.75
Absorbance	0.025(0.005)	0.060(0.004)	0.140(0.002)	0.175(0.004)
69.6				
0.25(0.02)				

Cr, ppb[2]	9.95	19.9	39.8	49.75
Absorbance	0.020(0.004)	0.049(0.005)	0.11(0.01)	0.14(0.01)
69.6				
0.18(0.007)				

* Standard deviation for 5uℓ aliquots given in parentheses
1) H_2 gas employed
2) no H_2 gas utilized

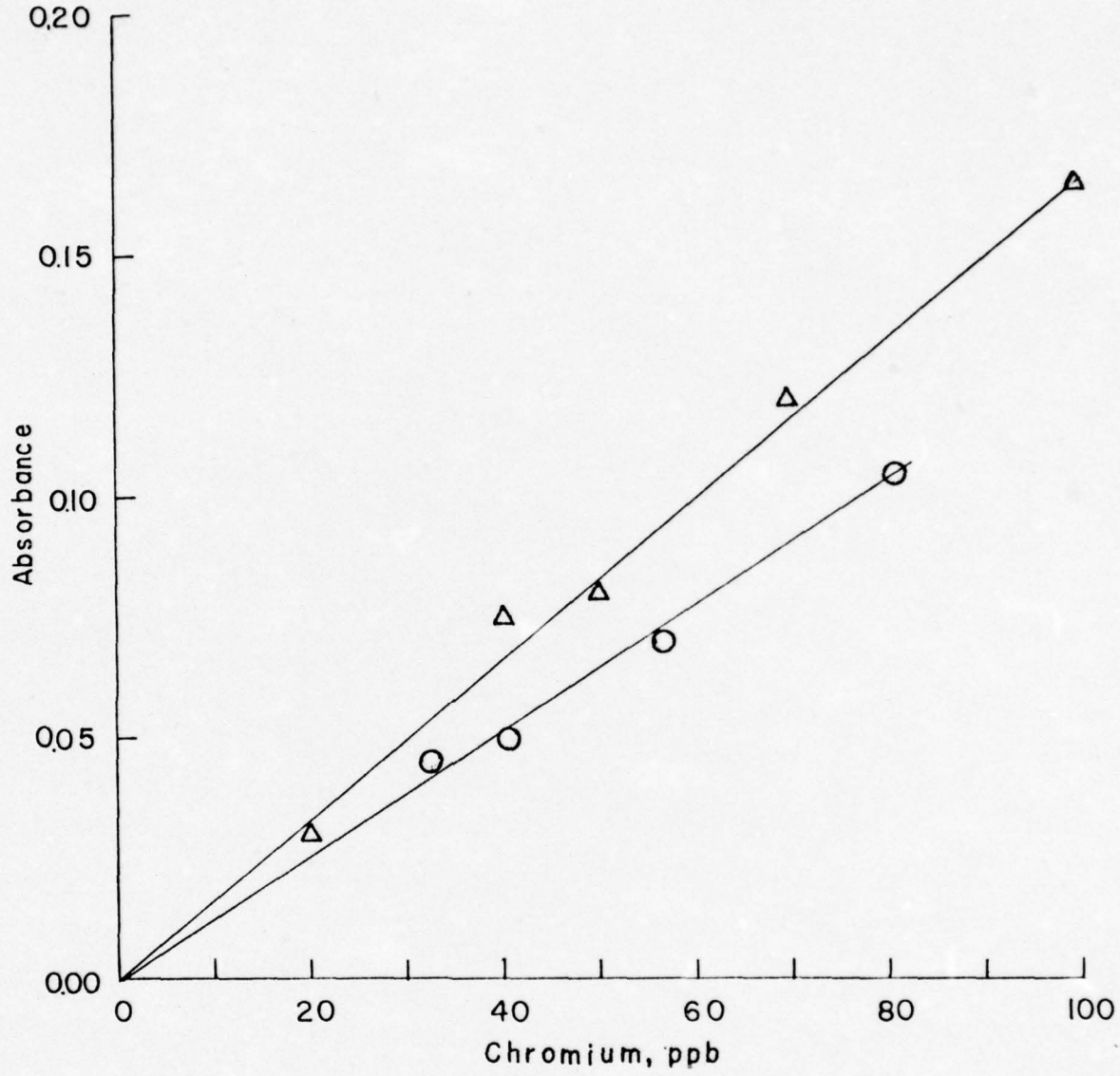


Figure 14. Analysis of Chromium (VI) and Chromium (III) by the Aliquot Method. Δ Chromium (XI), O Chromium (III).

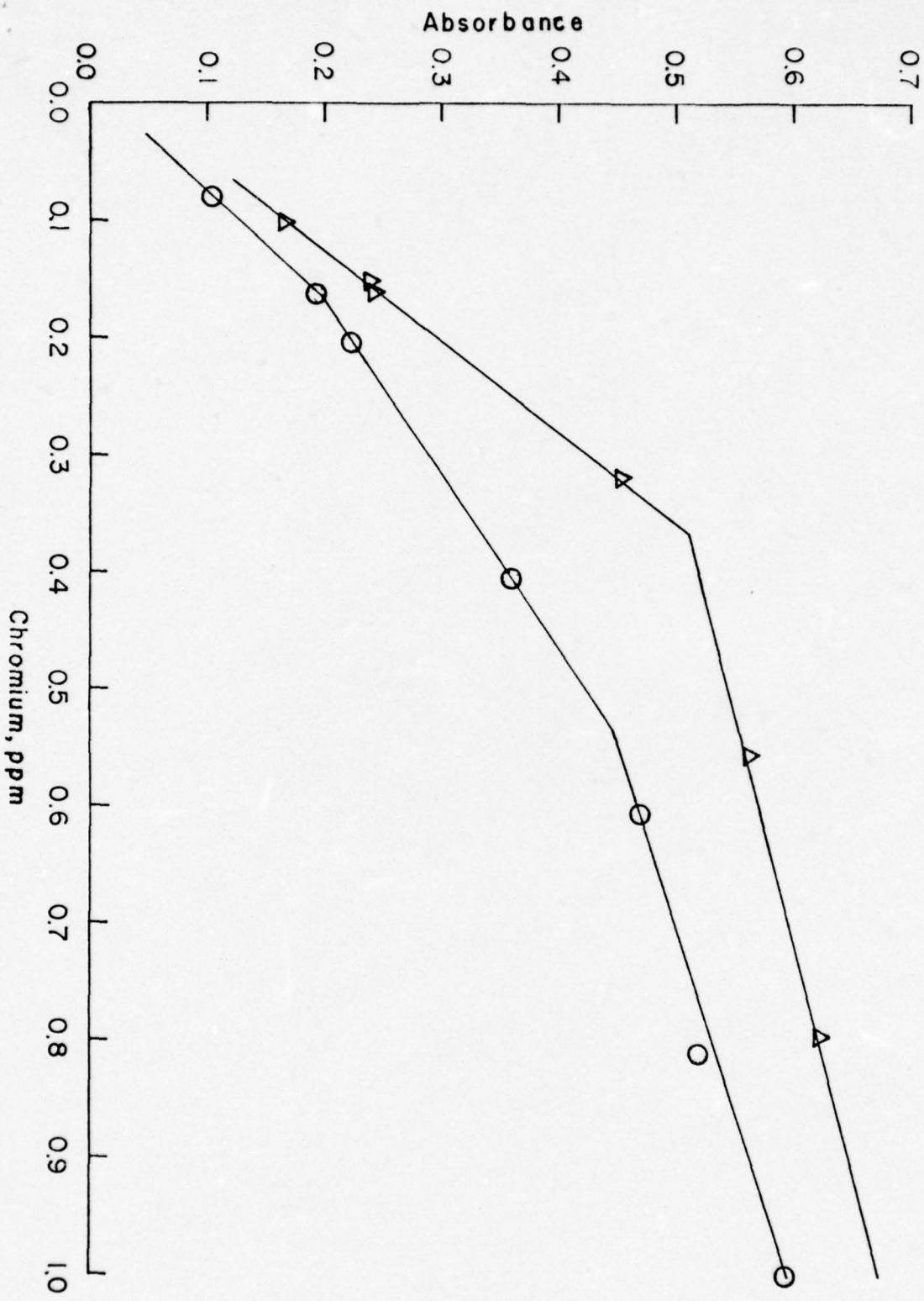


Figure 15. Determination of Chromium Using the Aliquot Method and Linear Voltage Programming. Δ Chromium (VI), O Chromium (III)

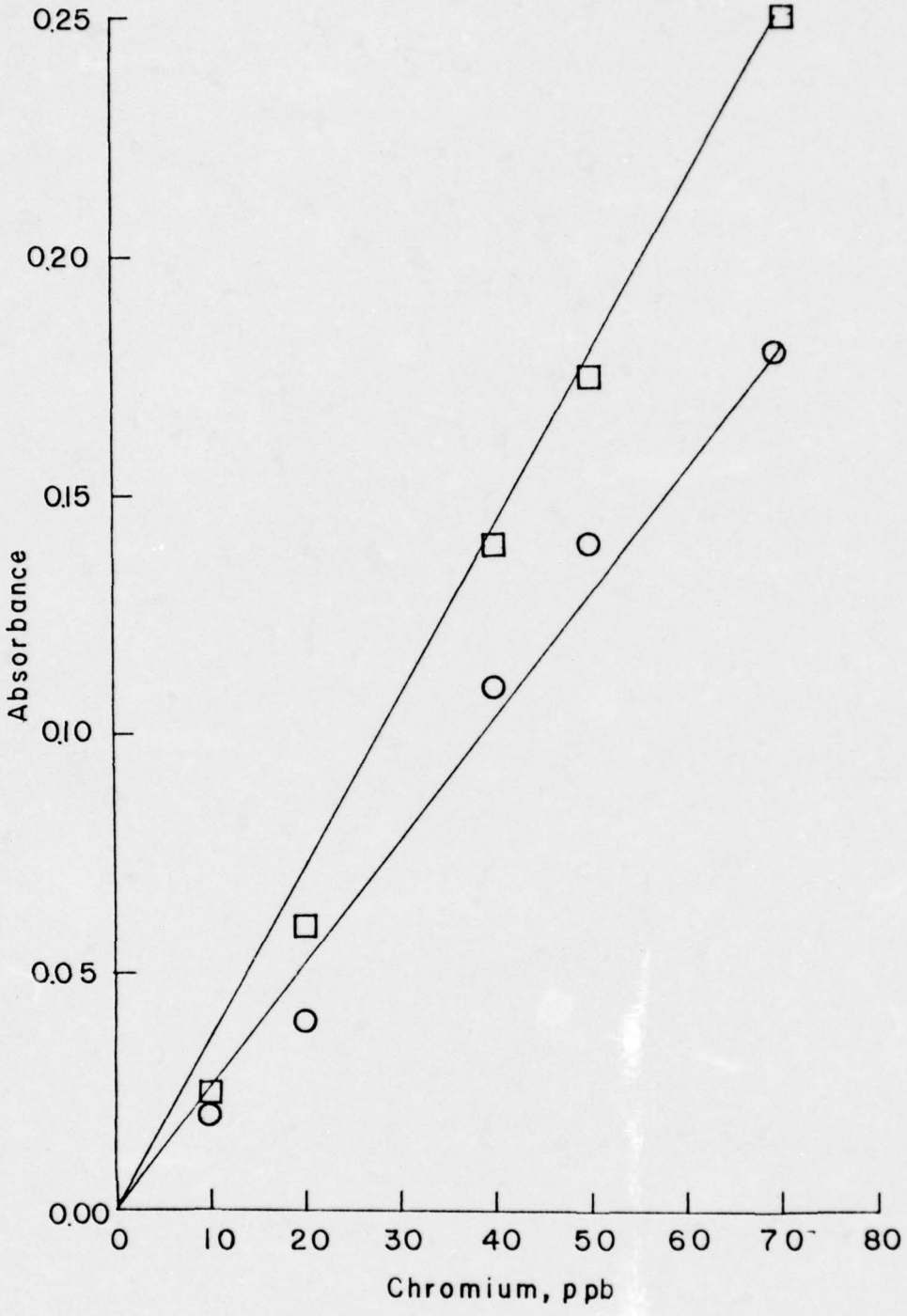


Figure 16. Enhancement of the Chromium Atomic Absorption Signal by Hydrogen Gas with a Carbon Tube Atomizer. □ H_2 gas, O no H_2 gas.

SILVER

The soaking method was utilized for silver in the hope of attaining the necessary sensitivity to analyze natural waters which commonly contain less than 2 ppb silver (1). The instrument and HCL parameters were adjusted according to the Varian Analytical Methods manual. An atomization setting of 22 was employed.

Silver: wavelength, 328.1 nm
slit width, 100μ
lamp current, 3 mA

All silver standards were freshly prepared by serial dilution of a standard silver nitrate solution (973) ppm). Baker A. R. silver nitrate (0.7664 g) was dissolved in 10-15 ml of concentrated nitric acid and diluted to 500-ml in a volumetric flask. For each silver concentration, five milliliter samples were pipetted into the 5-ml polypropylene beakers discussed earlier.

The calibration curve for a 100 second second soaking time (0-39 ppb) has two linear portions; the first portion extending between 0 and 27 ppb, Figure 17. For a 200 second soaking time, two ranges of approximate linearity are again observed with the first portion corresponding to 0-19 ppb. From the calibration curve for the region encompassing 48-780 ppb, two linear sections are found (48-194 ppb, and 194-780 ppb), Figure 18.

The sodium salts of nitrate, carbonate, sulfate, and bicarbonate were examined at a concentration of 1 nM for any effect on the absorbance of a 1 ppm silver solution (as silver nitrate). The results for sodium sulfate and bicarbonate were statistically identical to those for silver nitrate alone.

Interferences for Silver using the Soaking Method*

added electrolyte, 10^{-3}M	percent signal change , Ag 1 ppm
$NaNO_3$	-6.1%
Na_2CO_3	14.6
$NaHCO_3$	0.0
Na_2SO_4	0.0

*50 second soaking time, 100-fold concentration excess of electrolyte over silver.

One millimolar cadmium sulfate and manganese sulfate each gave no effects on the silver signal, but cupric sulfate (63 ppm Cu) increased the silver signal dramatically. Since copper has atomic transition lines at 3273.96 and 3279.82 Å of which the former is much more intense and silver has an atomic transition at 3280.68 Å (2), it is conceivable that copper atoms could

Interferences for Silver using the Soaking Method*

Added salt, 10^{-3}M	percent signal change, Ag, 1 ppm
$MnSO_4$	0
$CdSO_4$	0
$CuSO_4$	40.7

*50 second soaking time and 100-fold concentration excess for salt over silver.

absorb silver HCl radiation given the proper slit width. If the transmittance is set at 100% for the 3280.68 Å line used in silver analyses, the radiation from the copper HCL at this wavelength is approximately 5% T. However, no absorbance can be observed at the silver analytical wavelength using the copper HCL and a solution containing 1 mM cupric sulfate and 1 ppm silver. Thus, rather than the enhancement being a

direct result of copper absorption of silver HCL radiation, some other interaction must be the cause.

The sensitivities for the carbon tube and soaking methods for determining silver are listed in the following table.

	sensitivity, ppm	absolute sensitivity, g
carbon tube (5μℓ)	2.7×10^{-4}	1.35×10^{-12}
soaking, wire loop (5 ml)		
100 sec	5.2×10^{-4}	2.62×10^{-9}
200 sec	3.1×10^{-4}	1.55×10^{-9}

The calibration curve for silver employing the carbon rod is quite linear (0-39 ppb), Figure 19. With the exception of an atomization setting of 65 for the carbon tube atomizer power supply all conditions are similar to the zinc analysis.

In Figure 20, a calibration curve is shown for the determination of silver in the region 0-156 ppb by the aliquot method using IVP. The plot exhibits curvature toward the x-axis of concentration greater than 39 ppb silver. The sensitivities and absolute sensitivities are given for the aliquot method as well as the soaking method as a means of comparing the two trace analysis techniques. Although the aliquot method is less sensitive for the determination of silver, it is more rapid than the soaking method.

	sensitivity, ppm	absolute sensitivity, g
aliquot/method (5 μℓ)	1.72×10^{-3}	8.59×10^{-12}
Soaking method (5 ml)		
100 sec soak	0.52×10^{-3}	2.62×10^{-9}
200 sec soak	0.31×10^{-3}	1.55×10^{-9}

Figure 20. Determination of Silver by the Aliquot Method with LVP.*

Ag, ppb	15.6	59	78	117
absorbance	0.04(0.004)	0.100(0.005)	0.170(0.008)	0.225(0.003)
	156			
	0.255(0.007)			

* Standard deviation for 5 μℓ aliquots given in parentheses.

References:

1.) R. D. Ediger, At. Abs. Newsletter, 12, 151 (1973)

2.) W. F. Meggers, C. H. Corliss and B. F. Scribner, Tables of Spectral Lines Intensities, NBS Monograph, Part 1, U.S. Dept. of Commerce (May, 1975).

Silver Determination by Atomic Absorption Spectrometry

Figure 17. Soaking Method

absorbance	0.22(0.01)	0.27(0.01)	0.36(0.01)	0.405(0.009)
concentration, ppb	48.5	97.0	194	291
	0.46(0.06)	0.62(0.05)		
	390	780		

Figure 18, Soaking Method

a) 100 sec. soak

absorbance	0.03(0.0)	0.065(0.003)	0.14(0.01)	0.190(0.002)
concentration, ppb	3.88	7.76	19.4	27.2
	0.220(0.006)			
	38.8			

b) 200 sec. soak

absorbance	0.05	0.11	0.235	0.26	0.29
concentration, ppb	3.88	7.76	19.4	27.2	38.8

Figure 19, Carbon Tube Method

absorbance	0.06(0.01)	0.18(0.02)	0.47(0.04)	0.66(0.02)
concentration, ppb	3.88	7.76	19.4	27.2
	0.91(0.02)			
	38.8			

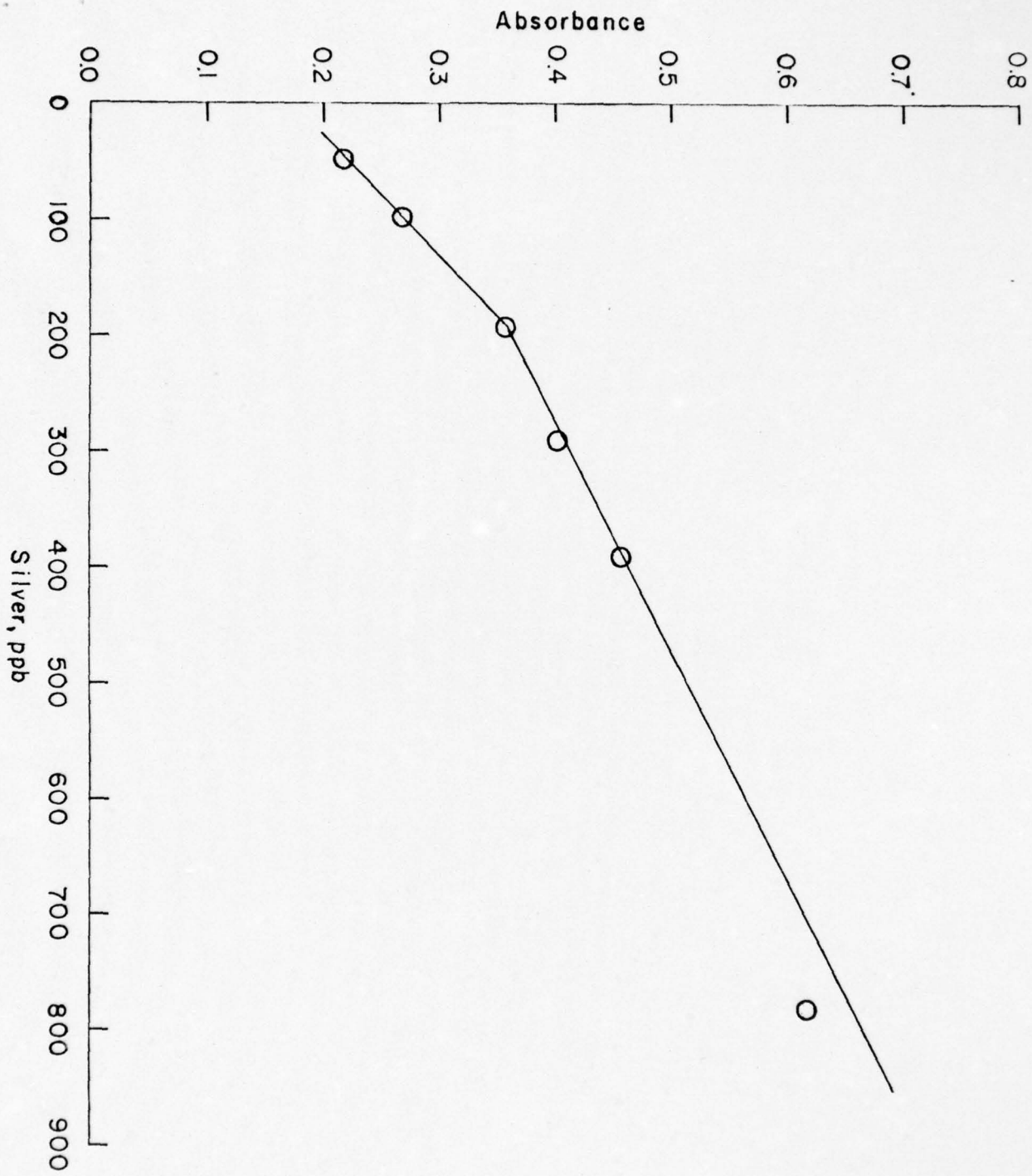


Figure 17. Silver Determination by the Spontaneous Preconcentration Method (100 second soaking time) over the Range 0-1 ppm.

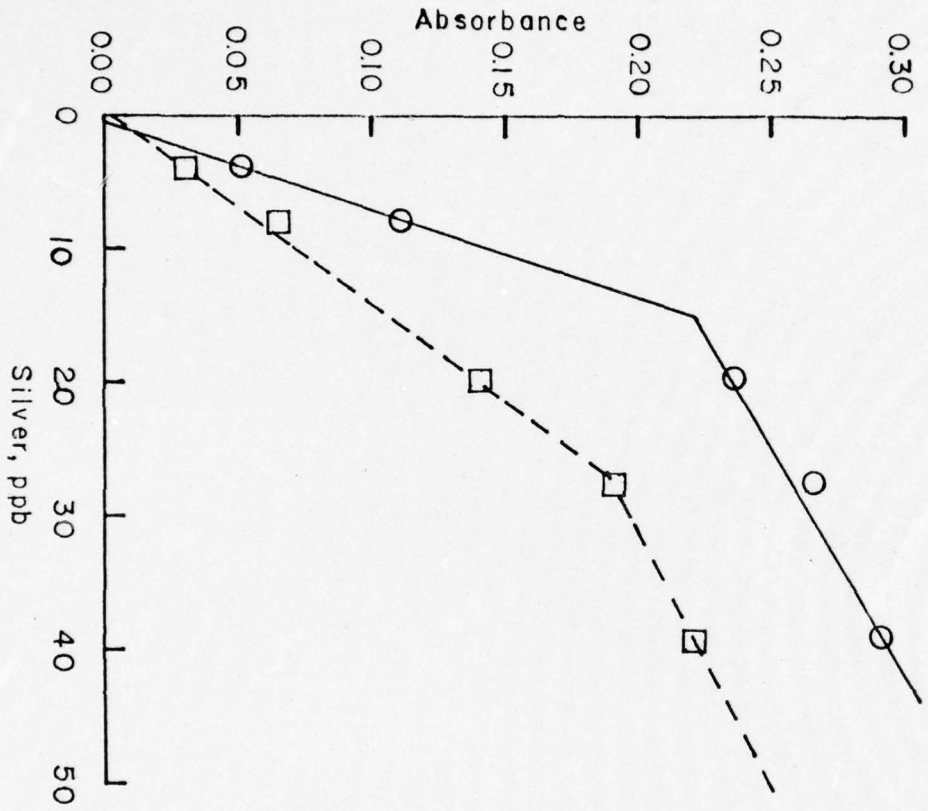


Figure 18. Analysis of Silver by the Soaking Method. O 200 second soaking time, 100 second soaking time.

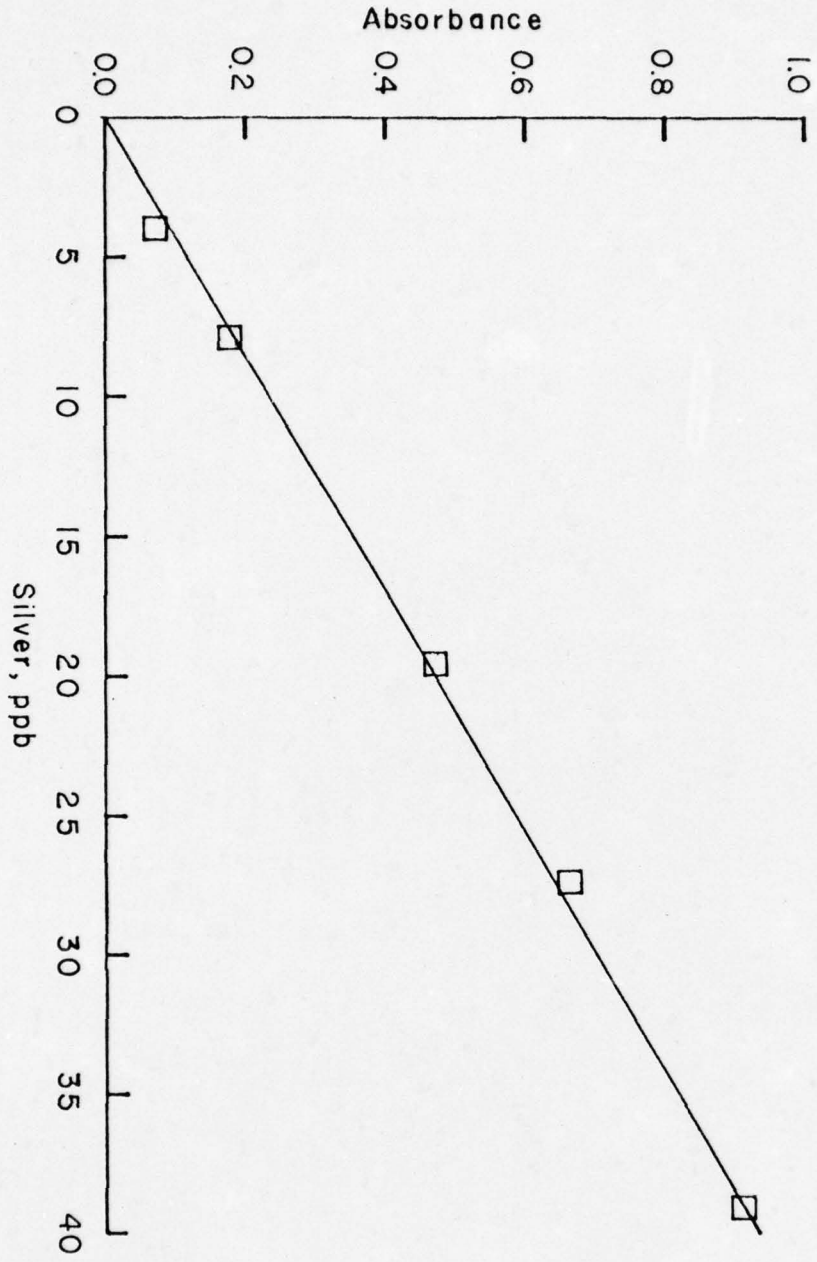


Figure 19. Silver Determination by the Carbon Tube Method.

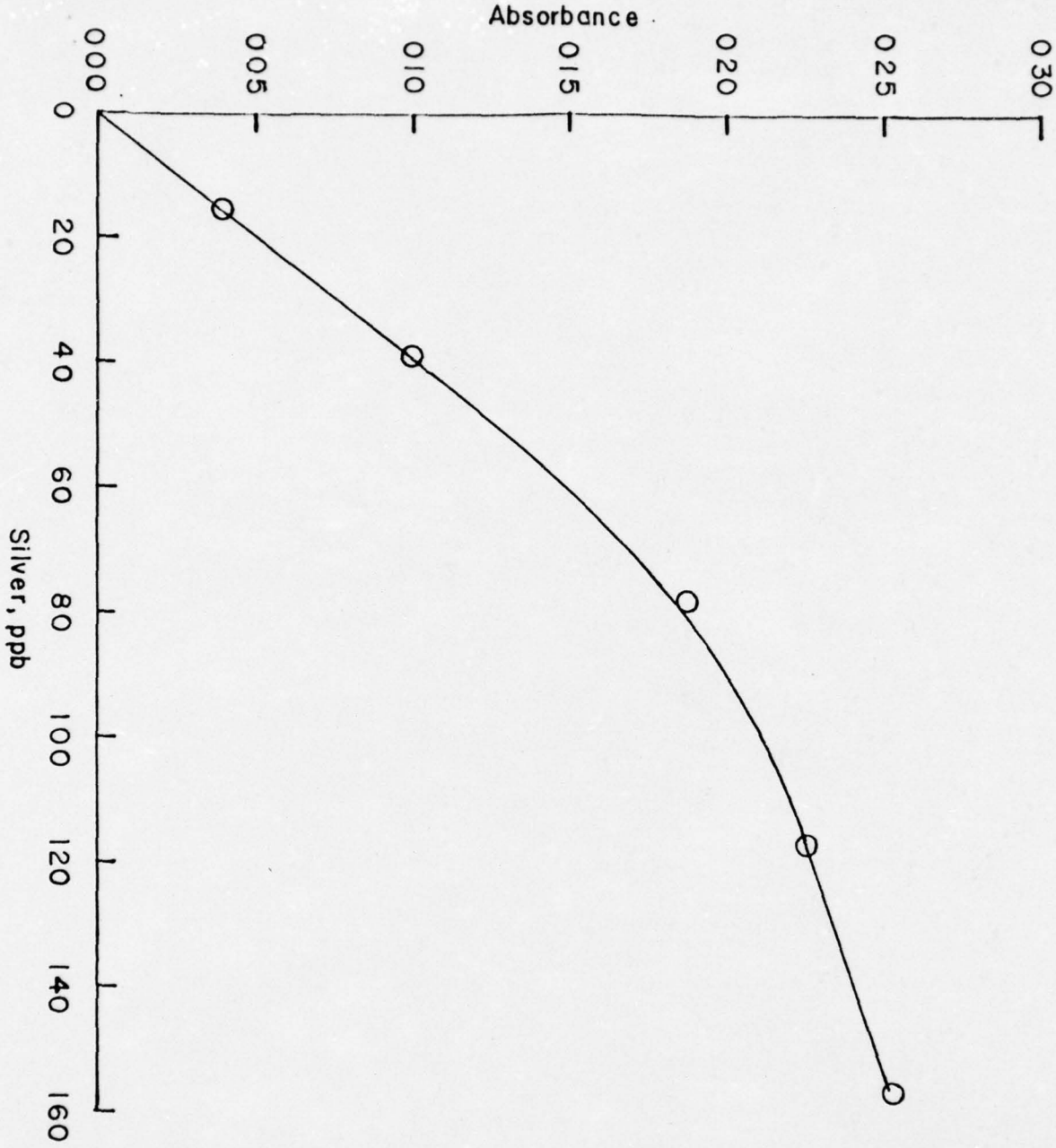


Figure 20. Analysis of Silver by the Aliquot Method.

MANGANESE

Sensitivities reported for the analysis of Manganese by atomic absorption spectroscopy are quite good (0.033 µg/ml) (1) which requires careful cleaning of all materials used in preparing Manganese solutions. The procedure recommended by Karin (2) has been followed and has been described in detail under the subheading Zinc.

All Manganese determinations were carried out using both the aliquot and soaking methods. The instrument settings for the Varian AA-5, Varian Techtron Manganese Hollow Cathode Lamp and the Hydrogen Continuum Lamp were adjusted according to Varian's manual "Analytical Methods for Flame Spectroscopy" (1).

Manganese: wavelength, 279.5 nm
slit width, 50µ
lamp current, 5mA

The standard, stock solution of Manganese was prepared by dissolving 1.801 grams of $MnCl_2 \cdot 4H_2O$ (Matheson, Coleman and Bell, reagent grade) in doubly distilled, deionized water and enough concentraded HCl (Baker, A.R.) to bring the pH between 3-4 upon dilution to 500 ml. in a volumetric flask. Standard solutions were prepared by subsequent dilution of the stock solution.

A 5 µl sample size was employed in both the wire loop techniques and the carbon rod technique, the latter used as a reference method, by means of a 5µl autopipette (autopette). For the wire loop technique, the inert gas flow of N_2 was adjusted to 1.959 liters/min and during atomization a reducing atmosphere of H_2, at a flow of 225 ml/min. and during atomization a reducing atmosphere of H_2, at a flow of 225 ml/min.

The Variac settings were as follows: 12-drying cycle, 35-atomization cycle. These settings gave the best signals. All absorbance measurements were determined from peak heights since the peaks are quite sharp and duration times are extremely short. Selenium analysis has been done previously in our labs, recording both the integrated absorbance and the peak height absorbance. Peak height measurements gave results between 95 and 98 percent of the integrated absorbance. Therefore, peak heights were used as the absorbance values.

During the course of the Manganese analysis, modifications were made on the support for the atomizer. With the aid of the U.N.O. machine shop, an adaptor was constructed to fit the atomizer to the commercially available Varian AA-5 burner base, which fits on the optical rail and is equipped with controls for horizontal, vertical and rotational alignment. This would increase the precision of optical alignment.

The calibration curve for Manganese over the concentration curve of 0.05 ppm - 0.500 ppm is shown in Figure 21. Between 0.200 ppm and 0.500 ppm curvature to the concentration axis is observed. The curve intersects the origin of the calibration plot indicating no background absorbance due to non-atomic absorption was observed. For the concentration range between 200 ppb and 1.00 ppm a less sensitive wavelength of 321.7 nm may yield a linear calibration curve (1).

An expanded calibration curve in Figure 22 for Manganese solutions over the concentration range of 1.0 ppb - 100.0 ppb indicates there is curvature towards the concentration axis above ~ 20 ppb. Again the curve goes through the origin indicating no background absorbance due to non-atomic absorption. Non-atomic background correction on both calibration curves using the hydrogen continuum lamp confirmed zero background absorption. The same wire loop was employed in both calibration curve determinations.

Sensitivities for the determination of Manganese by the aliquot method were calculated according to reference 3. In order to calculate the sensitivity, a concentration giving an absorbance of 0.1 is employed.

Manganese:

	Sensitivity (ppm)	Sensitivity (grams)
Figure 21	1.9×10^{-3}	9.6×10^{-12}

As a reference method, the Varian Techtron Model 63 Carbon Rod Atomizer was used to analyze the Manganese standard solutions. A calibration curve employing the carbon rod atomizer is seen in Figure 23. There is greater sensitivity with the carbon rod method.

Manganese:

	Sensitivity (ppm)	Sensitivity (grams)
Carbon Rod	2.8×10^{-4}	1.4×10^{-12}

The calibration curve exhibits similar shape as that for the aliquot method. There is linearity to approximately 0.260. Between 0.200 and 2.0 ppm curvature towards the concentration axis is observed.

A homemade power supply was employed to dry and atomize the sample for the carbon rod analysis (4). A drying setting of 20 volts and an atomization setting of 80 volts were used for the determination of Manganese. A nitrogen flow rate of 4 liters/min. was used as recommended by the Varian Techtron Model 63 manual (3). Hydrogen, although recommended by the Varian manual, was not employed.

An interference study by the aliquot method was obtained. Sodium salts of anions and transition metal sulfates were added to a standard manganese solution and peak height absorbances were recorded. The % signal change was calculated by the following equation:

$$\% \text{ signal change} = \frac{(Ab_{ave}Mn - Ab_{ave}(Mn + \text{interferent})) \times 100\ \%}{Ab_{ave}Mn}$$

The results are shown in the following table:

10^{-3} M	Salt	% Signal change, Mn 200 ppb
$CuSO_4$	$CuSO_4 \cdot 5H_2O$	-54
$CdSO_4$	$3CdSO_4 \cdot 8H_2O$	-19
$NaNO_3$	$NaNO_3$	-16
Na_2SO_4	Na_2SO_4	-30
NaCl	NaCl	-1

All of the interferent salt solutions caused a depression in the manganese signal. Although it is realized that upon addition of the respective anions, sodium ion is added, this could not be avoided, nor separated. In the case of the transition metal interferences, sulfate ion was added. Therefore, the change in signal can only be considered to be caused by cation and anion of the respective interferent.

The actual benefit of such interferent calculations are in doubt. As indicated by Smeyers-Verbeke et.al, in an extensive study of interferents, changes in the concentration of the interferent of interest with the same concentration of analyte yielded varying signal changes (5). In other research, in which Sensmeier et.al. employed a tantalum strip atomizer, it was reported that interferents gave increased or decreased silver signals. When a solution of silver containing all the interferents was analyzed, there was no effect on the silver signal (6). Previous results in our lab also show that there are no general trends in interference studies (4, 7).

To further substantiate the results mentioned above, a solution of 0.209 ppm Mn containing each of the interferents at a 10^{-3}M concentration led to a decrease in signal which obviously could not be deduced quantitatively from the results of the individual interferents. The % signal change of this solution was 40.

The problem of interference to an atomic absorption measurement can best be circumvented by the method of standard additions. In this method a small volume of unknown sample is added to a constant volume of each of the standard solutions. A Beer's Law Plot is constructed, and at the point the curve intersects the concentration axis, the unknown sample concentration is obtained.

At the time the calibration curve was obtained for the carbon rod atomizer, Figure 23, samples from the army were analyzed. Results are shown in the following table:

Sample Number	Absorbance (ave)	Concentration Found (ppm)
15	1.25	0.110
21	1.59	0.155
22	1.54	0.150
23	1.53	0.145
24	1.39	0.130

Attempts were made to use the aliquot method in determining the unknown army sample concentrations. However, due to large matrix effects, there were problems with reproducability. Several attempts were made to remove these effects, including Linear Voltage Programming (4), but all attempts failed. The aid of a standard additions plot might help explain this problem, but due to the limited volumes of unknown sample available, this was not possible. Through future research we hope to explain this problem.

Many calibration curves, other than the representative ones described here in exhibit slight changes in shape and range of linearity. One parameter that can account for this change is the wire loop construction. Since the wire loops are hand-constructed, reproducability is only fair. With the aid of the U.N.O. machine shop, a template was recently constructed to improve the shape and reproducability problem. Results of this improvement will be discussed in our next quarterly report.

The soaking method (8) was also investigated for manganese analysis. The results were spurious. There were soaking times as long as 1500 seconds with little or no signal obtained.

The mechanism, during the soaking analysis, for an analyte to preconcentrate on the wire loop has been described by an ion-exchange mech-

mechanism (8). Manganese being a +2 cation would therefore be expected to preconcentrate on the wire. It is anticipated that future surface studies of the wire surface and mechanistic studies of the solution-wire interface will better explain the preconcentration phenomenon.

One last point is worth mentioning. A quantitative determination of the relative concentrations of manganese that would be detected by the carbon rod method and not by the aliquot method has been computed. The calculation is as follows:

$$\frac{10^6\ \mu g/g \times (\text{sensitivity (g) (aliquot)} - \text{sensitivity (g) (carbon rod)})}{5 \times 10^{-3}\ \text{ml sample volume}}$$

The results are as follows:

	Result
Figure 21 vs. Figure 23	1.6 ppb

At a concentration which gives 1% absorption, there is only a difference of 1-2 ppb between the two methods. This is quite small and is offered here to emphasize that sensitivity measurements must be inspected carefully.

BIBLIOGRAPHY

1. Analytical Methods for Flame Spectroscopy, Varian Instrument Division, 611 Hansen Way, Palo Alto, California 94303
2. R. W. Karin, J. A. Buono, J. L. Fasching, Anal. Chem., 47, 2296 (1975).
3. Instruction Manual for Model 63 Carbon Rod Atomizer, Varian Techtron, p. 1-9, (1972).
4. M. P. Newton, Ph.D. Dissertation, L.S.U.N.O., (1974).
5. J. Smeyers-Verbeke, Y. Michotte, P. Van der Winkel and D. L. Massart, Anal. Chem., 48, 125, (1976)
6. M. R. Sensmeier, W. F. Wagner, and G. D. Christian, Z. Anal. Chem., 277, 19 (1973).
7. J. V. Chauvin, Thesis, L.S.U.N.O. (1972).
8. M. P. Newton and D. G. Davis, Anal. Chem., 47, 2003 (1975).

MANGANESE DETERMINATIONS BY A. A| SPECTROSCOPY

Figure 21 Aliquot Method

Absorbance				0.114	0.134	0.188	0.205
Concentration, ppm				0.050	0.100	0.200	0.300
Standard Deviation				0.00	0.009	0.004	0.005

Figure 2, Con't.

0.210	0.221	0.222*
0.400	0.500	1.00
0.006	0.00	0.005

Figure 22 Expanded Working Curve, Aliquot Method

Absorbance	.003	.023	.042	0.114	0.134
Concentration, ppb	1.0	6.0	10.0	50.0	100.0
Standard Deviation	0.00	0.002	0.003	0.00	0.009

Figure 23 Carbon Rod Method

Absorbance	0.156	0.802	1.14	1.91	2.18	2.44	2.58	2.7[illegible]
Concentration, ppm	0.010	0.050	0.100	0.200	0.300	0.400	0.500	1.00
Standard Deviation	0.020	0.035	0.067	0.045	0.003	0.133	0.028	0.035

* not shown on calibration curve

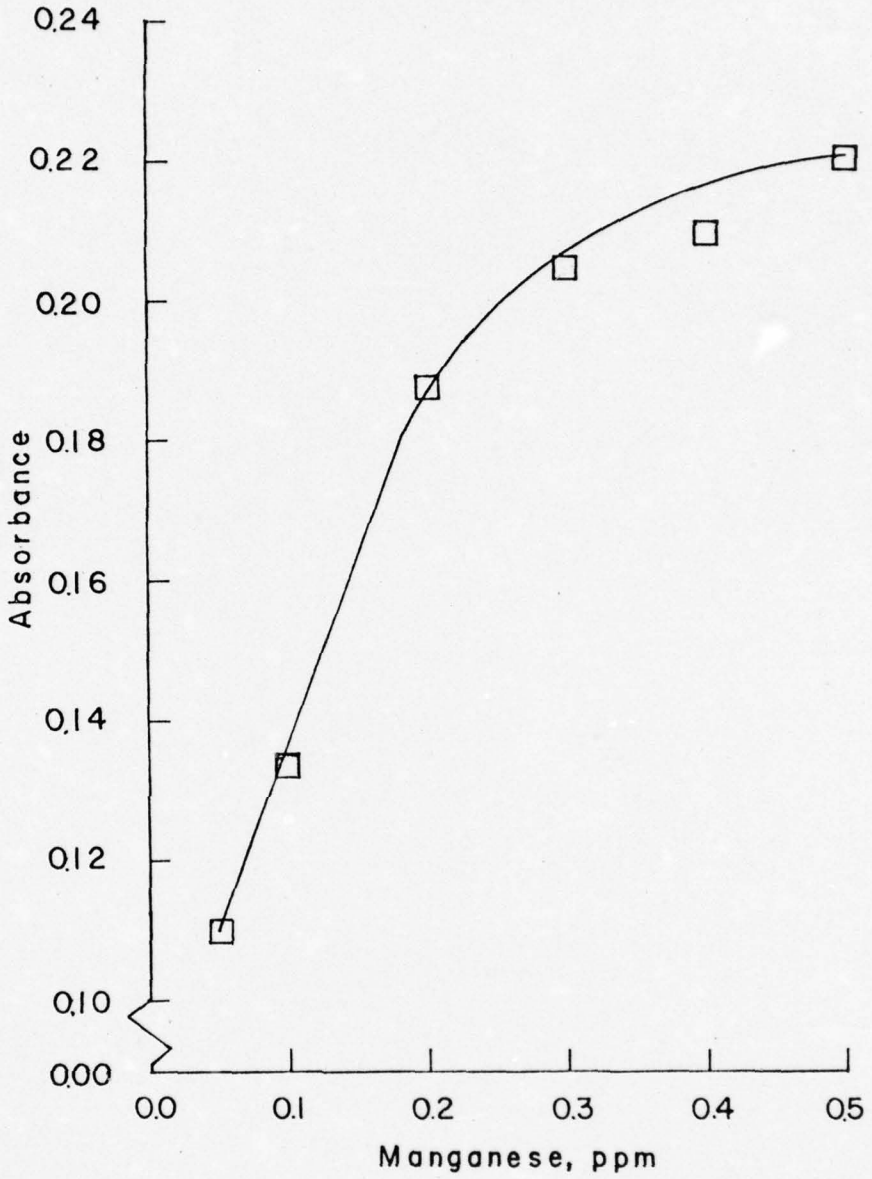


Figure 21. Calibration Curve for the Determination of Cadmium by the Aliquot Method.

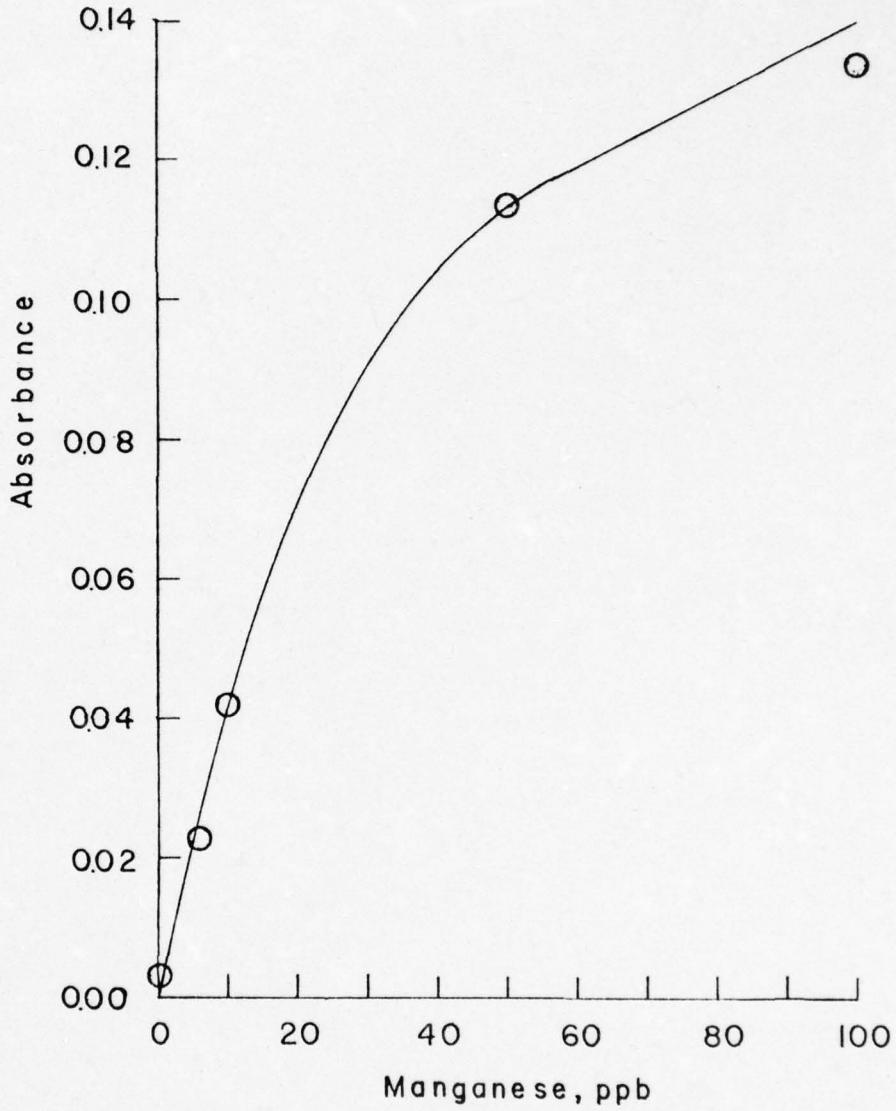


Figure 22. An Expanded Working Curve for the Determination of Manganese by the Aliquot Method.

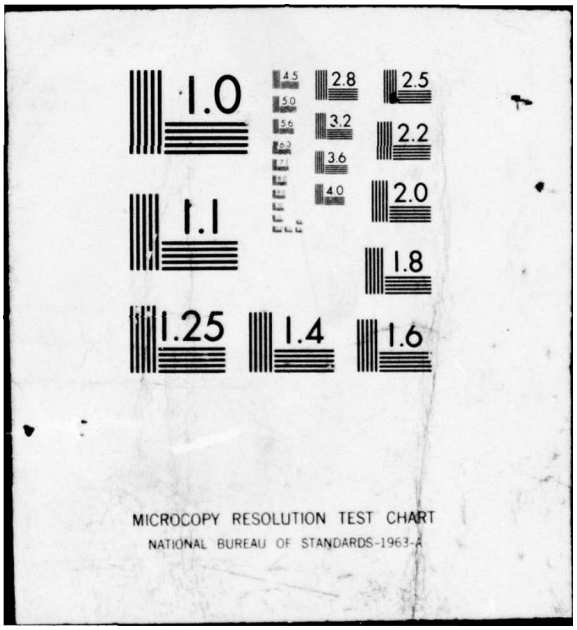
AD-A032 016 NEW ORLEANS UNIV LA DEPT OF CHEMISTRY F/G 7/4
ANALYSIS BY FLAMELESS ATOMIC ABSORPTION.(U)
OCT 76 C L YUAN, J V CHAUVIN, J F MOLINA DAMD17-75-C-5048
UNCLASSIFIED 357-30-5105 NL

2 OF 2
AD
A032 016



END

DATE
FILMED
1-77


1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
6.3
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

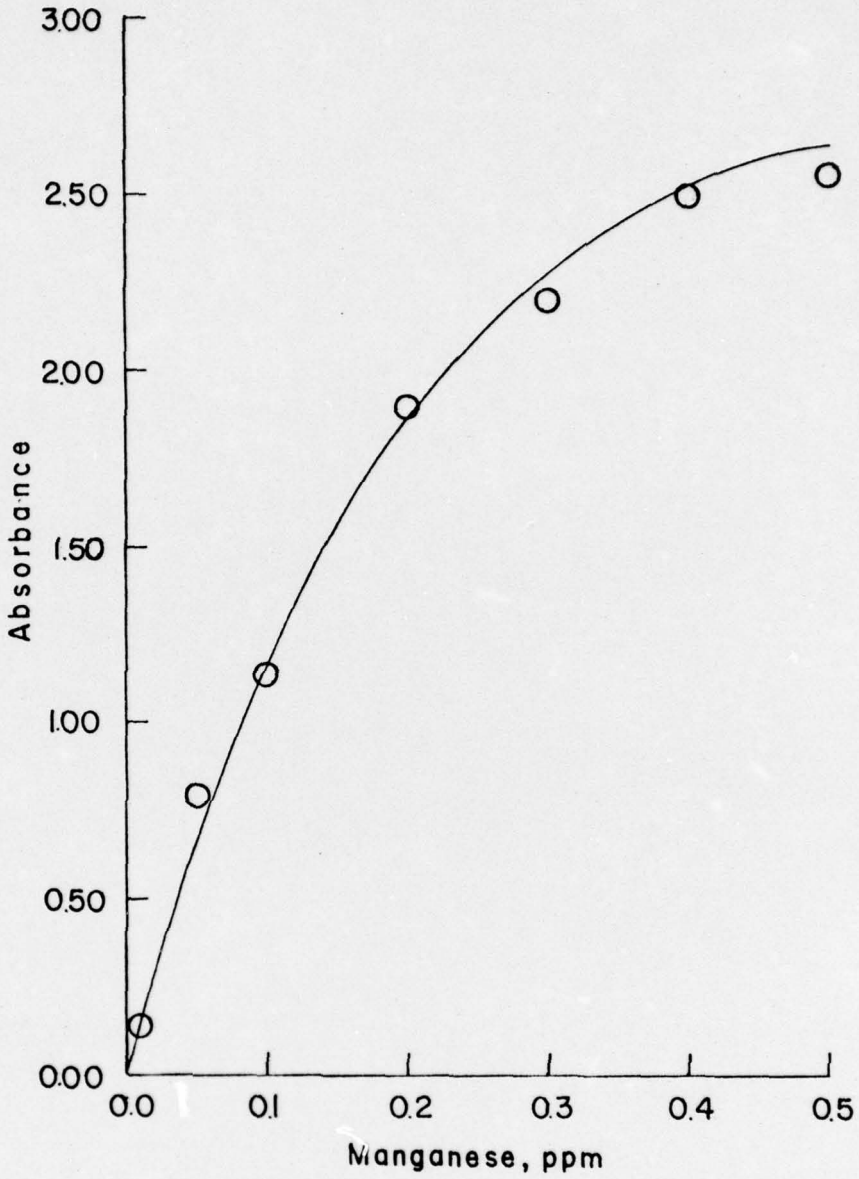


Figure 23. Analysis of Manganese by the Carbon Tube Atomizer over the Range, 0-0.5 ppm.

CADMIUM

All cadmium determinations were carried out using the aliquot method and the Perkin-Olmer 306 AAS. The recommended operating conditions are (1)

Cadmium: Wavelength
Slit width setting
Lampcurrent: 10 ma

Atomization settings of 38-42 and a drying setting of 20 were utilized. Higher drying settings yielded erratic absorbance signals - suggesting that some sample may be valatilized at high drying temperatures. Either argon or nitrogen were used as the sheathing gas since both yeilded similar sensitivities. A Nitrogen flow rate of 2.44 ℓ/min and a hydrogen flow rate of 204 ml/minute resulted in the best sensitivity and increased loop life.

Two stock 1000 ppm Cd. solutions have prepared from anhydrous $CdCl_2$. One of these is about six months old and consists of 1.6310 grams of $CdCl_2$ dissolved in 1 liter of distilled, deionized water. The other solution is about one week old and was prepared by dissolving 1.6310 g of $CdCl_2$ and about 2/3 ml of concentrated HNO_3 in enough distilled, deionized water to yield 1 liter of solution at a pH of 2. The nitric acid may be necessary to prevent absorption losses onto the container walls since 0.1 ppm standards prepared from each of the stock solutions yeilded very different absorbance readings. The sample prepared from the pH 2 stock read 0.17 absorbance units higher than a 0.1 ppm standard prepared from the older, unacidified stock solution.

Figure 24 shows the calibration curve extablished for Cadmium.

	Sensitivity, ppb	Sensitivity
Cadmium, 5μℓ aliquot	.88	4.4×10^{-12} g

Figure 24, Aliquot Method 5μℓ Sample

Cd concentration, ppb	50.2	99.5	149.7	198.9
Absorbance	0.256	0.440	0.576	0.640
Standard Deviation	0.022	0.030	0.028	0.006

BIBLIOGRAPHY

(1) Instructions Model 306 Atomic Absorption Spectrometer, Perkin-Elmer, Norwalk, Conn., 1972.

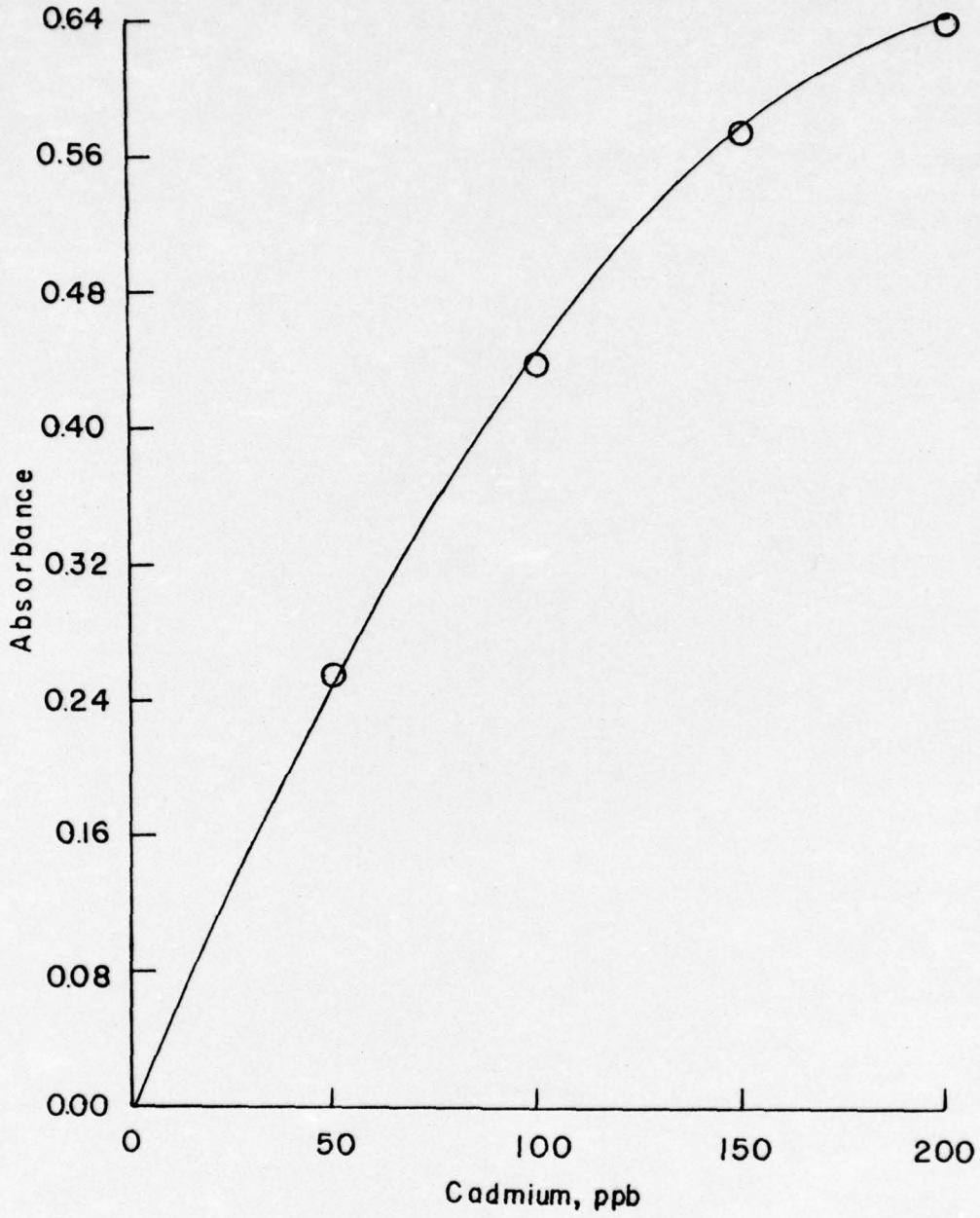


Figure 24. Calibration Curve for the Determination of Cadmium by the Aliquot Method over the Range 0-0.2 ppm.

COPPER

All glassware and polyethylene or propylene sample storage bottles are cleaned by soaking and scrubbing with micro™ soap solution, rinsed with copious amounts of tap water, then with 1:1 nitric acid, and finally with 1-2 mega-ohm distilled-deionized water. When necessary, films and stains that are not removed in the above procedure are treated with $K_2Cr_2O_7$-H_2SO_4 cleaning solution, then rinsed with tap water, and treated by the procedure described above.

The water used for the final rinse and for the preparation of solutions is made with a Corning Ultra-Pure apparatus set up as follows: tap water is passed through a Sears filter to remove dirt and large particulate matter; then through a Barnstead high capacity mixed resin deionizer; distilled in a glass of 1 liter capacity; collected in a polypropylene bottle from which it may be further purified by passage through two Corning filters - the first removes organics, the second is an ultar-pure deionizer. The conductivity of the water is monitored and the water is rejected if its resistance is less than 1 mega-ohm. Problems were encountered when the beads of the ultra-pure deionizer sloughed off into the storage vessel (a four gallon polypropylene aspirator bottle). Therefore the water was filtered through filter paper before it flows into the storage bottle. This stored water never yields any absorbance signal when analyzed as a blank.

All solutions are transferred to polypropylene bottles immediately after being prepared. Absorption losses on container walls do not seem to be a problem with copper - at least for storage periods of up to one month as shown in Table 1.

Table I

Absorbance of 1 Month Old and Freshly Prepared Copper Standards

Sample	Absorbance
1 month old 20 ppb Cu	.0090
Freshly prepared 20 ppb Cu	.0096
1 month old 30 ppb Cu	.0120
Freshly prepared 30 ppb Cu	.0126

Serial dilutions are usually made with a 50 ml-class A buret.

The 5 ml sampling cups were used directly from the package with no further treatment or cleaning. Disposable auto-pipet (5 microliter delivery) tips were rinsed several times with the solution being analyzed before being used to transfer that particular solution. It was not necessary to use a separate tip for each sample.

The results obtained with the soaking technique are very sensitive to the amount of loop immersed in the sample. In order to insure a reproducible soaking depth from sample to sample, it was determined that a volume of 6.8 ml in the sampling cup containing a magnetic stirring bar gave the greatest amount of loop submersion without wetting the contacts on the cell. 10 ml pipets graduated in 0.1 ml intervals are used to pipet samples into the sampling cup. The magnetic stirring bar is rinsed thoroughly with distilled water, dried, and placed in the sampling cup with ivory dipped forceps before the sample is pipetted.

The Perkin-Elmer Model 306 used for these studies (the Varian AA-5 was used for most other work) is a double beam instrument which can be operated with a simultaneous deuterium arc background corrector (DABC.) When the DABC is in use, the instrument becomes a single beam with the

hollow cathode and deuterium arc sources being passed alternately through the optical system. A multi-element (Co, Cu, Fe, Mn, Mo) Perkin Elmer HCL was operated at the recommended settings (1):

Copper: wavelength 324.8 nm
slit width setting: 4
Lampcurrent: 30 ma

In order to obtain corrected absorbance readings with the DABC, it is necessary to adjust the HCL until the images from both sources are superimposed. A recorder deflection of less than .05 absorbance units when the combined HCL and DABC beams are interrupted with a card indicates that the two sources are properly aligned. (1) Aqueous copper standards yielded similar absorbance readings with and without the DABC. The results reported in this annual report were obtained with the loop at the focal point of the HCL. An alternative procedure in which the loop would be located at the focal point of the DABC has not yet been examined.

A drying setting of 30 and an atomization setting of 70-76 on the NSU power supply were used for the analysis of copper. The best sensitivity for copper was obtained at atomization settings of 24-26 on the UNO power supply. An argon flow rate of 1.5 ℓ/min and a hydrogen flow rate of .15 ℓ/min gave the best results for copper.

Recorder expansions of x3, x10, and x30 are available. Usually an expansion of x3 or x10 is employed - the x30 expansion yields too much noise with the DABC in use. At x1, full scale deflection corresponds to a 10 mv, 1 absorbance unit signal. No other recorder sensitivities were available in the past although a 1 mv module is now available for use.

Soaking technique -

An open loop (figure 5) is used for the soaking method. 6.8 ml of solution are pipetted into a cup is raised to the position that yields the maximum amount of loop submersion without wetting the contacts and cell body. This position is used for all subsequent samples. The timer is set at 0 seconds, turned on, and when the hand passes the 10 second mark the cup is raised. At the appropriate time (usually 20 seconds later) the sampling cup is lowered. The rinsing cup containing distilled water, which is not stirred, is then raised and the loop rinsed for 2 seconds. The air-driven stirrer is left on continuously during the entire cycle. The loop is then dried for 5 seconds at a value of 30 on the drying variac. The brass enclosure is then moved into place over the loop, the hydrogren turned on, and 10 seconds later the sample is atomized. Occasionally the loop is cleaned at a setting higher than the atomization setting (with the drying variac) to remove any buildup. This buildup has not so far been encountered. The hydrogen is turned off after atomization or cleaning and a new cycle is begun. Argon flows continuously over the loop for both the soaking and aliquot methods of sampling

Aliquot Technique -

A closed single loop is used for the aliquot method. (Fig. 5)

The sampling cycle for the aliquot method consists of pipetting the sample onto the loop, drying at a setting of 30% until the sample is visibly dry, sliding the brass enclosure into place, turning on the hydrogen, and 10 seconds later atomizing the sample. The hydrogen is then turned off after power to the loop is discontinued and a new cycle begun. The aliquot method is considerably less time-consuming

and tedious than the soaking method.

Analysis of Data -

Peak heights are measured from an average baseline before the atomization peak with a millimeter ruler, recorded in millimeters, then converted to the appropriate absorbance reading through calculations involving the scale expansion used. At least 5 readings are taken on each sample. The standard deviation is calculated.

Results and discussion -

In the soaking method, sensitivity is increased if the sample is stirred while the loop is immersed in the solution. A 0.1 ppm copper solution was analyzed by soaking for 20 seconds. Absorbance readings of 0.021 and 0.014 were obtained for soaking with and without stirring, respectively. For the series of readings where the solution was not stirred during immersion, the solution was stirred in between soakings.

A soaking time versus absorbance study was performed and the results shown in Figure 25. Sensitivity can be improved by employing longer soaking times although the curve begins to level at longer soaking times.

Figure 26 shows the results of an absorbance versus concentration study using the soaking method while figure 27 depicts a calibration curve for a 5μl sample size using the aliquot method. A comparison of the sensitivities realized with both methods is shown in the following table.

	sensitivity, ppb	absolute sensitivity
Figure 26, soaking method (6.8 ml)	9 ppb	6.1×10^{-8} g
Figure 27, aliquot method (5 μl)	9 ppb	4.5×10^{-11} g

Although it originally appeared that deliberately oxidizing the loop by heating it to the atomization temperature without hydrogen would lead to increased sensitivity for the soaking method it appears that the limitation (decreased loop lift and poor precision) inherent in this method are too severe to warrant its adoption.

Attempts to oxidize the loop by soaking it in either a 1F HNO_3 solution or in a 3×10^{-3} F $K_2Cr_2O_7$, 0.18 F H_2SO_4 solution in order to increase the amount of copper that precontentrates on the loop were unsuccessful. No increase in sensitivity was observed after these treatments.

BIBLIOGRAPHY

(1) Instructions Model 306 Atomic Absorption Spectrophotometer, Perkin-Elmer, Norwalk, Conn., 1972.

Figure 25. Soaking Time vs. Absorbance for 100 ppb Cu - (6.8 ml)

Time (sec)	10	20	30	40	60	80	100
Absorbance	.012	.020	.030	.036	.045	.052	.060
SD	.002	.002	.002	.002	.002	.002	.004

Figure 26, Soaking Method, 20 Sec. submersion time, Unoxidized loop

Cu Conc., ppm	.1	.2	.3	.4	.5	.6
Absorbance	.059	.105	.128	.149	.173	.177
SD	.006	.002	.006	.008	.004	.006

Figure 27, Aliquot Method, 5µℓ sample

Cu Conc, ppb	48.9	100.7	150.2	201.2	249.2
Absorbance	.019	.045	.077	.097	.115
SD	.001	.003	.002	.008	.005

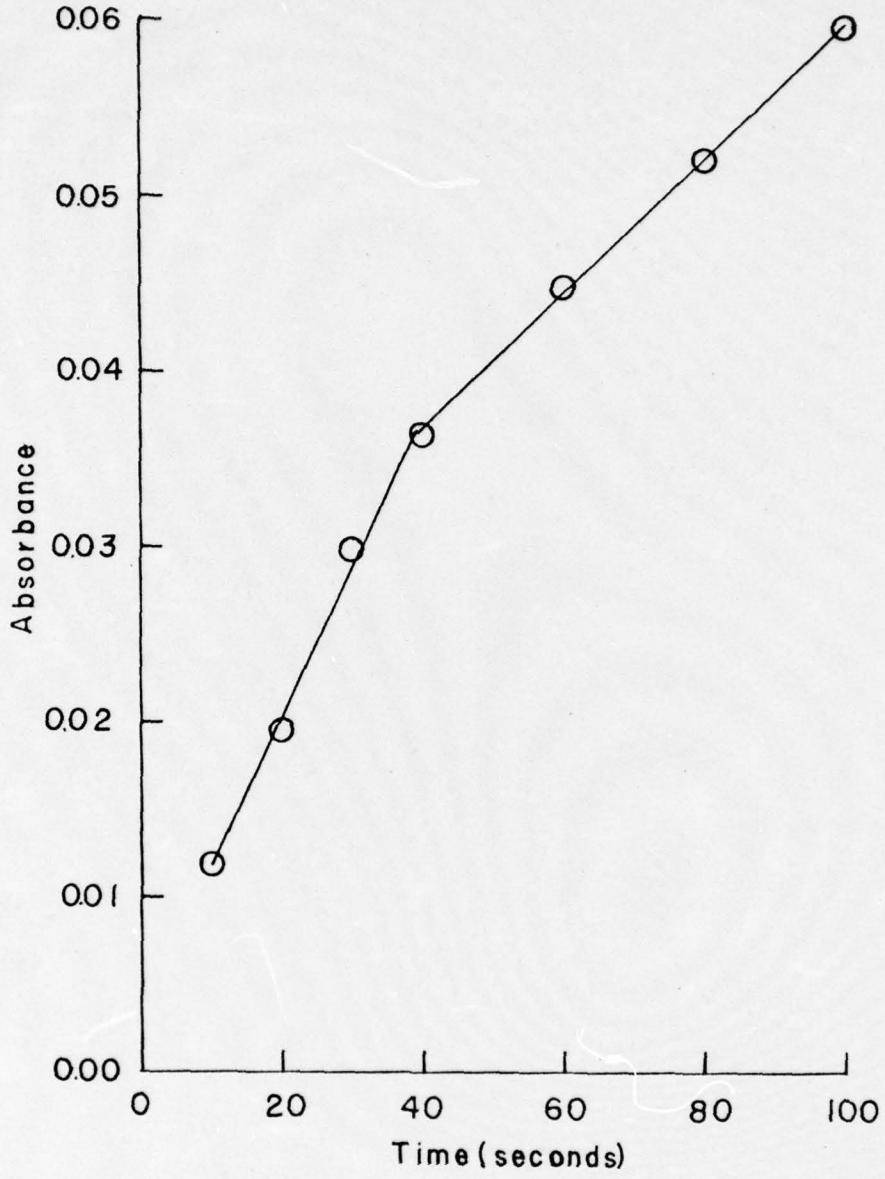


Figure 25. The Relationship between Absorbance and Soaking Time for a 0.1 ppm Copper Solution.

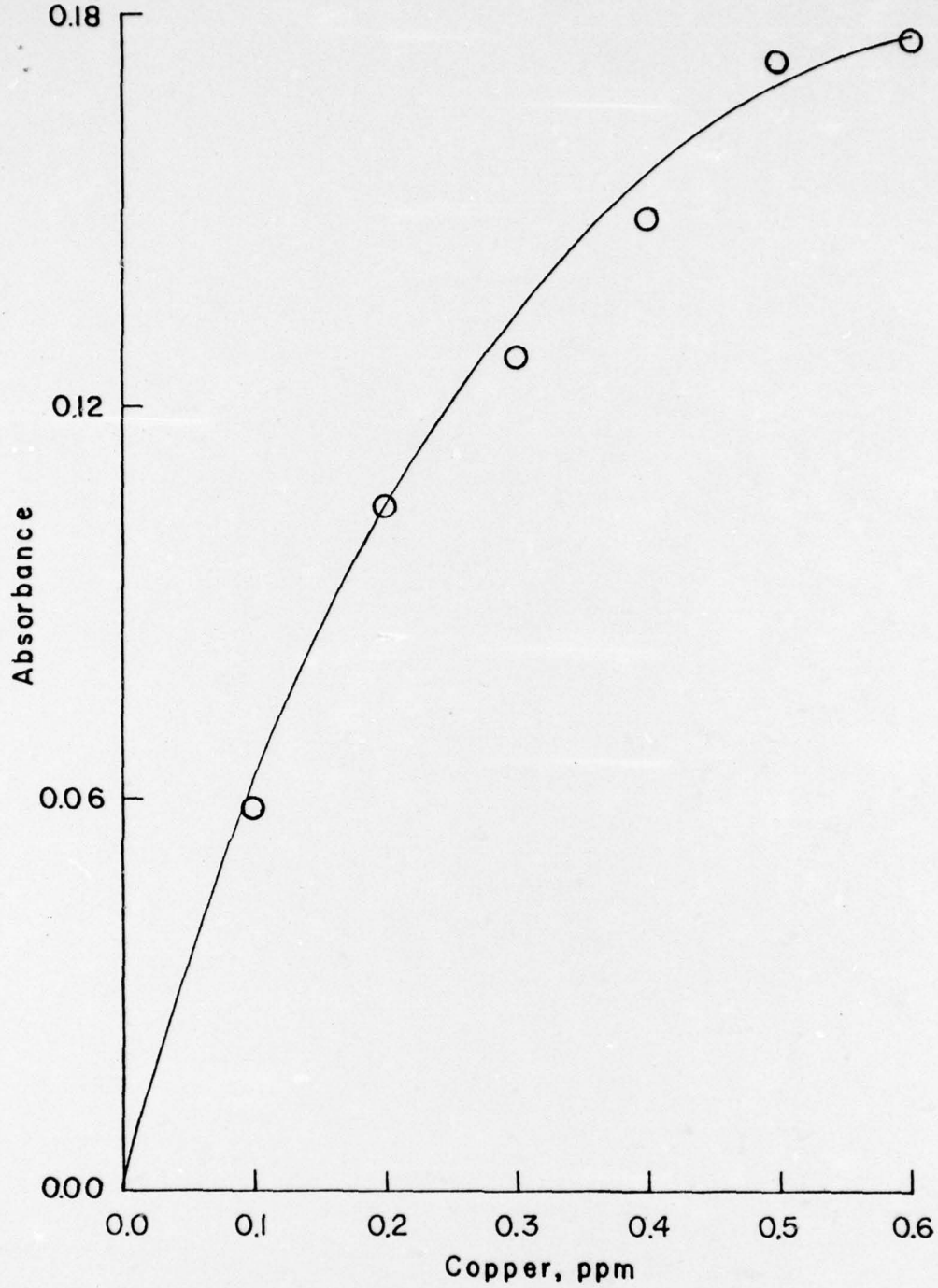


Figure 26. Working Curve for the Determination of Copper by the Soaking Method (20 second soaking times).

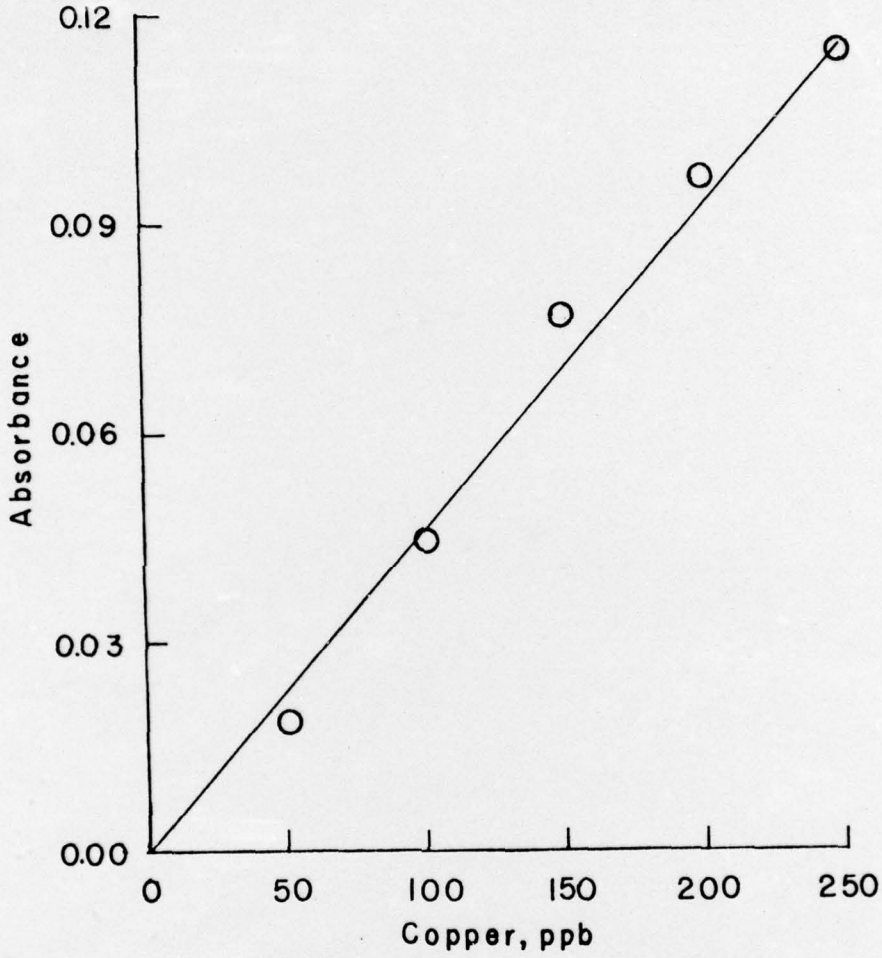


Figure 27. Calibration Curve for the Determination of Copper by the Aliquot Method.

LEAD

Using flame atomic absorption spectrometry the sensitivity calculated for the determination of lead is 0.11 ppm at 217.0 nm (1). In this work we will report the sensitivity and absolute sensitivity for lead using the wire loop aliquot method.

Experimental

Materials

Dissolve exactly 1.59852 g of lead nitrate (M. W = 331.23 g) in 1000 ml of doubly-distilled deionized water to make a 1,000 ppm lead stock solution.

All glassware and polyethylene or polypropylene containers are soaked in an Alconox solution and rinsed with tap water prior to immersion in a 50% nitric acid bath. After several days, the glassware and storage containers are taken out and rinsed thoroughly with copious amounts of tap water, followed by several rinses with doubly-distilled, deionized water. (2)

All solutions are transferred to polyethylene or polypropylene bottles immediately after preparation.

Instrument

The instrument is the Varian Techtron A.A.-5 atomic absorption spectrophotometer. A lead hollow cathode lamp (HCL) serves as the spectral source.

All instrumental parameters were adopted from Varian's Analytical Methods for Flame Spectroscopy (1)

Lead: Wavelength, 217.0 nm
slit width, 300 μ
lamp current, 5 mA.

The sample of 5μℓ was dispensed from an "autopette" 5μℓ dispensing pipet. The inert gas flow of N_2 was adjusted to 1.95/min and a hydrogen flow of 225 mℓ/min was employed during the atomization process. The Variac settings were 8 for the drying cycle and 20 for the atomization cycle.

The linear voltage programming technique was utilized to atomize the sample. Therefore, we can get more reproducible results by "cleaning" the wire loop during every run and, as a consequence, reduce memory effects. The peak height was measured in absorbance units. Full scale on the recorder was 1.0 absorbance units.

Calibration curves.

A calibration curve from 0.5 ppm to 50 ppm exhibits several ranges of approximate linearity which can be utilized: 0-1 ppm, 1-5 ppm, and 5-25 ppm. (see Figure 28.)

A calibration curve covering the range between 5 and 500 ppb shows a linear range of 0-70 ppb. The line intersects the origin of the calibration curve, indicating no background absorbance for the lead standards. The hydrogen continuous lamp was also employed to check for the presence of non-atomic absorption. A less sensitive analytical wavelength for lead at 283.31 nm (typical sensitivity = 0.23 μg/mℓ may prove adaptable to work in the higher concentration ranges (1,3).

From Figure 30, a sensitivity of 5.4 ppb (2.7×10^{-11} g absolute sensitivity) was obtained by finding the concentration that corresponded to an absorbance reading of 0.0044 absorbance units (1 % absorption - the definition of sensitivity). The alternate method, - (finding the

concentration that yields 0.1 absorbance unit and multiplying that concentration by 0.044) was not utilized (4). If we assume an absorbance of 0.1 to be on the linear portion of the calibration curve, from the extrapolation of Figure 29, we can get 6.16 ppb (3.08×10^{-11} g absolute sensitivity) as the sensitivity (12% deviation).

The detection limit was 4.7 ppb. (from Figure 30). Comparing 20 ppb solutions, detection limit is improved over flame work. (1). Here, we define the detection limit as the concentration of an element which will produce an average absorbance peak signal corresponding to twice the peak to peak noise of the base line.

Interferences

The effect of a 100-fold molar excess of the sodium salts of various common anions on the absorbance signals of lead were investigated. The percent signal change, which represents the extent of the interference, is calculated by:

$$\text{Signal Change} = \% = \frac{10^2 \times | \text{Absorbance (pb) + added electrolyte) - Absorbance (Pb)}.}{\text{Absorbance (Pb)}}$$

Table of Interferences for Pb using the aliquot method

added electrolyte (10-3M)	salt source	percent signal change on Pb (1.0 ppm).	background absorbance
1. $NaNO_3$	$NaNO_3$	-16.3	0.008
2. NaOAc	$NaOAc \cdot 3H_2O$	-36.3	0.011
3. NaF	NaF	-30.5	0.005
4. NaI	NaI	-94.7	0.029
5. Na_2SO_4	Na_2SO_4	-78.2	0.029
6. Na_2CO_3	$Na_2CO_3 \cdot H_2O$	-65.9	0.006
7. Na_3PO_4	$Na_3PO_4 \cdot 12H_2O$	-27.9	0.010
8. Na_2HPO_4	Na_2HPO_4	-28.8	0.009

All of the above sodium salts suppressed the signal of lead. Sodium iodide, in particular, depressed the lead signal. The background absorbance, which was checked by the hydrogen continuum lamp, was measured here also. The background absorbance of the lead solution containing NaI as the interferent was relatively large (The absorbance of that solution, measured with the Pb HCL was 0.024.). It could be non-atomic background absorption which is caused by molecular absorption anbd/or light scattering (5). It should be subtracted from the total signal. The combined effect of both anion and cation contributes t the decrease in signal. The interferences from phosphate, carbonate, iodide, fluoride and acetate were removed by adding 1g EDTA per 100 mℓ of sample (6) in flame atomic absorption work.

The absorbances of two lead solutions, each reportedly containing 1 ppb lead, are compared below. The absorbances obtained from the commercial standard (Harleco) and the standard utilized in this study agree fairly well.

	(1) Pb, 1 ppm (Harleco)	(2) Pb, 1 ppm (C. Yuan)
Absorbance (Avg.)	0.455	0.420
* S.D.	0.0087	0.0092
* R.S.D.	1.926	2.20 %
Difference	----	7.6 %

* S.D.: standard deviation
R.S.D.: relative standard deviations

Since the signal obtained from each standard solution may not be constant for long periods of time, it is worthwhile to note the change in absorance of a 1 ppm lead solution on a day to day basis.

	(1) June 7	(2) June 9
Absorbance	0.455	0.381
% Change	———	-16.3%

In addition, the 1 ppm lead solution was analyzed before and after several intervening standard solutions. The results indicate relatively small memory effects.

	(1)	(2)
Absorbance	0.381	0.40
% Change	———	+4.98%

BIBLIOGRAPHY

(1) Analytical Methods for Flame Spectroscopy, Varian Instrumental Division, 611 Hansen Way, Palo, California 94303.

(2) West, M. "Quarterly Report on Contract DAMD, 17-75-C-5048." March, 1976.

(3) Manning, D. C. and Vollmer, J., Atom. Abs. Newsletter, 1967, 6, 38.

(4) Instruction Manual for Model 63 Carbon Rod Atomizer, Varian Techtron p. 1-9 (April, 1972).

(5) Culver, B. R. and Surles, T., Interference of Molecular Spectra due to Alkali Halide in Non-Flame Atomic Absorption Spectrometry, Anal. Chem. 47 (6), 920 (1975).

(6) Robinson, J. W. "Atomic Absorption Spectroscopy." Marcel Dekker Inc., New York, p. 131 (1966).

Data:

Calibration curve of lead by aliquot method.

(I.) Rough curve, Figure 28

concentration, ppm.	0.5	1	5	10	15	20*	25*	50*
absorbance	0.18	0.315	0.550	0.664	0.715	0.784	0.808	0.931

(II.) Delicate curve, Figure 29

concentration, ppb	10	20	30	40	50	70
absorbance	0.0071	0.0116	0.0234	0.0345	0.0410	0.058

100*	200*	500*
0.069	0.152	0.34
0.0012	0.0026	0.0028

(III.) Detailed curve, Figure 30

concentration, ppb	30*	25*	20*	18	15	13
absorbance	0.0182	0.0150	0.0125	0.0146	0.0130	0.0109
(ABs. standard deviation)	0.0033	0.0010	0.0020	0.0005	0.0009	0.0012

10	5
0.0090	0.0040
0.0005	0.0008

* not shown on Figure.

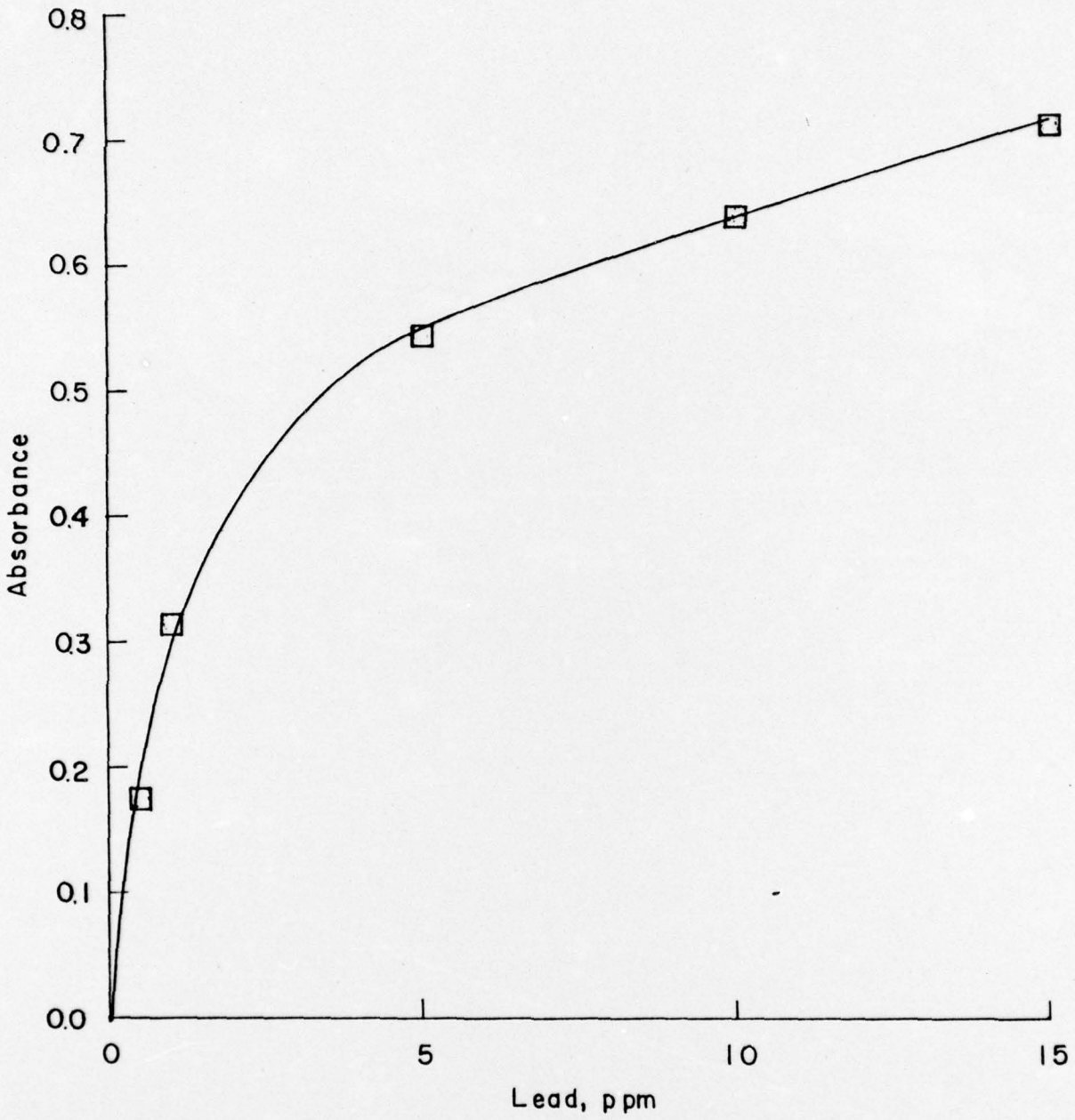


Figure 28. Calibration for the Analysis of Lead by the Aliquot Method over the Range 0-15 ppm.

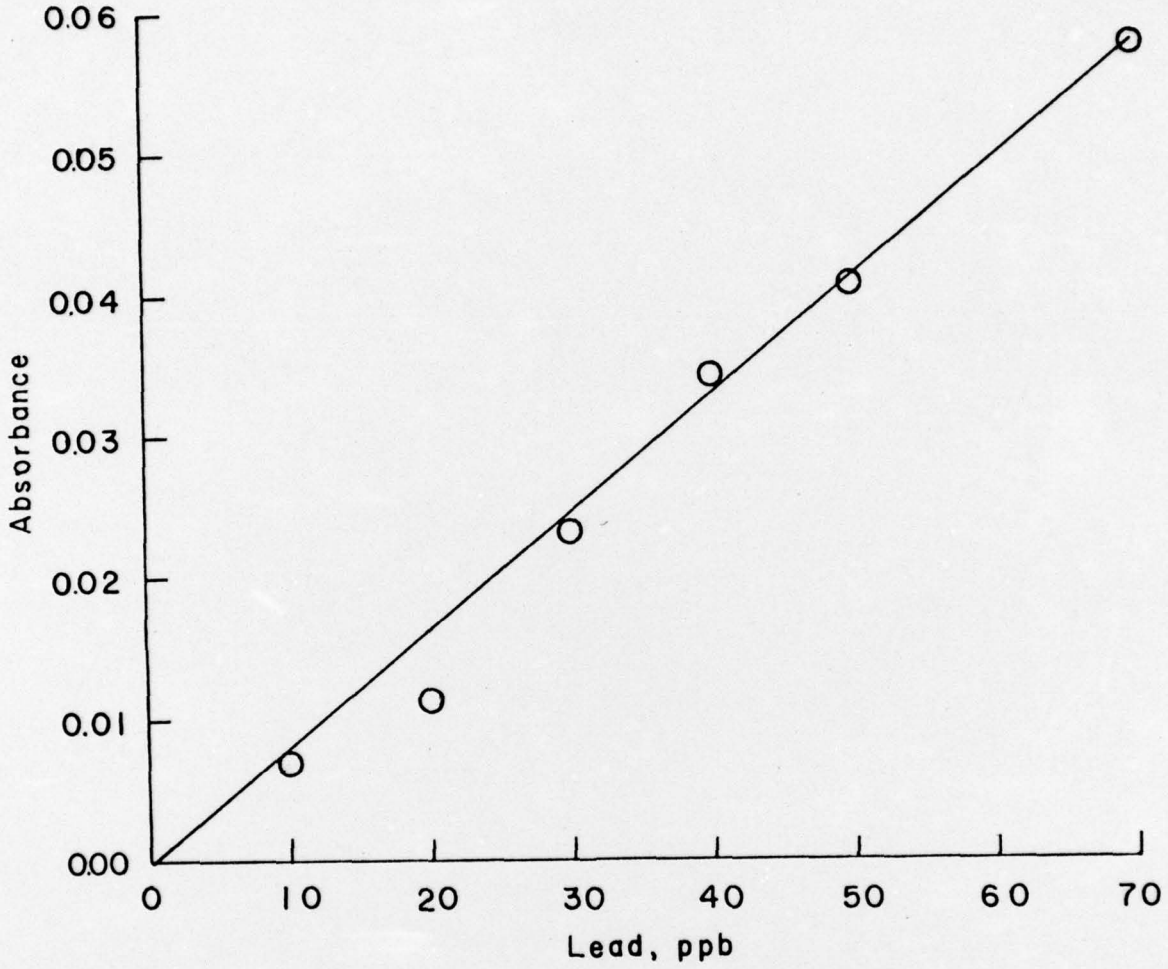


Figure 29. Working Curve for Lead Analysis in the Range 0-70 ppb with the Aliquot Method.

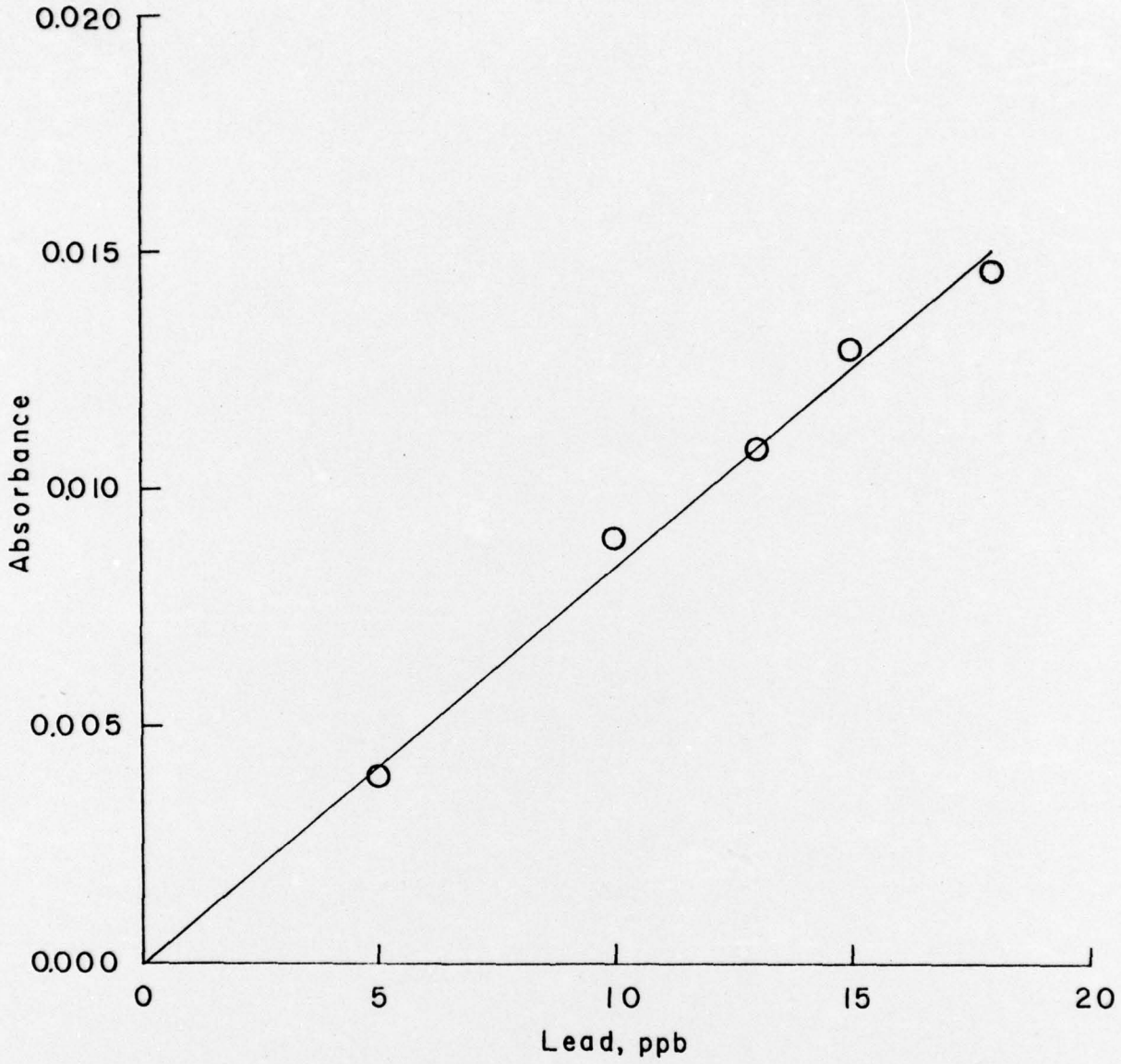


Figure 30. Expanded Working Curve for Lead in the Range 0-18 ppb.

Temperature versus Variac Setting

In order to further characterize the tungsten rhenium wire loop atomizer, the optimum atomization temperature was determined for a variety of elements using an optical pyrometer. A Leeds and Northrup 8632 C Optical Pyrometer, a single adjustment potentiometer type, was employed for the temperature measurements. The observed temperatures varied from 890°C, corresponding to a variac setting of 20 (that used to atomize lead), to 1700°C which corresponds to a variac setting of 40, Figure 1. The latter setting is high enough to atomize any of the elements studied by the wire loop atomizer technique. Aggett and Sprott (1) found a temperature range of 300-1560°C for the tantalum ribbon and a range of 270-1500°C for the carbon rod (2). However, the temperature stated for each element corresponded to the minimum temperature at which atomization could be observed.

(1) J. Aggett and A. J. Sprott, Anal. Chem. Acta, 72, 49 (1974

(2) Instruction Manual for Varian Techtron Model AA-5 Atomic Absorption Spectrophotomer, Varian Techtron Pty. Limited, Melbourne, Australia (October, 1971).

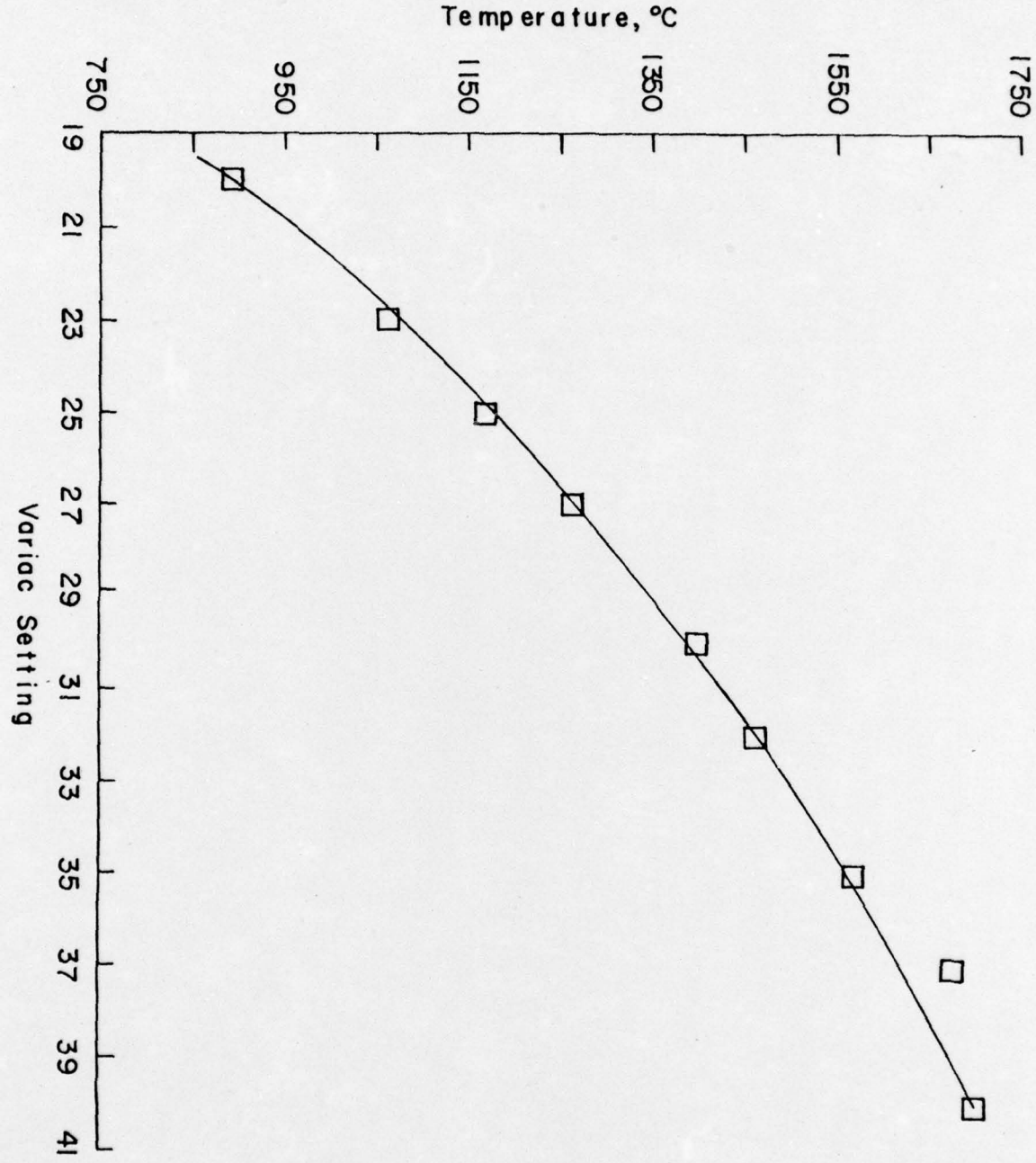


Figure 31. The Relationship between Atomizer Temperature and Variac Setting as Determined with an Optical Pyrometer.

Annual Report

Distribution List

4 copies	HQDA (SGRD-RP) WASH DC 20314
25 copies	Environmental Protection Department. ATTN: SGRD-UBG US Army Medical Bioengineering Research and Development Laboratory Fort Detrick, Frederick, MD 21701
12 copies	Defense Documentation Center(DDC) ATTN: DDC-TCA Cameron Station Alexandria, VA 22314
1 copy	Superintendent Academy of Health Sciences, US Army ATTN: AHS-COM Fort San Houston, TX 78234
1 copy	Dean School of Medicine Uniformed Services University of the Health Sciences Office of the Secretary of Defense 6917 Arlington Road Bethesda, MD 20014