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Separation and Determination of Arsenic (V) and Arsenic (III) in Sea Water by Solvent Extraction and Atomic Absorbtion Spectrophotography Via the Hydride Generation Technique

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SEPARATION AND DETERMINATION OF ARSENIC(V) AND ARSENIC(III) IN SEA WATER BY SOLVENT EXTRACTION AND ATOMIC-ABSORPTION SPECTROPHOTOMETRY VIA THE HYDRIDE GENERATION TECHNIQUE

BY

SAMUEL ASARE AMANKWAH

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
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MASTER OF SCIENCE THESIS

BY

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1983

ABSTRACT

Arsenic(III) and arsenic(V) species exist in sea water at concentration levels of less than 0.2 ng/ml to greater than 50 ng/ml. The concentration levels of these species in sea water are currently questionable due mostly to possible interferences.

A reliable analytical method has been developed to separate and determine these species in sea water. The method involves the extraction of APDC-As(III) complex into a chloroform layer at a pH range of 4.0-4.5. Wet ashing of the chloroform layer followed by reduction of arsenic(V) to arsenic(III) by potassium iodide makes it possible to determine arsenic by the atomic absorption spectrometry-hydride generation technique. The various parameters such as pH, percent APDC, interferences, efficient reducing agents and wet ashing methods have been investigated in this study.

A detection limit of 0.031 ppb and a sensitivity of 0.140 ng/ml have been achieved. Precision as judged by % RSD (0.6-5.4) indicates good reproducibility of the results when synthetic sea water samples spiked with arsenic(III) and natural sea water samples are analyzed.

ACKNOWLEDGMENTS

It is a pleasure to record my sincere thanks to Professor James L. Fasching, my thesis supervisor, for his direction, tuition and encouragement. I also wish to thank my research group members for their valuable technical assistance. I am grateful to W. E. Johnson, A. Kocsi, and C. L. Strate for their assistance in various ways. In addition, nods of thanks go to Dorothy Morancy who typed this manuscript.

PREFACE

The manuscript form was adopted and the manuscript from this thesis will be submitted to Talanta.

There are seven appendices and these are:

1. Introduction and Review of Literature.
2. Elimination of Reagent Blank in the Determination of Arsenic by Atomic Absorption Spectrometry via the Hydride Generation Technique.
3. Interference studies of some trace elements and organics on the hydride generation of arsenic.
4. Wet Ashing.
5. Reduction of Arsenic(V) to Arsenic(III).
6. Data Treatment.
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SEPARATION AND DETERMINATION OF ARSENIC(V) AND ARSENIC(III) IN SEA WATER BY SOLVENT EXTRACTION AND ATOMIC-ABSORPTION SPECTROPHOTOMETRY VIA THE HYDRIDE GENERATION TECHNIQUE

ABSTRACT

Arsenic (V) and arsenic(III) in sea water have been separated by a solvent extraction technique. Arsenic(III) is determined by atomic absorption spectrometry--hydride generation method. Arsenic (III) is first separated from a mixture of As(III) and As(V) by complexing with ammonium pyrrolidinedithiocarbamate (APDC) in the pH range 4.0-4.5. The arsenic(III)-ADPC complex is then extracted into a chloroform layer. Wet ashing, employing a mixture of concentrated nitric acid and perchloric acid (1:1), was performed on the chloroform layer to get rid of all organics.

Total arsenic was determined by first reducing arsenic(V) to arsenic(III) by potassium iodide and the total arsenic(III) extracted by the solvent extraction method followed by atomic absorption-hydride generation analysis. Arsenic(V) was determined by difference.

The low detection limit of 0.031 ppb, high sensitivity and precision make the method suitable for analysis of open ocean waters.

INTRODUCTION

Solvent extraction has often been used in the separation of trace elements from sea water matrix before its subsequent analysis by atomic absorption spectrophometry or neutron activation (1,2,3,4,5). However, the literature concerning arsenic speciation by solvent extraction is sparse. A few articles have been reported which include the use of dithiocarbamates and ammonium molybdate as the complexing agents (6). Puttemans and Massart (7) have reported a method for differential determination of arsenic(V) and arsenic(III) species by solvent extraction and electrothermal atomic absorption spectrometry. With their method arsenic(III)--ammonium pyrrolidinedithiocarbamate(APD C) complex was extracted quantitatively from acidic media into a chloroform layer. Arsenic(III) was stripped off into an aqueous medium by Cu(II) before analysis by graphite-furnace atomic absorption spectrometry. The detection limit of their method was not determined but good extraction recoveries were reported.

Toshihiko Kamada (8) has also studied the extraction behavior of a rsenic(III) and arsenic(V) with ammonium pyrrolidinedithiocarbamate, sodium diethyldithiocarbamate (DDDC) and dithizone in organic solvents. With his method the organic layer was analyzed directly by graphite furnace atomic absorption spectrophotometry. He indicated that 9-60 parts per billion levels of arsenic species in aqueous medium could be determined.

These methods are subject to interferences when applied to sea water matrix because the extracted APDC, DDDC, or HDEDTP complexes of arsenic(III) contain complexes of other metals such as Cu and Ni which may interfere with the analysis (8). In addition, interference due to the dithiocarbamate itself and other organics associated with it are a problem in the analysis. To solve the problem of interference, a method involving solvent extraction, wet ashing to eliminate organic interferences, which is followed by selective determination of arsenic(III) by the hydride generation technique has been developed. APDC as the chelating system with chloroform as the organic solvent was used for the extraction step. Results for optimum pH, chelate concentration, accuracy, precision, sensitivity and detection limits of the developed method will be subsequently discussed.

EXPERIMENTAL

Apparatus

A Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer equipped with an electrothermal quartz cell furnace, a chart-recorder and an Arsenic Electrodeless Discharge line source powered by an 8-watt power supply source was used for all analysis. The Perkin-Elmer MHS-10 Mercury/Hydride Generation system was connected to the quartz cell via two traps containing calcium chloride to remove the water vapor. The carrier gas used was argon and the flow rate was regulated by a flowmeter. Figure 1 shows the assembly of the system.

The electrothermal quartz cell was 1.7 cm in diameter by 18.8 cm long with open ends. Graphite sleeves were used for heat dissipation. Nichrome wire (diameter = 0.0253 ins.; resistance = 1ohm/ft) was wound around the tube to a sufficient length (about 4 ft.) to reach a temperature of about 900°C by resistance heating. To insulate the tube and to maintain a uniform temperature distribution around the tube, asbestos was wrapped around it followed by glass cloth. Power to the resistance wire was supplied by a variable transformer.

Reagents

All solutions were prepared from analytical grade chemicals. Distilled deionized water was used for all solutions.

Standard arsenic(III) solution (1 mg/ml). Prepared by dissolving 1.322 g of As_2O_3 primary standard (MCB) in 100 ml basic solution.

Standard arsenic(V) solution (1 mg/ml). Preapred by dissolving 4.1650 g of $Na_2HAsO_4 \cdot 7H_2O$ (Mallinckrodt) in 1000 ml solution.

Sodium borohydride solution (5%). Prepared by dissolving 5 g of sodium borohydride powder (Fisher) in 100 ml deionized water followed by the addition of 1 pellet of potassium hydroxide. The resulting turbid solution was filtered through 0.45 μm filter membrane to obtain a clear solution. This solution was prepared on bi-weekly basis following the procedure of Fraser and Bye (9,10).

The mineral acids, concentrated nitric acid (Fisher) and concentrated hydrochloric acid (Fisher) were redistilled before use in a pyrex distilling kit. All cleaned pyrex glass is assumed to be free from arsenic impurities (11).

Synthetic sea water was prepared by dissolving 254.0 g of NaCl, 105.0 g of $MgCl \cdot 6H_2O$, 39.1 g of Na_2SO_4, 11.0 g of $CaCl_2 \cdot 2H_2O$, 7.2 g of KCl, 2.03 g of $SrCl_2$, 0.27 g of H_3BO_3 and 19.2 g of $NaHCO_3$ in 10 liters of deionized water. All reagents were obtained from Mallinckrodt.

Ammonium acetate buffer pH 4.5. Equal volumes of 4N sodium acetate (Fisher) and 4N glacial acetic acid (Fisher) were mixed.

Ammonium acetate buffer pH 6.1. 470 ml ammonium hydroxide (Fisher) were added to 430 ml glacial acetic acid.

Potassium iodide was obtained from Fisher Scientific Company.

Atomic absorption standards for lead (996 ppm), iron (1013 ppm), cobalt (988 ppm), zinc (1000 ppm), cadmium (1000 ppm), copper (1000 ppm), mercury (1000 ppm) and nickel (997 ppm) were obtained from Alpha Analytical Laboratories. These solutions were prepared from chloride salts except lead, nickel and mercury which were nitrate salts.

Ammonium pyrrolidinedithiocarbamate (APDC) solution (1%). One gram APDC (Eastman) was dissolved in 100 ml deionized water. The resulting solution was filtered through a 0.45 μm filter membrane followed by extraction with chloroform to purify it. The purified APDC solution was prepared as needed.

The organic solvent, chloroform, was used as purchased from Fisher Scientific Company.

Each stock standard solution was diluted to give an appropriate concentration before use.

PROCEDURE

I. All glassware was cleaned by washing it several times in 4 molar nitric acid and then rinsed it in deionized water until it was neutral to litmus paper.

II. Synthetic sea water was spiked with an appropriate concentration of arsenic(V) and arsenic(III) solution. This procedure was used in the various studies.

III. Natural sea water was collected from Narragansett Bay. It was filtered through a 0.45 μm filter membrane (Millipore) to remove any particulate matter. Analysis of the filter membrane showed no retention of arsenic. The pH was lowered to 2 using hydrochloric acid and the solution stored in a polyethylene bottle (following the recommendation by Robertson) (12). It was assumed that the As(III)/As(V) ratio did not change at that pH value. To study the two valency states of arsenic, a 10 liter sea water sample (either synthetic or natural) was divided into two 5 liter parts. In one aliquot about 100 g of potassium iodide was added to reduce all arsenic(V) to arsenic(III). The resulting solution was used for the total arsenic determination. The other aliquot was used for arsenic(III) analysis.

EXTRACTION

A 300 ml sea water (synthetic or natural) sample was placed in a 500 ml separatory funnel. Using the ammonium acetate buffers, the pH was brought to within the range 4.0-4.5. Ten ml of purified 1% APDC was added to the solution followed by 25 ml of chloroform. The solution was shaken for 20 minutes on a horizontal mechanical shaker. After the separation of the two layers, the chloroform layer was drained into a 150 ml erlenmeyer flask. The aqueous layer was discarded. Wet ashing was performed on the chloroform layer according to the following method: 10 ml of concentrated nitric acid and 10 ml of 70% perchloric acid were added to the chloroform layer. To prevent bumping and spattering, glass beads were added and the flask was fitted with a short-stem funnel. This was boiled to white dense fumes of perchloric acid on a hot plate. Ten ml of deionized water was then added to the sample in the flask and again boiled to white dense fumes of perchloric acid. The resulting solution was then cooled down to about 40°C. About 1 gram of potassium iodide was added to reduce arsenic (V) to arsenic(III). The solution was made up to 50 ml in a volumetric flask with 1 molar hydrochloric acid.

Atomic absorption spectrophotometrtic analysis of arsenic(III) via the hydride generation technique was performed on 15 ml aliquots of the preconcentrated sample. Arsenic(III) levels in the aliquots were determined by the standard addition method. To investigate the optimal chelate concentration for complexation and extraction, the experiment was repeated using 10 ml of 0.25%, 0.5%, 1% or 2% purified APDC in separate experiments. The optimal pH for complexation and extraction was also determined by repeating the experiment under various pH conditions. Synthetic sea water was used as blank in all experiments. The flow chart for the extraction procedure is shown in Figure 2.

RESULTS AND DISCUSSION

The arsenic species which are known to occur in sea water are arsenite, arsenate, dimethylarsinate $(CH_3)_2AsO(OH)$ and methylarsonate $(CH_3)AsO(OH)_2$ (20,21).

The methods for the determination of dimethylarsinate and methylarsonate at natural sea water levels have been developed only recently (22). At the moment, the borohydride-based reduction systems which generate methylarsines from methylated arsenic compounds is not well established and therefore cannot be reliably used to determine the methylated arsenic compounds. The technique used in this work only identifies inorganic arsenic(III) and (V) compounds. The organoarsenic compounds were excluded from the study because current estimates of their concentration in sea water is less than the inorganic As species.

The method for the separation of arsenic(III) from arsenic(V) as discussed above is based on the fact that the dithiocarbamate selectively complexes with arsenic(III) but not with arsenic(V) (17). No arsenic(V) complexes are reported. This is probably due to the high stability of the arsenic(V) oxy-anions over a wide pH range, and the instability of dithiocarbamates in very acid solution and steric effects (17).

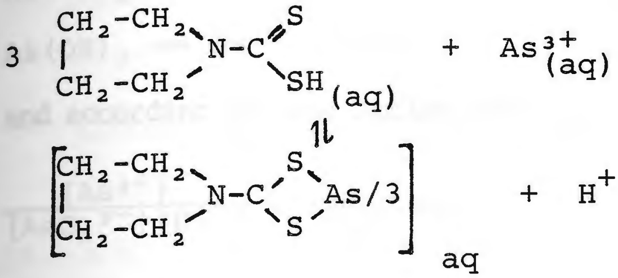
The determination of As(V) is based on the assumption that

$$As(V) = As_{Total} - As(III)$$

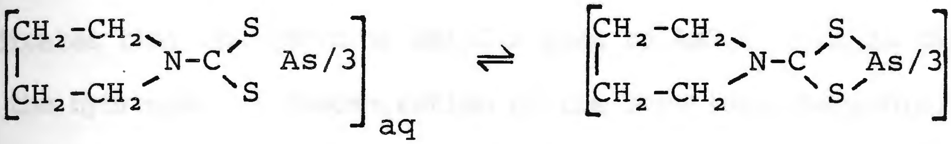
As_{Total} is defined here as As(III) + As(V) excluding organo-arsenic(V) compounds which do not form complexes with dithiocarbamates and not reduced to As(III) by potassium iodide. It is also assumed that inorganic As(V) is completely reduced to As(III) by potassium iodide before separation by dithiocarbamate extraction (19).

pH Effect

The reaction between arsenic(III) and ammonium pyrrolidine dithiocarbamate is pH dependent. The reaction equation is depicted below,



(1)



(2)

Consideration of equations (1) and (2) shows that an increase in the concentration of dithiocarbamate, as well as a decrease in hydrogen ions, will shift the equilibrium to the right. Consequently, the second equilibrium will also be shifted to the right and more of the arsenic(III) species will be extracted. While a decrease in H^+ ion concentration favors more extraction and stability of the dithiocarbamate, an increase in H^+ concentration favors the availability of As(III) ions which are required for complexation with APDC. The pH dependence of As(III) availability can be illustrated by the following equilibria (16):

$$As(OH)_3 \rightleftharpoons AsO_3{}^{3-} + 3H^+$$

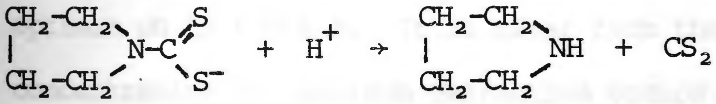
$$As(OH)_3 \rightleftharpoons As^{3+} + 3OH^-$$

and according to mass action law

$$\frac{[As^{3+}]}{[AsO_3{}^{3-}][H^+]^6} = \text{Constant}$$

The product $[H^+][OH^-]$ is constant and this expression clearly indicates that the ratio of As(III) ions to $AsO_3{}^{3-}$ ions is dependent on the hydrogen ion concentration of the solution; therefore, As(III) is available for complexation with APDC in strongly acidic solution.

The dependence of the stability of APDC on pH is also illustrated by the following equation (14):



It is clear from these equations that any analytical method to be used for the study of arsenic involving complexation with APDC requires a careful control of the pH of the medium.

Figure 3 shows the study of the effect of pH on the complexation and extraction for the method developed. The study indicates that the optimal pH for complexation and extraction is within the 4.0-4.5 range. The decrease in the amount of arsenic(III) extracted at pH greater than 5 is probably due to non-availability of arsenic(III) ions. The decrease in efficiency at low pH (<4.0) is probably due to the breakdown of the APDC to pyrrolidine and carbon disulfide.

Concentration Dependence of APDC

From equation (1) an increase in APDC concentration should result in a shift of the equilibrium to the right. Consequently, more of the APDC-arsenic(III) complex will be extracted. The optimum concentration of APDC necessary to bring about maximum extraction of the complex was studied. Figure 4 shows a graph of atomic absorption signal versus percent APDC. The graph was obtained from the preconcentration of 50 ng of As(III) from 300 ml synthetic sea water using varying amounts of APDC. The extraction was done at the optimum pH of 4.0-4.5. It is clear from the graph that the minimum concentration for maximum extraction occurs when APDC is 1 or 2 percent (w/v). In subsequent analyses 1 percent APDC was used. To compensate for the breakdown of APDC in the pH range used for the extraction, 10 ml portions of the 1%(w/v) concentration of APDC solution were used.

Sensitivity and Detection Limit

The sensitivity and detection limit obtained for the analysis of arsenic using the above method is shown in Table I. The sensitivity was obtained from a plot of percent absorption versus concentration (ng/ml) in triplicate analysis. The value of 0.140 ng/ml obtained is comparable to reported values for other methods involving the use of solvent extraction (23).

The detection limit was determined from the relationship D.L. = $\bar{X}\pm 3\ \sigma bl$ according to Zief and Mitchell (14). In this relationship D.L. is the Detection Limit and $\bar{X}$ is the average value of ten determinations of the blank and σbl is the standard deviation from these determinations.

The detection limit of 0.031±0.005 ng/ml for the standard addition method was based on preconcentrated volume of 50 ml from which 10 ml aliquots were used for the analysis. This was used for routine work. A lower detection limit of 0.006±0.0007 ng/ml was obtained from a calibration curve based on the analysis of a preconcentrated volume of 10 ml which was analyzed as one sample. The values obtained (Table I) are very low and indicate that the method can be used for sea water analysis.

Percentage Recovery and Precision Studies Using Synthetic Sea Water

Tables II and III show the results for percentage recovery and precision studies respectively. These results were obtained by the standard addition method. Figure 5 shows a typical standard addition curve obtained from spiked synthetic sea water.

Percent recoveries range from 95 to 105. The precision data in Table III were obtained on day-to-day basis. The percent relative standard deviation of 0.6-0.8 indicates that the results from the analysis are very reproducible.

Analysis of Natural Sea Water

The method was applied to the analysis of natural sea water samples from Narragansett Bay. The day-to-day analysis on one sample was done to study the precision of the method. From the results shown in Table IV it was assumed that for the short period of this study there was no change in the As(III)/As(V) ratio. The percent relative standard deviation of 1.7–5.4 indicates good reproduciblity.

Interference Studies

The sea water matrix contains traces of metals such as Cu, Ni, Fe, Pb, Co, Zn, Cd, and Hg. It has been reported that APDC forms complexes with all these elements (12,8) and that during the extraction and determination of arsenic, these elements are likely to be present in the sample solution. Severe interference by Cu and Ni in the hydride-generation analysis of arsenic has also been reported (18). Studies were, therefore, carried out to investigate the effect of traces of Cu(II) and Ni(II) on the determination of arsenic using the hydride-generation technique. The results for the study are shown in Table V. They indicate that Ni(II) and Cu(II) did not interfere below 5 parts per million levels. Since these elements occur in sea water below 5 ppm (1) one should not worry about their interferences when using a hydride generation technique to analyze for arsenic in sea water matrix. There were no interferences from Fe(III), Pb(II), Co(II), Zn(II), Cd(II) and Hg(II) at 1000 parts per million levels.

Studies were also conducted to investigate the interference effects of APDC and pyrrolidine on the hydride generation of arsenic.

The results obtained indicate that APDC and pyrrolidine interfere severely at trace levels. In addition to forming gaseous products from reduction by sodium borohydride, pyrrolidine complexes with arsenic to form an arsenic-amido derivative during stripping off of As from As-APDC complex with concentrated nitric acid. Since this derivative is more soluble in chloroform than in an aqueous medium, much of the arsenic is lost before analysis of the aqueous layer by hydride generation. Wet ashing before hydride-generation analysis was used to eliminate this problem. Wet ashing of the chloroform layer retains all the arsenic by breaking down any arsenic-amido derivative which might have been formed by the breakdown of As-APDC complex.

Wet-Ashing and Reduction of As(V) to AsIII

Experiments were carried out to find the best systems for wet ashing and the reduction of arsenic(V) to arsenic(III). Nitric acid and perchloric acid in the ratio 1:1 was found to be the simplest system for wet ashing among others tried as shown in Table VI. A recovery of 100±1% arsenic was achieved when this system was applied to spiked synthetic sea water. The organic matter was pyrrolidine and APDC.

Table VII shows the percent recovery of As(V) for various reductive systems studied. Potassium iodide (KI) alone was found to be the best reducing agent of the following combinations: KI, KI+$Na_2S_2O_3$; KI+$Na_2S_2O_3$; KI+Na_2SO_3; KI+Na_2SO_3+$Na_2S_2O_5$ tested. The sulfites, metabisulfites and the thiosulfate all produced SO_2 or H_2S upon reaction with borohydride and these gaseous products also interfere with the arsine generation.

CONCLUSIONS

The characteristic features of this method can be summarized in three steps;

1. Preconcentration of sample by solvent extraction;
2. Wet ashing on the organic layer;
3. Determination of arsenic by hydride generation-atomic absorption technique.

The method has the following advantages: a; Combination of wet ashing and hydride generation makes the method free from interferences. The sensitivity is therefore significantly improved. b; The detection limit of 0.031+.005 ng/ml is lower than reported values from other methods (15,17,8). c; Twelve samples can be analyzed a day and this makes the method economically usable for routine analysis of sea water samples.

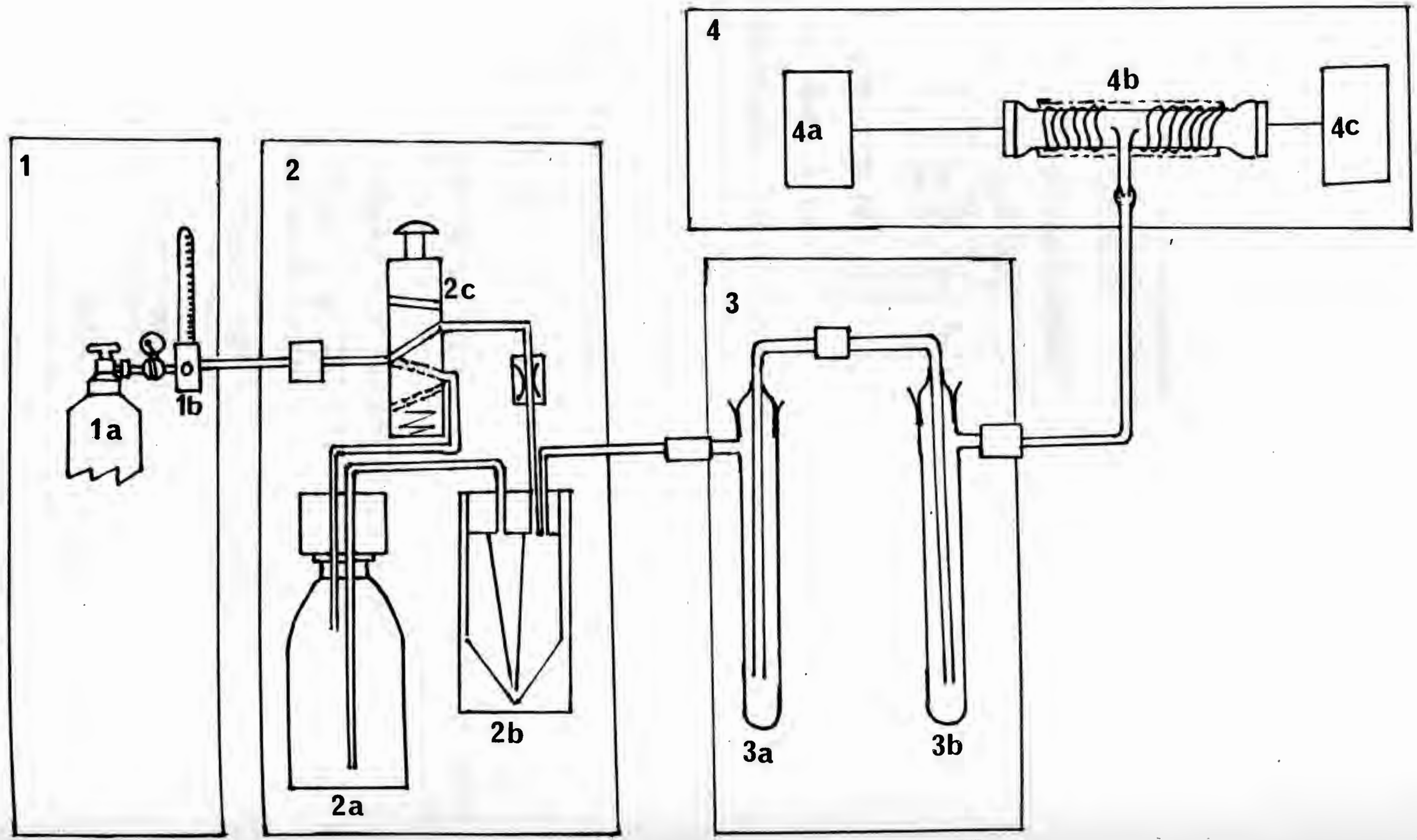
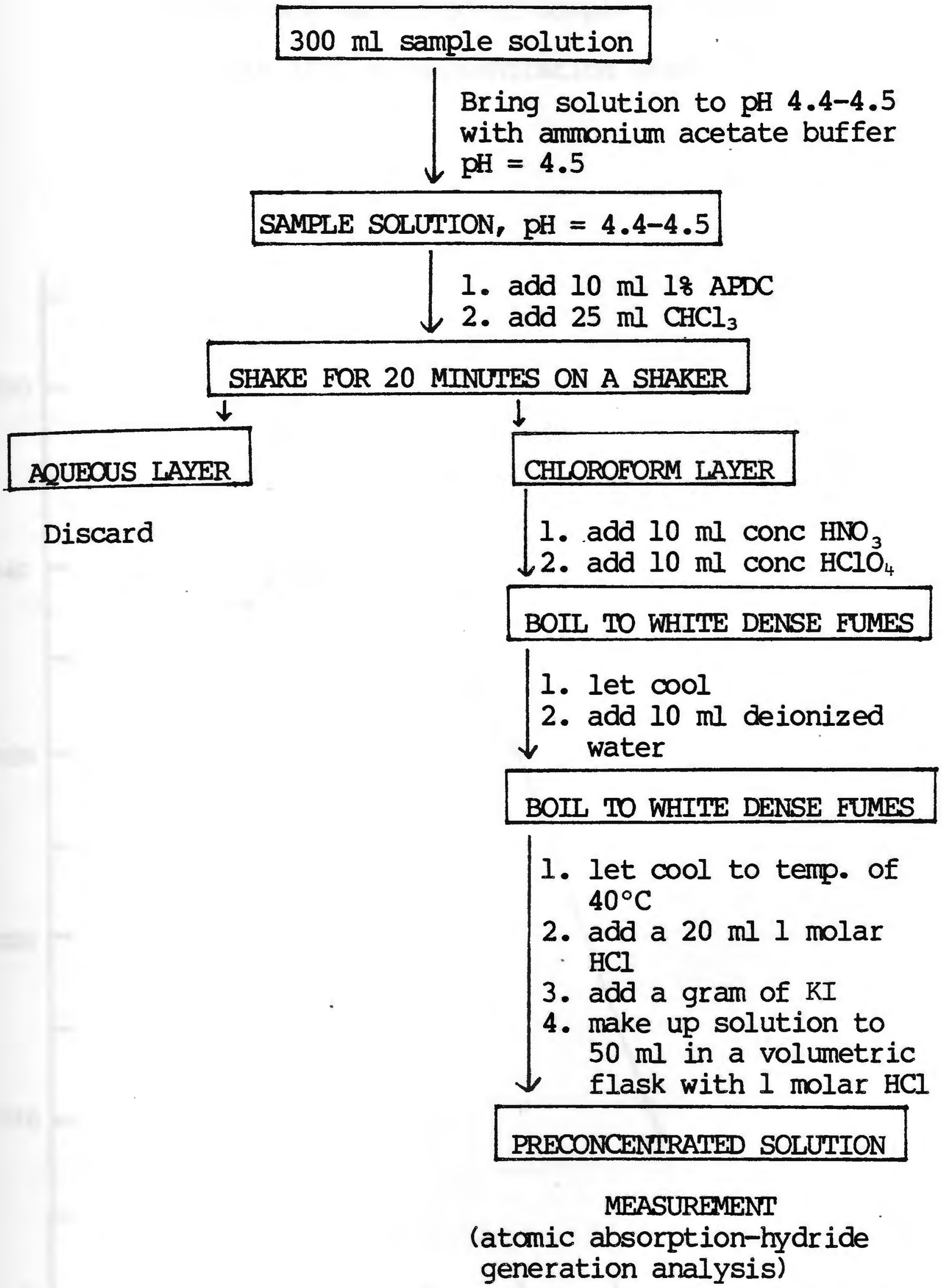


FIGURE 1. Perkin-Elmer Atomic Absorption Spectrophotometric–MHS-10 Hydride Generation Assembly

1a, Argon Gas Cylinder; 1b, Flowmeter; 2, Perkin-Elmer MHS-10, 2a, sodium borohydride container; 2b, reaction vessel; 2c, plunger; 3a&b, contains calcium chloride pellets to remove water vapor; 4, Perkin-Elmer Atomic Absorption Spectrophotometer 403; 4a, arsenic electrodeless discharge lamp;

FIGURE 2

FLOW CHART DIAGRAM FOR THE EXTRACTION



300 ml sample solution

Bring solution to pH 4.4-4.5 with ammonium acetate buffer pH = 4.5

SAMPLE SOLUTION, pH = 4.4-4.5

1. add 10 ml 1% APDC
2. add 25 ml $CHCl_3$

SHAKE FOR 20 MINUTES ON A SHAKER

AQUEOUS LAYER

Discard

CHLOROFORM LAYER

1. add 10 ml conc HNO_3
2. add 10 ml conc $HClO_4$

BOIL TO WHITE DENSE FUMES

1. let cool
2. add 10 ml deionized water

BOIL TO WHITE DENSE FUMES

1. let cool to temp. of 40°C
2. add a 20 ml 1 molar HCl
3. add a gram of KI
4. make up solution to 50 ml in a volumetric flask with 1 molar HCl

PRECONCENTRATED SOLUTION

MEASUREMENT
(atomic absorption-hydride generation analysis)

FIGURE 3

Absorbance Versus pH of Sample Solution

(in APDC preconcentration step)

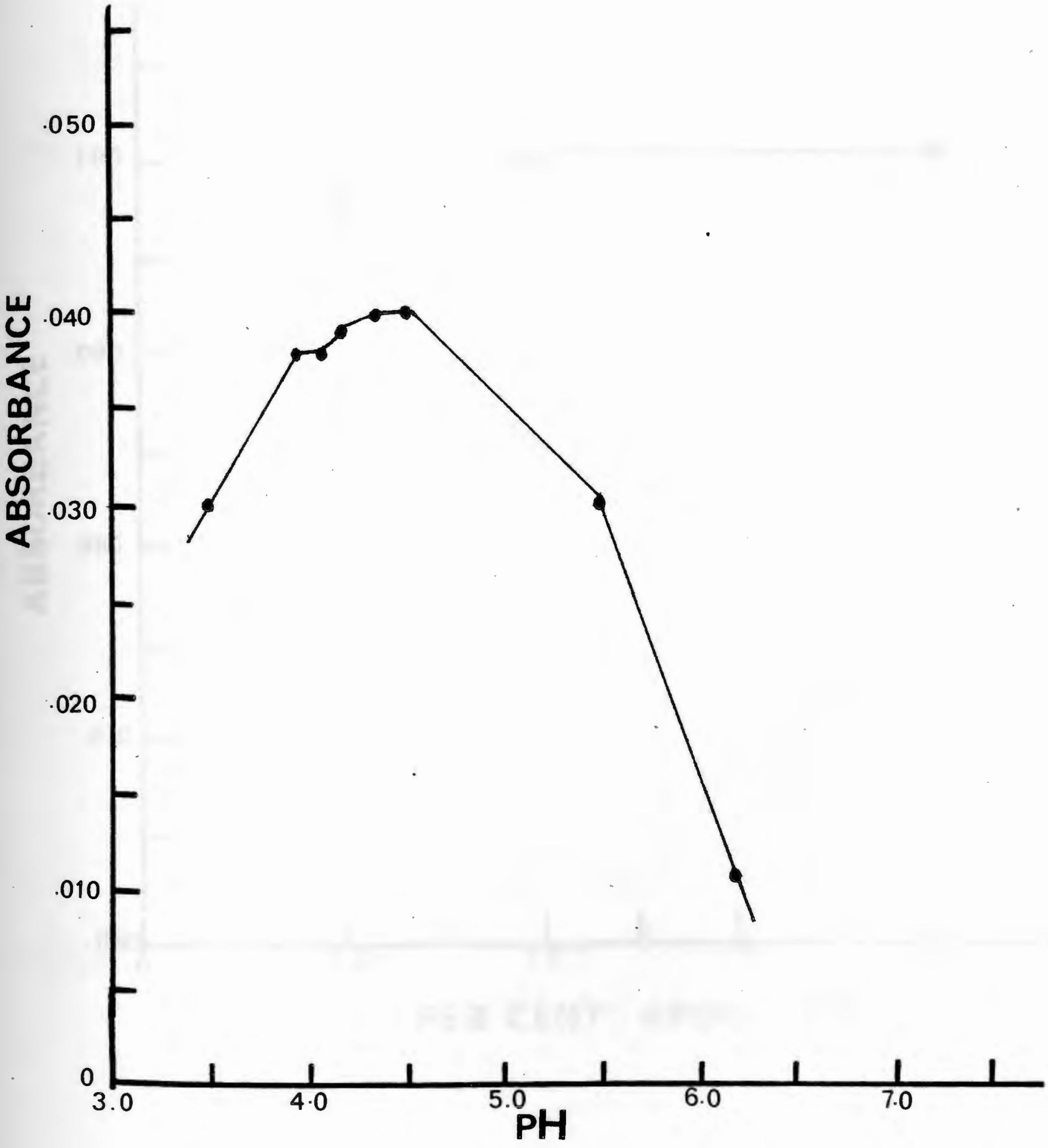


FIGURE 4

Absorbance Versus Percent of APDC (w/v)

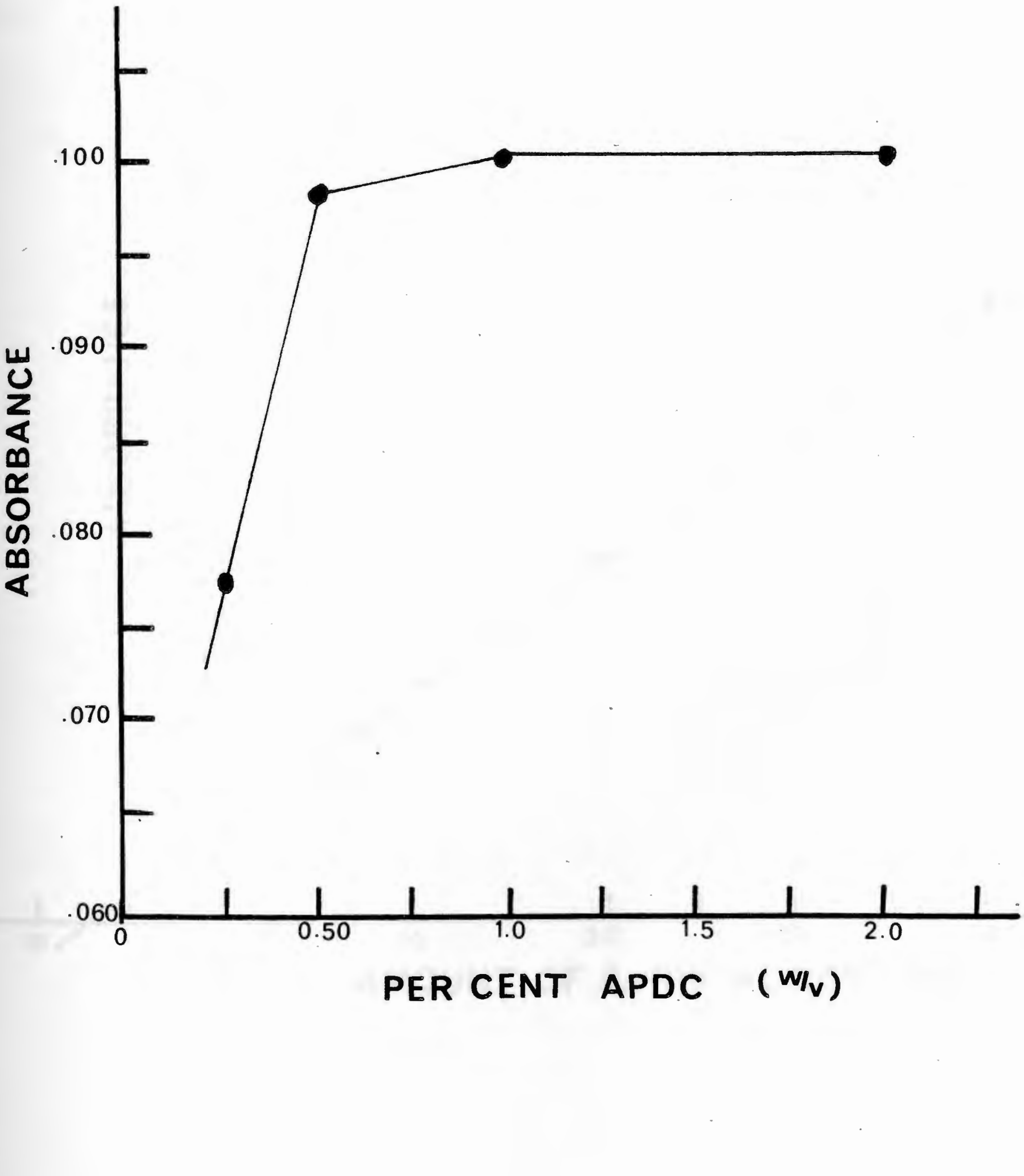


FIGURE 5

Standard Addition Curve for Arsenic(III)

in Synthetic Seawater

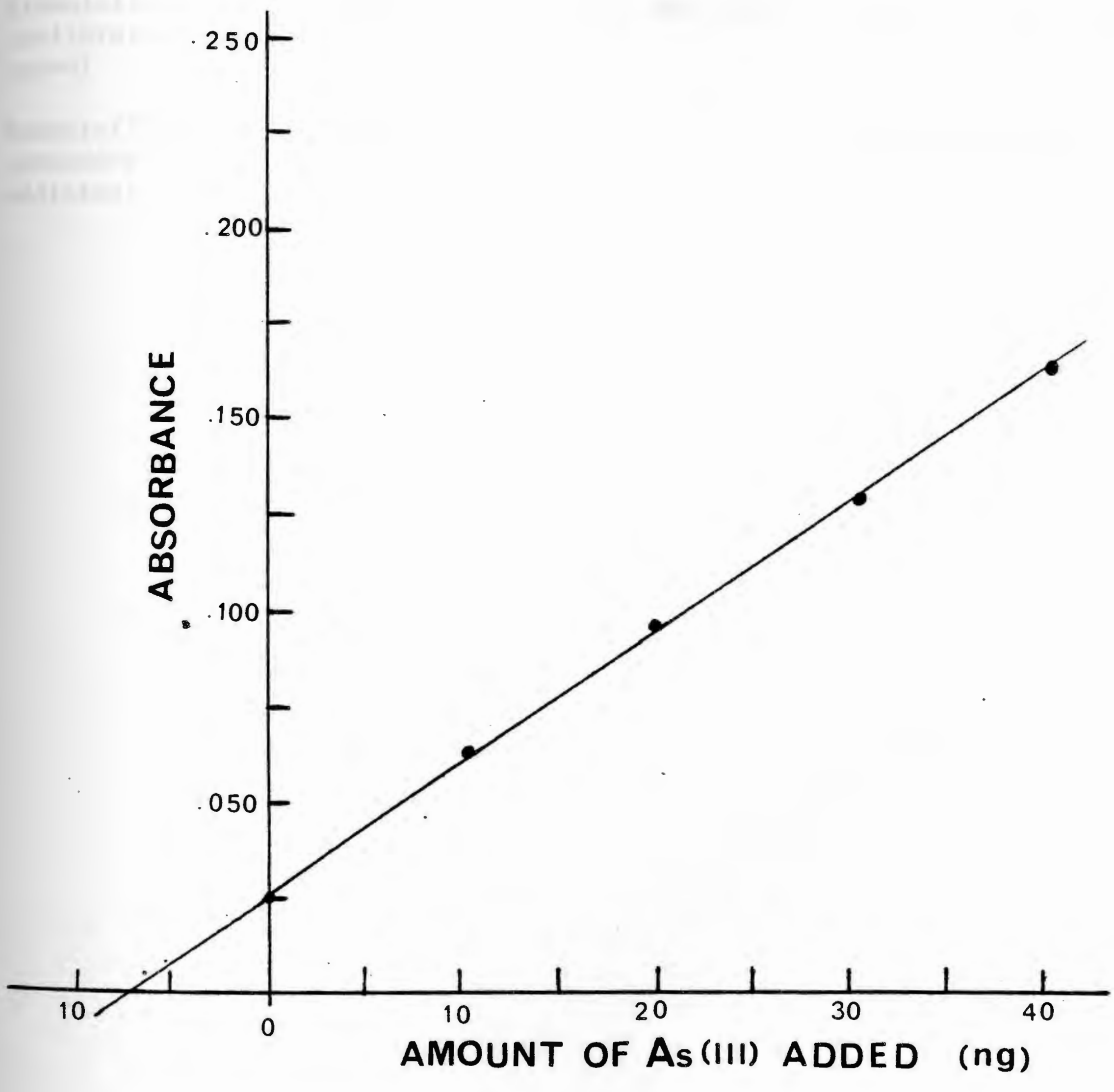


TABLE I

DATA FOR SENSITIVITY AND DETECTION LIMITS STUDIES
(Results for triplicate analysis)

	Volume of preconcentrated solution	Sensitivity	Detection limit
Arsenic(III) (calibration curve)	10 ml	0.14 ± 0.006 ng/ml	0.006 ± 0.0007 ng/ml
Arsenic(III) (standard addition)	50 ml	-	0.031 ± 0.005 ng/ml

TABLE II

ACCURACY DATA FOR RECOVERY OF ARSENIC(III) AND ARSENIC(V)

Sample #	As(III) added (ng)	As(V) added (ng)	Percent total As(III + V) recovered	Percent As(III) recovered	Percent As(V) recovered
1	30	-	103.3	103.3	-
2	300	30	99.4	100.6	96.7
3	30	300	98.8	100.0	98.7
4	40	40	95.0	95.0	95.0
5	10	10	105.0	105.5	100.0

TABLE III

PRECISION DATA FOR ARSENIC(III) AND ARSENIC(V) IN SYNTHETIC SEA WATER FOR A 300 ml SAMPLE

Sample no.	As(III) added (ng)	As(V) added (ng)	As(III) found (ng)	As(V) found (ng)
1	150	150	148	146
2	150	150	146	145
3	150	150	148	148
4	150	150	148	147
		Mean ($\bar{X}$)	147.5	146.5
		Standard Deviation	0.89	1.2
		% RSD (Sr)	0.6	0.8

TABLE IV

PRECISION OF ARSENIC(III), ARSENIC(V) AND TOTAL ARSENIC IN NATURAL SEA WATER FOR A 300 ml SAMPLE

Analysis	As(III) found (ng)	Total As found (ng)	As)V) (ng) (by difference)
1	15	144	129
2	14	140	126
3	15	145	130
4	16	140	124
Mean (X)	15	142.3	127.3
Standard Deviation	0.82	2.4	2.8
% RSD	5.4	1.7	2.2

TABLE V

As(III) INTERFERENCE STUDIES OF Cu(II) AND Nickel(II)

I.

Cu(II) Concentration (ppm)	Absorbance
0	0.880
1	0.875
5	0.594
200	0.484
1000	0.440

II.

Ni(II) Concentration (ppm)	Absorbance
0	0.877
1	0.870
5	0.560
10	0.440
100	0.165
1000	0.011

TABLE VI

COMPARISON OF ASHING PROCEDURES

System	Percent recovery
Dry ashing with oxygen plasma	50±10
HNO_3/H_2SO_4	99±0.5
$HNO_3/HClO_4$	100±1
$HNO_3/H_2SO_4/HClO_4$	100±0.5

TABLE VII

REDUCTION OF ARSENIC(V) TO ARSENIC(III)
(a triplicate analysis of 20 ng of As(V))

Reductive System	% Recovery as As(III)
KI	100±0
KI + Na_2SO_3	75±7
KI + $Na_2S_2O_3$	85±5
KI + $Na_2S_2O_5$	42±10
KI + Na_2SO_3 + $Na_2S_2O_5$	50±8

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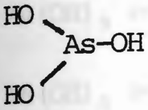
APPENDIX I

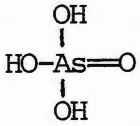
INTRODUCTION AND REVIEW OF LITERATURE

INTRODUCTION

Arsenic speciation as defined by T. M. Florence (25) is the determination of the individual physico-chemical forms of the element which together make up its total concentration in a sample. The various forms of arsenic in sea water which have been reported are ortho-arsenious acid(I), ortho-arsenic acid(II), methyl arsonic acid(III), and dimethylarsinic acid(IV) (5).

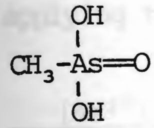


I.



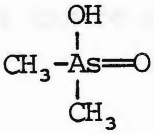
$$\mathrm{HO{-}\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{As}}{=}O}$$

II.



$$\mathrm{CH_3{-}\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{As}}{=}O}$$

III.



$$\mathrm{CH_3{-}\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{As}}{=}O}$$

IV.

The aqueous chemistry of arsenic is complicated and the various species of arsenic found in aqueous medium is dependent on the pH of the medium. The two valency states of arsenic are exhibited in the various species which have been reported. For example, arsenic is in the +3 state in arsenious acids and +5 state in arsenic acids and the organo-arsenic compounds. Due to the amphoteric nature of arsenic, the arsenious acid can dissociate not only as an acid but also as a base (30) as depicted below

$$As(OH)_3 \rightleftharpoons AsO_3^{3-} + 3H^+$$

$$As(OH)_3 \rightleftharpoons As^{3+} + 3OH^-$$

Combining these equations with the water dissociation constant and applying the mass action law, it can be shown that

$$\frac{[As^{3+}]}{[AsO_3^{3-}][H^+]^6} = \text{constant}$$

It is seen from this expression that the ratio of As^{3+} ions to AsO_3^{3-} ions is strongly dependent on the hydrogen ion concentration of the solution and that As^{3+} is present in an appreciable amount only in strongly acid solution. This is especially important in dithiocarbamate extraction since arsenic should be in the As(III) form for complexation to take place.

Arsenious acid may also exist as the meta-form, that is, $HAsO_2$ (56). Its equilibria in aqueous solution at a pH of about 8.0 can be represented as

$$AsO_2^- + H^+ \rightleftharpoons HAsO_2$$

and

$$AsO^+ + OH^- \rightleftharpoons HAsO_2$$

The other form of arsenious acid which exists in aqueous solution can be formulated as $H_3As(OH)_6$ or $As(OH)_3(H_2O)_3$ and its equilibria in solution at a pH of about than 7.0 can be represented as (4)

$$[As(OH)_4(H_2O)_2]^- + H^+ \rightleftharpoons As(OH)_3(H_2O)_3$$

$$[As(OH)_2(H_2O)_4]^+ + OH^- \rightleftharpoons As(OH)_3(H_2O)_3 + H_2O$$

The arsenic acid in an aqueous medium is relatively more stable. The acid is not ionized into As^{5+} as is the case with arsenious acid. This partly explains why the APDC-As(V) complex is not known. The equilibria of the acid might be represented by the following equations:

$$H_2AsO_4 \rightleftharpoons H_2AsO_4^- + H^+$$

$$H_2AsO_4^- \rightleftharpoons HAsO_4^= + H^+$$

$$HAsO_4^= \rightleftharpoons AsO_4^{\equiv} + H^+$$

It is clear from these equilibria of the various forms of arsenic in aqueous medium, that any analytical method which is to be developed and used to determine arsenic species at trace levels should take into account the matrix conditions which determine which equilibria exist in solution and hence which species are being analyzed.

A number of methods have been developed to study the speciation of arsenic in aqueous medium. Among these methods are electreophoresis and ion-exchange chromatography (49,51,50), paper chromatography (61), high performance liquid chromatography (9), gas chromatograph (29), differential pulse polarography (36), selective hydride evolution (47,1), cold traps with spectrophotometry (64,6,4,39,72) and solvent extraction followed by either flame, graphite furnace atomic absorption spectrophotometry (41,55,40,18) or neutron activation (32).

However, the study on the speciation of arsenic by solvent extraction followed by hydride generation analysis using the atomic absorption spectrophotometry has not been reported. The probable reason why studies have not been done in this direction is the possible interferences of organics which accompany the extraction procedure and which interfere with the hydride generation of arsenic. This study eliminates these organics by wet ashing. Trace element interferences are further eliminated by the selective hydride generation of arsenic from the sample matrix. The method is very sensitive and reliable and therefore applicable to the determination of the low levels of arsenic species in sea water.

LITERATURE REVIEW:

ARSENIC SPECIATION BY SOLVENT EXTRACTION.

The low levels of arsenic species in sea water (0.20-50 ppb) (3) require that sea water samples should be preconcentrated before analysis by atomic absorption spectrophotometry. Solvent extraction techniques have seldomly been used in this preconcentration step. The published reports make use of dithiocarbamates or molybdates as the chelating agents (16). Whereas dithiocarbamates selectively complex with arsenic(III), molybdates complex with both inorganic arsenic(V) and organo-arsenic compounds in the +5 state and this makes the separation of As(III) from As(V) possible.

A solvent extraction technique for the separation and Solvent extraction technique for the separation and determination of As(III) and As(V) using dithiocarbamates was probably first utilized by Shiro Gohda (65) to study the valency states of arsenic and antimony in sea water. In his method As(III) was separated from As(V) by extracting their diethyldithiocarbamates with chloroform and then back-extracted into dilute nitric acid. As(V) was collected in the aqueous phase by thionalide co-crystallization. The separated species were determined by neutron activation analysis. Although his method appeared to be convenient, nitric acid back-extraction has several drawbacks associated with it as has been reported by J. J. Lo et al. (44). For example, the kinetics are generally slow and acid extraction is poor for certain metals.

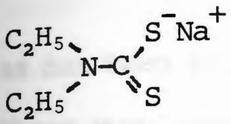
Toshihiko Kamada (40) has also studied the extraction behavior of arsenic(III) and arsenic(V) with ammonium pyrrolidinedithiocarbamate, sodium diethyldithiocarbamate and dithizone in organic solvents. He found out that APDC-MIBK extraction system was the best and As(III) was extracted in the pH range 4.0-5.6. Separation and determination of As(III) and As(V) in natural waters based on the extraction of arsenic(III) with ammonium-sec-butyl dithiophosphate, back-extraction into water, and measurement by graphite-furnace atomic absorption spectrometry has also been reported by Chakraborti et al. (13). A detection limit of 6 ng/L was reported.

The solution conditions and other parameters affecting the ammonium pyrrolidinediethiocarbamate methyl isobutyl ketone extraction system for graphite-furnace atomic absorption spectrometric determination of As(III) and As(V) have been studied by Subramanian et al. (71). They reported that arsenic(V) is not extracted over the entire range of pH and acidity studied. Using both direct and nickel matrix modifier, the results for total arsenic agreed with results by electrothermal atomization.

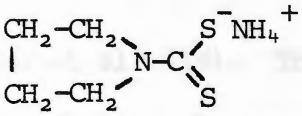
A comprehensive study for the differential determination of arsenic(V) and arsenic(III) species by solvent extraction and electrothermal atomic absorption spectrometry has been recently reported by Puttemans and Massart (55). With their method arsenic(III) was extracted quantitatively from acidic media with ammonium pyrrolidinedithiocarbamate (APDC). As(III) was stripped off into aqueous medium by Cu(II) before analysis by graphite-furnace atomic absorption spectrometry. Good extraction recoveries were reported.

CHEMISTRY OF THE EXTRACTION OF ARSENIC(III) BY DITHIOCARBAMATE

By far the most important of the dithiocarbamates used for the analysis of arsenic are the diethyldithiocarbamates (DDDC) and the ammonium pyrrolidinedithiocarbamates (APDC). The structures are shown below:

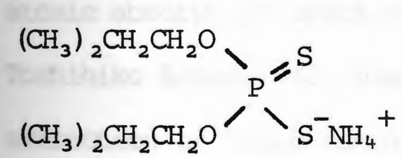


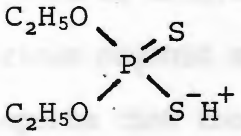
DDDC



APDC

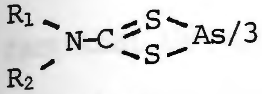
The use of dithiophosphates in the study of arsenic speciation has seldomly been reported. The determination of arsenic(III) using ammonium-sec-butyl dithiophosphate (13) and diethyldithiophosphoric acid (HDEDTP) (55) have been reported. The structures of these compounds are shown below:



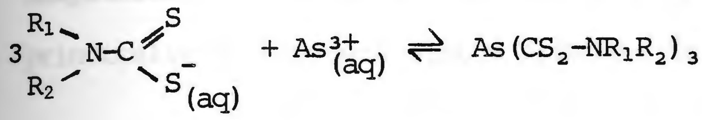


HDEDTP

The dithiocarbamates form with arsenic(III) analytically useful complexes of the general type



as has been elucidated by Vaciago et al. (14). The formation of these complexes which are pH dependent can be represented by the equation



The arsenic(III)-dithiocarbamate complex is extracted into an appropriate organic solvent which is then analyzed for arsenic by atomic absorption spectrometry or by neutron activation analysis. Toshihiko Kamada (40) has studied various organic solvents for the extraction of these complexes. He reports that the extraction efficiency of the solvents increases in the order methyl isobutyl ketone (MIBK) > nitrobenzene (NB) > carbon tetrachloride (CCl_4). The other solvents which have been reported to have good extraction efficiency are chloroform and Freon-TF.

The analytical application of dithiocarbamates is based on the fact that the dithiocarbamates selectively complex with arsenic(III) but not with arsenic(V). The reason for this differential complex formation with arsenic(III) but not with arsenic(V) are two-fold: (1) the dithiocarbamates are bulky groups and, therefore, it is less likely that five of these will conveniently surround the relatively small arsenic atom and (2) As^{5+} unlike As^{3+} is not available for complexation at the pH for optimum extraction because arsenic(V) is principally in the more stable arsenate form.

DETERMINATION OF ARSENIC BY THE HYDRIDE GENERATION TECHNIQUE

Since the introduction of hydride generation technique for the analysis of arsenic by Holak (37), several papers have been published on this subject (63,26,59). The method is presently well-established and it is frequently used for routine analysis of hydride forming elements at trace levels.

The basic principle for analysis of arsenic by the hydride generation technique is that arsenic(III) is selectively reduced to arsine by sodium borohydride solution in an acidic medium. The reaction can be represented by the following general equations although the mechanism for the reduction is not well understood.

$$BH_4^-{}_{(aq)} + 3H_3O^+ \rightarrow B(OH)_3 + 10[H]$$

$$As^{3+} + 3[H] \rightarrow AsH_3 \uparrow$$

The gaseous arsine produced is swept into a pre-heated furnace at a temperature of about 900°C by a carrier gas, usually argon or helium.

In the furnace, AsH_3 is decomposed into arsenic and hydrogen atoms. Atomization followed by absorption of arsenic resonance radiation makes it possible to measure the amount of arsenic present in the sample.

$$AsH_{3\,(g)} \xrightarrow{\text{Decomp.}} As_{(g)} \xrightarrow{\text{Vaporization}} As_4 \xrightarrow{\text{Decomp.}} As_2 \xrightarrow{H} As_{(g)} \quad (35,36).$$

Under mild acidic conditions arsenic(V) is not reduced by borohydride solution. This is probably due to the fact that arsenic(V) is exclusively in the arsenate form. The arsenate ion might, however, be very slightly ionized into As^{5+} ions in very strong acidic conditions and a reduction to arsine by borohydride solution might then take place according to the following equilibria,

$$H_3AsO_4 + 5H^+ \rightleftharpoons As^{5+} + 4H_2O$$

$$As^{5+} + 3[H] \rightarrow AsH_3 \uparrow$$

[H]-from borohydride solution

FURTHER EXPERIMENTS AND DISCUSSSION

During the course of the studies certain conditions were required to be optimized. These included the following experiments which have been discussed in detail in the appendices

1. Elimination of reagent blank in the determination of arsenic(III) by atomic absorption spectrometry-hydride generation technique.
2. Interference studies of some trace elements and organics on the hydride generation of arsenic.
3. The method of wet ashing.
4. Reduction of arsenic(V) to arsenic(III).

APPARATUS

All atomic absorption spectra measurements were made by a Perkin-Elmer atomic absorption spectrophotometer and its accessories as described in the manuscript.

All pH measurements were made by a Corning pH Meter Model 7.

Dry ashing was done in a Low Temperature Asher Model 302 (LFE Corporation).

APPENDIX II

ELIMINATION OF REAGENT BLANK IN THE DETERMINATION OF ARSENIC BY ATOMIC ABSORPTION SPECTROMETRY VIA THE HYDRIDE GENERATION TECHNIQUE

INTRODUCTION

Since the birth of the determination of arsenic via hydride generation with subsequent analysis by atomic absporption in 1969 (37), there have been conflicting reports about the causes and the elimination of the reagent blank signal associated with the determination. Knudson et al. (42) attributed this reagent blank to sodium borohydride contamination. R. D. Wauchope (11) in his paper on the application of a rapid arsine generation technique to soil, water and plant samples had observed that the reagent blank was produced from 20-40% hydrochloric or perchloric acid and that the signal was dependent on the hydrogen flow which swept the arsine into the furnace for atomization. No attempt was made to eliminate this blank. Others (W. Holak (37); D. D. Siemer et al. (67); Braman et al. (8,7); E. A. Grecelius (15) have attributed this blank to water vapor, carbon dioxide and hydrogen sulphide gas respectively. These researchers succeeded in eliminating the blank by using substances which absorb these gases such as sodium hydroxide, calcium chloride and phosphoric acid. Due to the different views on this subject, this study has included an investigation into the sources and elimination of the reagent blank in the hydride generation system which was developed in this study.

Reagents

Arsenic(III) stock solution was prepared by dissolving 1.322 g of As_2O_3 primary standard (Matheson, Coleman and Bell) in 10 ml 20% NaOH. The resulting solution was made up to the mark in 1000 ml volumetric flask (i.e. 1 mg/ml).

The arsenic(V) stock solution was prepared by dissolving 4.1650 g of $Na_2HAsO_4 \cdot 7H_2O$ primary standard (Mallinckrodt analytical reagent) in deionized water. The resulting solution was made up to the mark in a 1000 ml volumetric flask (i.e. 1 mg/ml).

Working solutions were made by dilutions from the prepared stock solutions.

The sodium borohydride solution 5% was prepared by dissolving 5 g of sodium borohydride powder (Fischer) in 100 ml deionized water followed by 2 pellets of potassium hydroxide. The resulting turbid solution was filtered through 0.45 μm filter membrane to obtain a clear solution. This solution was prepared on a bi-weekly basis since the study by Fraser and R. Bye (12,28) has shown that there is no change in the reactivity of sodium borohydride up to a period of three weeks. Concentrated hydrochloric and nitric acids were redistilled in pyrex glass distillation quickfit kit since pyrex does not contain any arsenic impurity (78). Two molar hydrochloric acid was prepared from the concentrated acid. Two molar nitric acid was prepared from the concentrated acid.

PROCEDURE

The instructions followed for the operation of the instrument were from the Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer manual and its manual for the accessory MHS-10 mercury/hydride generation system. (See Figure 1 in manuscript for schematic diagram of the assembly used in the analysis.)

Optimization of the system (i.e. optimal flow rate of carrier gas, correct positions of EDL and quartz tube) was done before any subsequent analysis.

For the study of the reagent blank, the Perkin-Elmer MHS-10 system was directly connected to the quartz-tube and 3% sodium borohydride solution (recommended concentration) was made to react with 10 ml 2 molar HCl in the reaction vessel and a reagent blank was observed.

The following experiments were designed and performed:

1. To investigate whether or not the reagent blank was due to the sodium borohydride solution used; different levels of sodium borohydride concentrations (3%, 4%, 5%, 6%) were used in the analysis;

2. To investigate any possible arsenic contamination in the hydrochloric acid, different hydrochloric acid concentration levels (1M, 2M, 3M, 4M,) were prepared and analyzed as before. Twenty milliliters of 1 ppb As(III) solution were added to the hydrochloric acid prior to reduction by sodium borohydride solution. In a separate experiment 10 ml of 4 molar HCl was added to 0.1 ml 5% sodium borohydride solution. The resulting solution was analyzed as before;

3. Concentrated hydrochloric acid was distilled and 1M, 2M, and 3M concentrations prepared from it. These solutions were analyzed as a reagent blank;

4. To investigate whether or not water vapor was also a source of the reagent blank: a trap containing calcium chloride was fitted

between the MHS-10 system and the quartz tube to remove any water vapor resulting from the vigorous and the exothermic reaction between the sodium borohydride and the 2 M HCl acid.

RESULTS AND DISCUSSION

Table I shows the absorbance values from the various sodium borohydride concentrations used. It can be seen from the table that there is no effect of the sodium borohydride solution on the absorbance due to the blank. This suggests that the reagent blank did not result from the sodium borohydride solution.

The results for the study with hydrochloric acid are shown in Table II. The Table indicates that different hydrochloric acid concentrations gave different peak heights for the blank. This suggests that the blank signal was probably an arsenic impurity in hydrochloric acid. The fact that the reagent blank peak height was increased after it was spiked with 20 ml 1 ppb As(III) confirms that the reagent blank was partly due to arsenic impurity in hydrochloric acid. The results from the distilled HCl show a significant decrease

TABLE I

ABSORBANCES FOR THE ANALYSIS OF VARIOUS CONCENTRATIONS OF SODIUM BOROHYDRIDE SOLUTION

Absorbance values	$NaBH_4$ concentration (% w/v)
0.099	3
0.088	4
0.099	5
0.099	6

TABLE II

AS(III) ABSORBANCE VALUES OF VARIOUS CONCENTRATIONS OF HYDROCHLORIC ACID

Hydrochloric Concentration (M)	Direct from bottle	Spiked with 20 ng As(III) standard	Redistilled
1	0.066	0.242	0.044
2	0.088	0.264	0.044
3	0.111	0.284	0.033
4	0.121	0.290	0.044

Absorbance value for 4M HCl after pre-reaction with 0.1 ml 3% $NaBH_4$ was found to be 0.040.

in reagent blank peak height. The probable reason is that the arsenic impurity was distilled off as arsenic trichloride. The results also indicate that the essentially identical peak heights as that from the distilled HCl was obtained when 2 molar HCl was made to react with 0.2 ml of 3% sodium borohydride solution before analysis for the reagent blank. These results further confirm that hydrochloric acid (analytical reagent) has a measurable arsenic impurity.

The results for the experiments involving the removal of water vapor indicate that water vapor was the major source of the reagent blank. Table III shows that the reagent blank is reduced to the noise level of the instrument when calcium chloride traps were fitted into the hydride generation system. The mechanism for absorption of water vapor may be due to hydroxyl radical produced during the free radical chain reaction as depicted below (20), where Q = heat energy:

$H_2 + Q \rightarrow 2H\cdot$

$H\cdot + H_2O \quad H_2 + OH\cdot$

$OH\cdot + OH\cdot \rightarrow H_2O_2$

$H\cdot + H\cdot \rightarrow H_2$

TABLE III

RESULTS FOR THE EXPERIMENT WITH CALCIUM CHLORIDE AS DRYING AGENT

Experiment #	Absorbance
1	0.006
2	0.006
3	0.008
4	0.006

CONCLUSIONS

The results of the experiment indicate that the sources of the reagent blank in the hydride generation technique are water vapor and arsenic impurity in the acid used in the analysis. The results show that simple distillation of the acid prior to its use in sample preparation frees it of any arsenic(III) impurity. The results also indicate that water vapor produced during the reaction could be removed by anhydrous calcium chloride. Any suitable drying agent could as well be used. Calcium sulphate (Drierite) is, however, not recommended since it has been reported that large amounts of arsine is adsorbed on to it (8). Reagent blank signals resulting from carbon dioxide and/or hydrogen sulphide were not observed with the system used.

APPENDIX III

INTERFERENCE STUDIES OF SOME TRACE ELEMENTS AND ORGANICS ON THE HYDRIDE GENERATION OF ARSENIC

INTRODUCTION

The reduction of arsenic(III) to its corresponding hydride followed by atomization of arsenic in a flame or flameless furnace is subject to organic and trace metal interferences as shown by this study.

Trace metal interferences in hydride generation following atomic absorption have been studied by many investigators (A.E. Smith (68), Braman et al. (8), Lansford et al. (43), Roulet et al. (58), Yamamoto et al. (80), Vigan and Wood (75), Daher and Saleh (17), Saleh (62). The trace metals which interfere severely as has been found by these researchers, are nickel(II) and copper(III) ions.

The work carried out in this study is the investigation of the various concentration levels of nickel(II) and copper(II) which interfere with hydride generation. Also the study of the effects of organics such as APDC and amines on hydride generation following atomic absorption were investigated. These organics were chosen for study because they were likely to be present in the sample solution which was analyzed for arsenic via the hydride generation.

EXPERIMENTAL

Reagents

1000 ppm Cu(II) solution was prepared by dissolving 2.650 g Cu(II) $Cl_2 \cdot 2H_2O$ in a litre of solution in a volumetric flask. 200 ppm and 2 ppm of Cu(II) solution were prepared from this stock solution.

100 ppm, 10 ppm and 1 ppm nickel(II) solutions were prepared

from nickel(II) atomic absorption standard in concentration of 997 ppm.

1% (w/v) ammonium pyrollidine dithiocarbamate was prepared by dissolving 0.500 g APDC in 50 ml of deionized water. This was filtered through an 0.45 μm filter membrane followed by extraction with chloroform.

Pyrrolidine was used as purchased from Fisher.

Atomic absorption standards, lead (996 ppm), iron (1013 ppm), cobalt (988 ppm), cadmium (1000 ppm), were obtained from Alpha Analytical Laboratories.

Two molar HCl was prepared from the concentrated solution.

PROCEDURE

Standard solutions of arsenic(III) containing 100 ng were prepared from the stock solution as described in the manuscript.

Interferences of trace elements:

One ml of the appropriate concentration of the trace element was added to 11 ml solution containing 100 ng of arsenic(III). The solution was then analyzed for arsenic by atomic absorption spectrometry-hydride generation technique.

Interferences by APDC and Pyrrolidine:

APDC. Two-fifths of a milliliter or 0.6 ml of 1% APDC were analyzed alone and also added to 11 ml of solution containing 100 ng arsenic(III) followed by atomic adsorption spectrophotometric analysis.

Pyrrolidine. One-half of a milliliter and 1 ml pyrrolidine were first analyzed separately and then 0.5 ml of pyrrolidine was added to a 11 ml solution containing 100 ng arsenic(III) and the resulting solution analyzed as above. The experiment was repeated using 1 ml pyrrolidine.

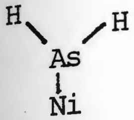
RESULTS AND DISCUSSION

Trace Element Interference

There were no interferences with the hydride generation of arsenic for the following elements at 1000 μg levels: Fe^{3+}, Pb^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+}. Nickel(II) and copper(II) interfered severely at this concentration level. Figure 1 shows the atomic absorption signal (absorbance) versus the various concentration levels of Ni(II) or Cu(II) added to 100 ng arsenic(III) solution. It is clear from the graph that Ni(II) and Cu(II) interfere in hydride generation to a significant degree when they are above 5 ppm in concentration in arsenic solution matrix.

A few reports have suggested a possible interferencemechanism by these elements. Smith et al. (70) have suggested that these elements form a precipitate with borohydride solution. Elemental nickel or copper is probably formed and this precipitate prevents the evolution of arsine from the reaction mixture.

Another reason for the interference has been offered by Saleh and Al-Daher (17). They explain that the elemental copper or nickel form a surface for chemisorption of arsine on to it as is shown below,



The other reason they have offered is that arsine gas is decomposed on the copper metal surface according to the reaction equation depicted below and thus arsine is not made available for atomization in the quartz tube,

$$nCu + AsH_3 \rightarrow Cu_nAs + 3/2\ H_2$$

where absorption of resonance energy occurs.

Brown et al. (76) have attributed this interference of copper to the reaction of NO_3^- ion, if present in solution, with the reduced copper to produce the species NO_2^-, NO_2, NO which interfere with the analysis since these species might absorb the same resonance energy as arsenic.

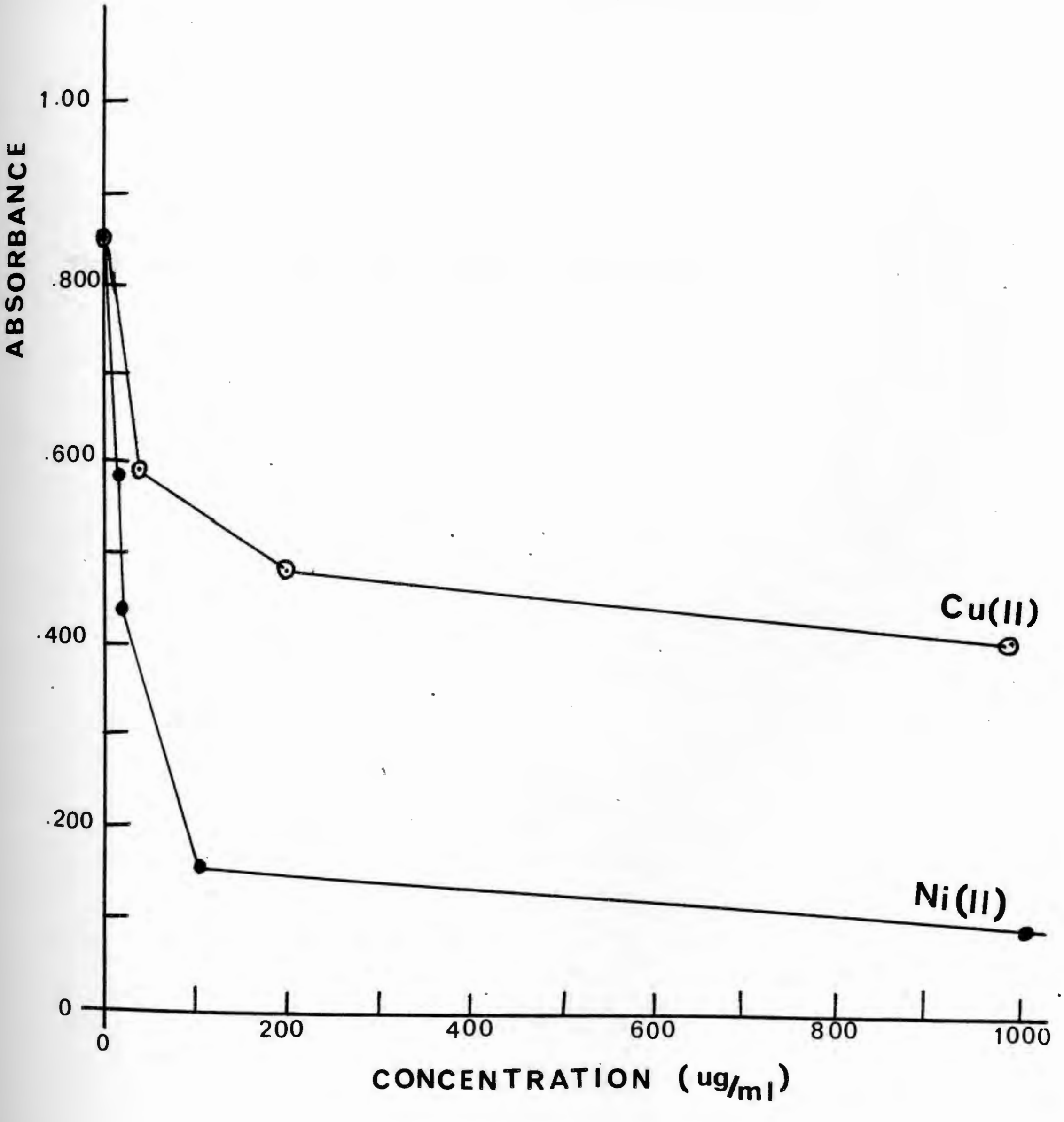
Although the explanations cited above somewhat clarify the chemical nature of these interferences, further studies are needed to completely establish the nature of these interferences and the mechanism of how they interfere.

Interference of APDC and Pyrrolidine

Preliminary studies during the development of the method indicated that APDC and pyrrolidine interfered significantly in the hydride generation. An investigation was therefore carried out to determine the tolerable levels of these compound in the analysis without interfering with arsine generation since these compounds were

FIGURE 1

Absorbance of 150 ng As(II) Versus Concentration of Cu(II) or Ni(II) Added



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suspected to be impurities in the sample from the extraction procedure. Figures 2 and 3 show the atomic absorption spectrum of 100 ng of As(III) with various amounts of APDC solution and pyrrolidine. The salient features of these spectra are the unusual peaks due to APDC and pyrrolidine alone. Also note how these peaks decrease in height in the presence of arsenic(III) ions.

FIGURE 2

Atomic Absorption Spectra of the Effect of APDC on As(III) Reduction to Arsine

A - 100 ng As(III) standard in 10 ml 1 molar HCL
B - 100 ng As9III) standard in 10 ml 1 molar HCl + 0.4 ml 1% APDC
C - 0.6 ml APDC in 10 ml 1 molar HCl
D - 0.4 ml APDC in 10 ml 1 molar HCl
E - 100 ng As(III) standard in 10 ml 1 molar HCl + 0.6 ml 1% APDC

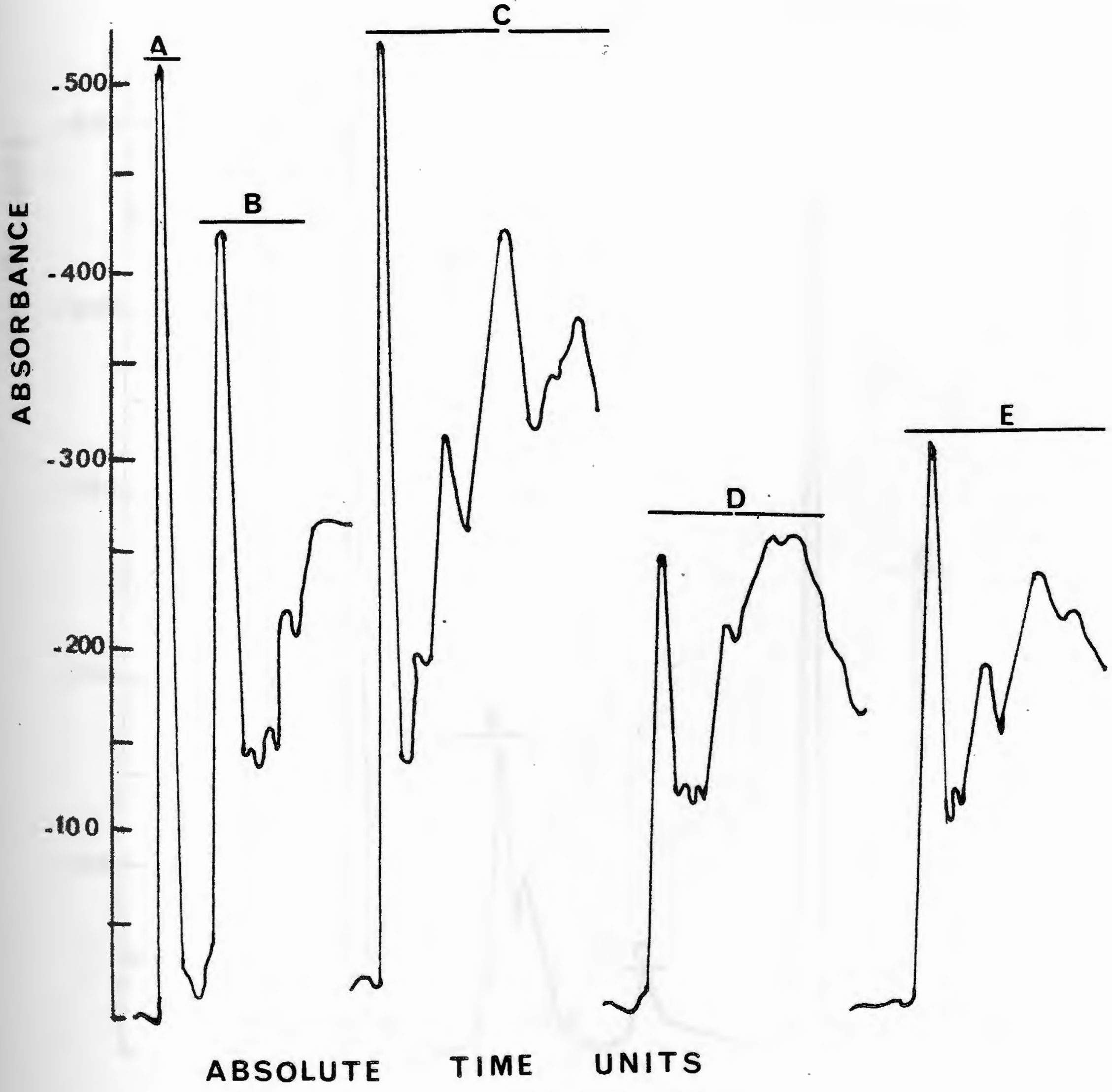


FIGURE 3

Interference Study of Pyrrolidine on Arsenic(III)

Reduction to Arsine

A - 100 ng As(III) standard in 10 ml 1 molar HCl (two analysis of As)
B - 100 ng As(III) standard in 10 ml 1 molar HCl + 1 ml pyrrolidine
C - 300 ng As(III) standard in 10 ml 1 molar HCl + 1 ml pyrrolidine
D - 100 ng As(III) standard in 10 mo 1 molar HCl + 1 0.5 l pyrrolidine
E - 1 ml pyrrolidine in 10 ml 1 molar HCl

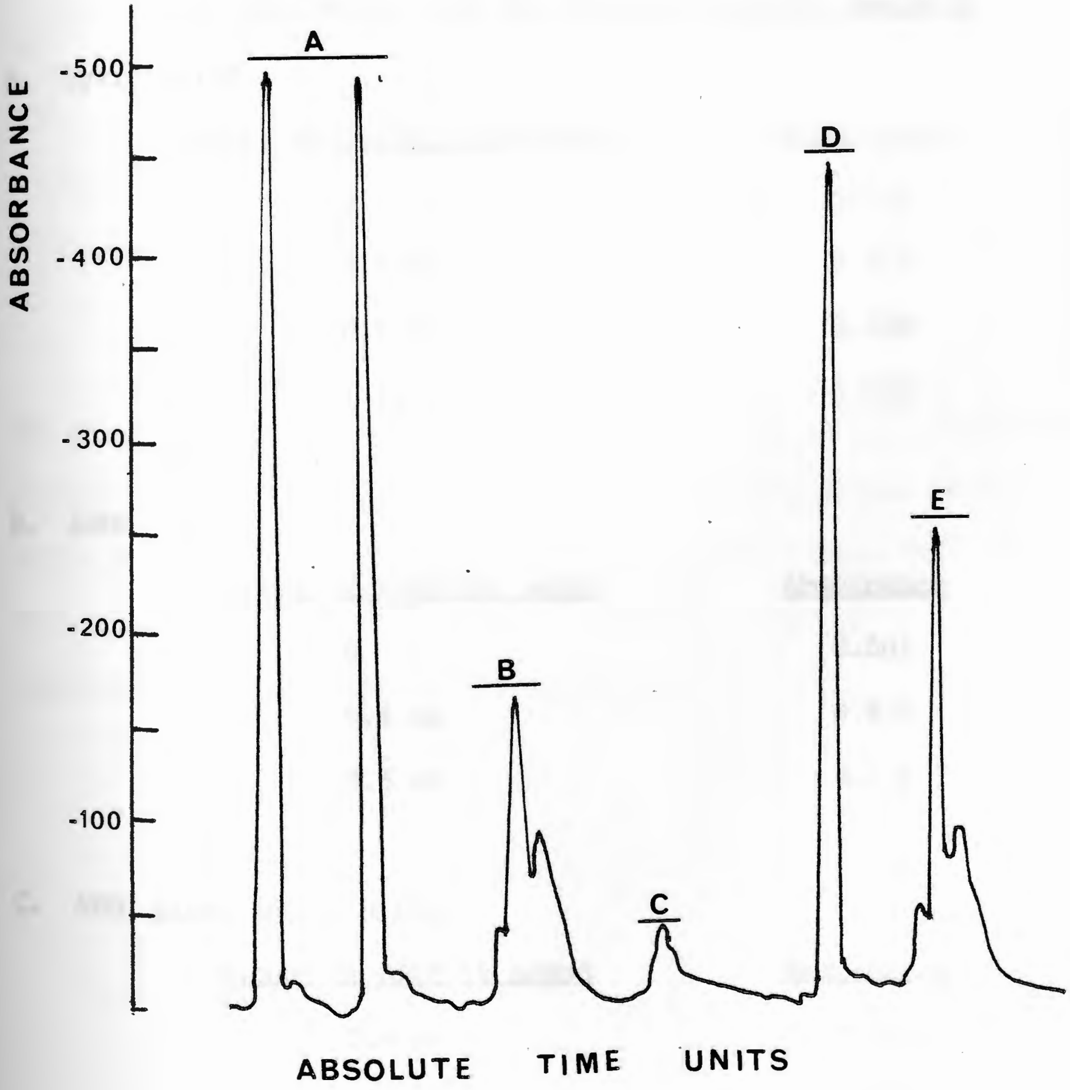


Table IV shows some quantitative work done on the effect of pyrrolidine and APDC on the analysis of 100 ng of arsenic(III). The trend is that both the absorption peaks due to the 100 ng arsenic(III) alone and APDC or pyrrolidine alone decrease in height when APDC or pyrrolidine is added to the 100 ng As(III) before analysis.

TABLE IV

ABSORBANCE VALUES FROM THE STUDIES OF THE EFFECT OF APDC AND PYRROLIDINE ON 100 ng OF As(III) ANALYSIS

A. Pyrrolidine

Amount of pyrrolidine added	Absorbance
0	0.523
0.4 ml	0.473
0.5 ml	0.330
1 ml	0.152

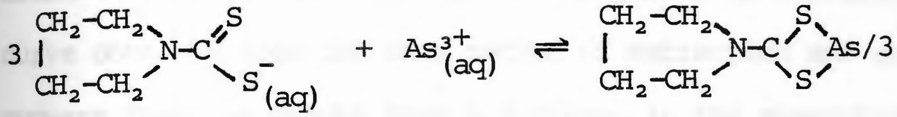
B. APDC

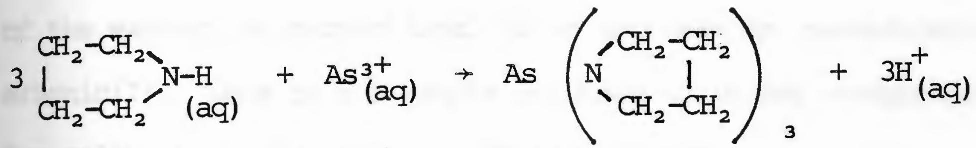
Amount of APDC(1%) added	Absorbance
0	0.501
0.4 ml	0.420
0.6 ml	0.280

C. APDC alone in 0.6 M HCl

Amount of APDC 1% added	Absorbance
0.6 ml	0.501
0.4 ml	0.245

A possible explanation for this observation is that sodium borohydride reacts with APDC or pyrrolidine to produce some gaseous products which absorb the same resonance energy as arsenic. The decrease in the peak heights of arsenic(III) spectrum in the presence of either APDC or pyrrolidine is due to the fact that APDC or pyrrolidine react with the arsenic(III) ions and, therefore, remove them from the solution matrix according to the following equations:





The peaks observed after addition of the various amounts of APDC or pyrrolidine to the arsenic(III) solution before analysis as shown in Table IV are due to the unreacted APDC or pyrrolidine. This means that all of the 100 ng arsenic(III) ions were used up by the APDC or pyrrolidine according to the equations above.

During the preliminary studies, appropriate concentrations of arsenic(III) were extracted with APDC into a chloroform layer. The arsenic(III) was stripped off from the APDC-As(III) complex into an aqueous layer using concentrated nitric acid. The aqueous layer was analyzed for arsenic directly without wet ashing by the hydride-generation technique. Figure 4 is a calibration curve obtained by analyzing the various concentrations of arsenic by the extraction method described above. Figure 5 is a standard addition curve obtained from the same method of extraction and analysis. It appears from the graphs that a decrease in the absorption peak height of the extract is proportional to an increase in concentration of arsenic(III) ions in the sample solution which are unexpected trends for calibration and standard addition curves.

FIGURE 4

Calibration Curve for Extraction System Without Wet Ashing: Absorbance Versus Concentration

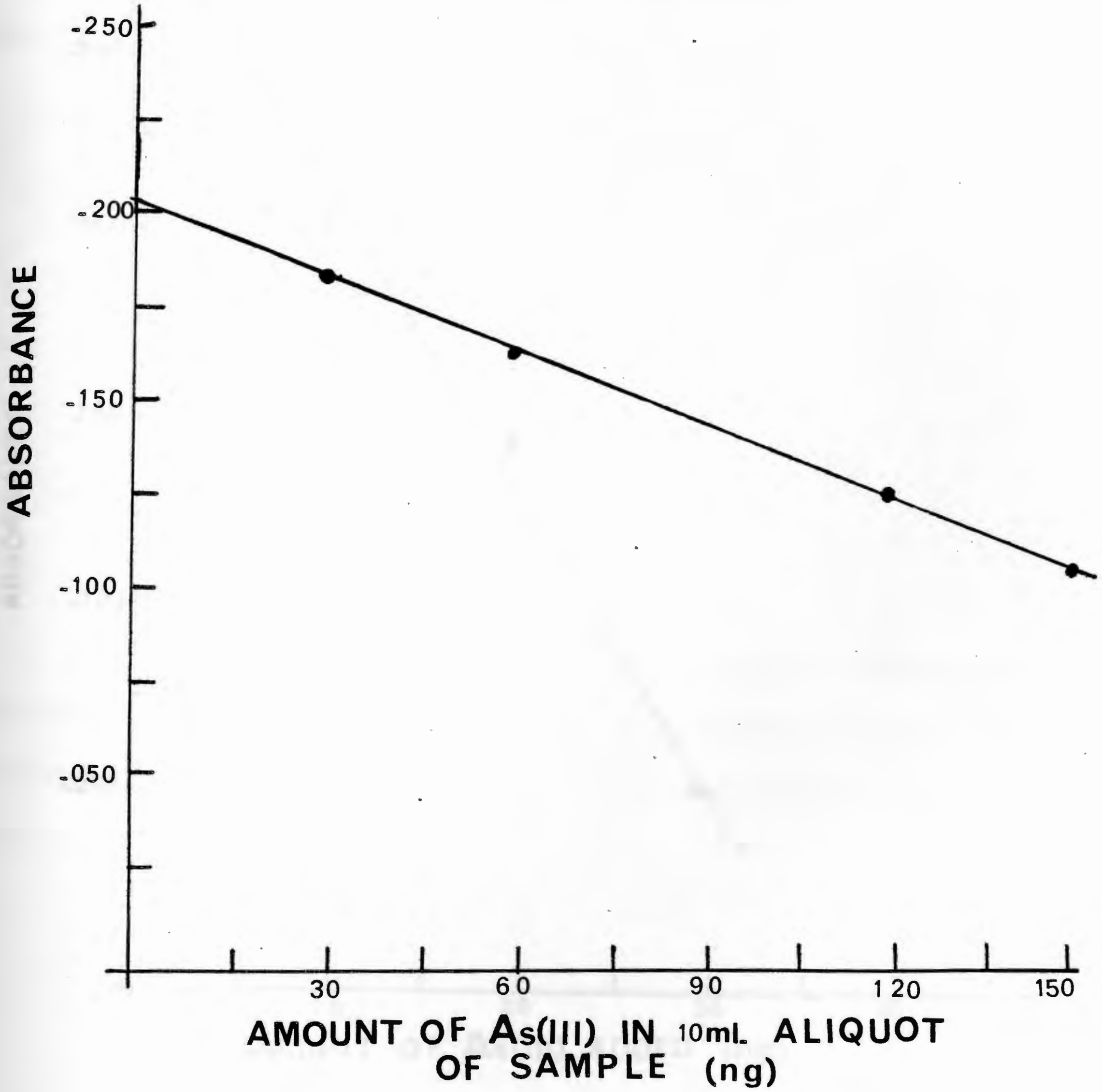
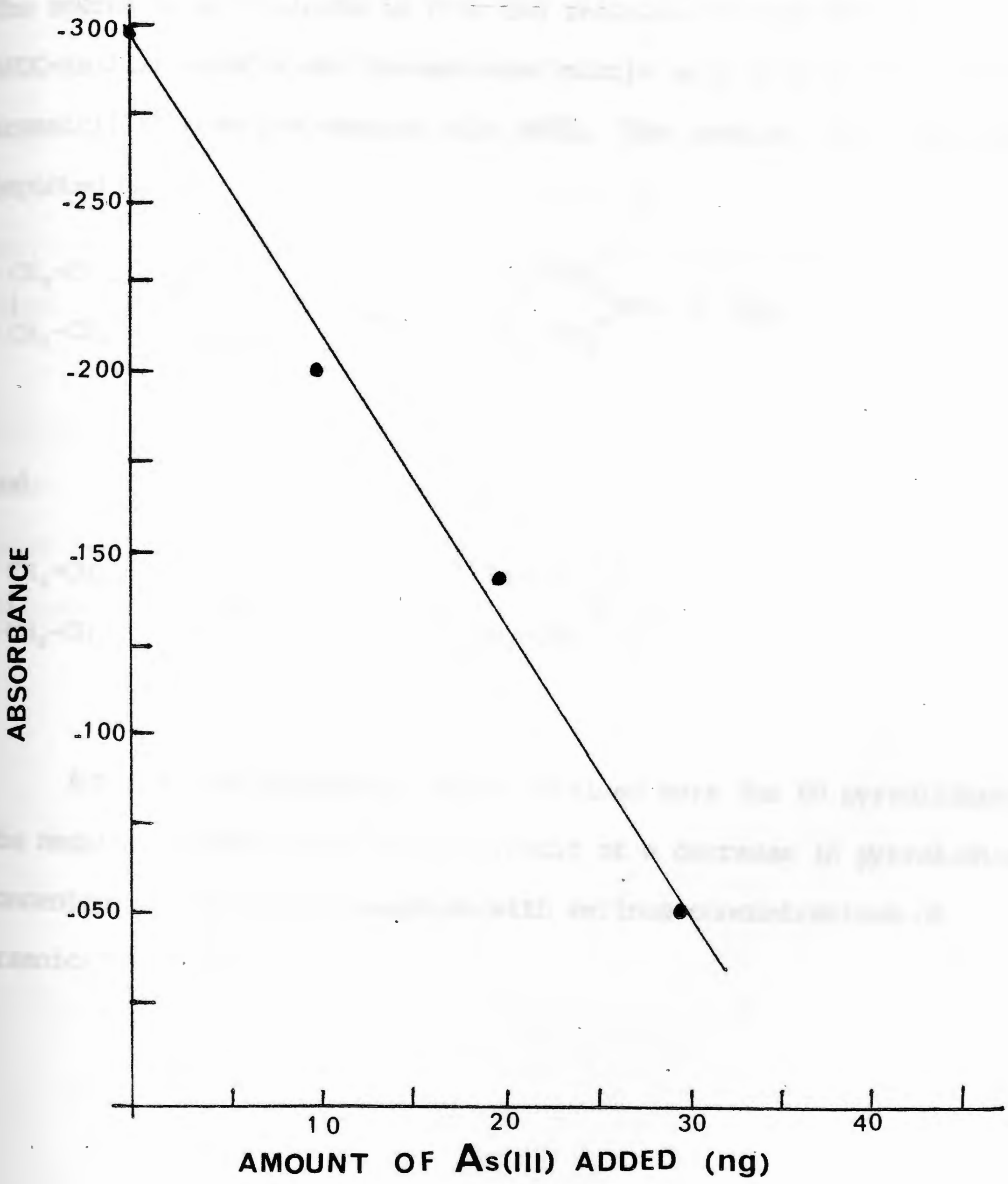
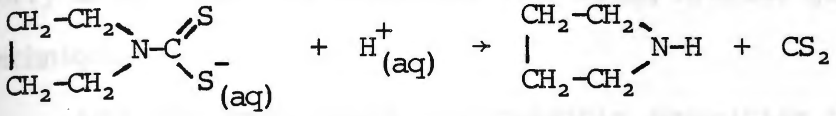


FIGURE 5

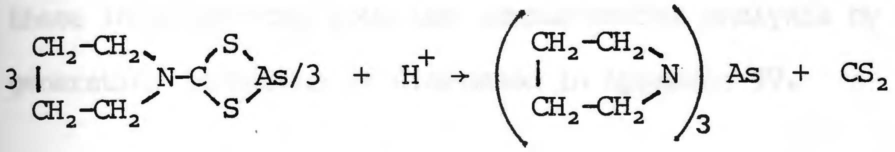
Standard Addition Curve for Extraction System Without Wet Ashing: Absorbance Versus Amount of As(III) Added



This unusual trend can be accounted for by equation 3 (69). The source of pyrrolidine is from the reaction between APDC or APDC-As(III) complex and concentrated nitric acid used to strip off arsenic(III) from its complex with APDC. The reaction equations are depicted below:



and



Actually the absorption peaks obtained were due to pyrrolidine. The negative linear graph is as a result of a decrease in pyrrolidine concentration due to its reaction with various concentrations of arsenic(III) ions.

CONCLUSIONS

The trace elements Fe^{3+}, Pb^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+} do not interfere with hydride generation of arsenic. Nickel(II) and copper(II) interfere at concentration levels above 5 ppm. Since these elements occur in sea water below 5 ppm (18) one should not worry about their interferences when using hydride generation technique.

APDC and pyrrolidine, the possible impurities in the preconcentrated sample using APDC as the complexing agent, interfere severely in hydride generation of arsenic. A way of eliminating these interferences from the sample before analysis by the hydride generation technique is discussed in Appendix IV.

APPENDIX IV

WET ASHING

INTRODUCTION

Systems with organic contaminants adversely affect subsequent analysis by hydride generation and it is often necessary to oxidize the organics to volatile compounds which can be removed from the sample medium thus enabling trace metals to be analyzed without interference. The method of ashing has been used to bring about this oxidation. There are several methods for ashing which have been reported in literature. Each report is based on one of the following classifications: (a) dry or wet depending on the application of a gaseous or liquid reagent, (b) higher or lower temperature and, (c) high or normal pressure.

To circumvent the problem of elemental loss, a low-temperature dry ashing technique was recommended (31). This method employs the use of oxygen plasma which is formed by passing oxygen through a high-frequency electromagnetic field. In the process, oxygen is activated and reacts with the sample. This causes a slow burning within a temperature range of about 50 to 250°C. Although this method is effective, it has one drawback, the ashing is slow if a large sample is to be ashed. Recently, it has been reported by Walsh et al. (76), that there are losses of arsenic during the low temperature ashing of atmospheric samples. Low temperature ashing of samples containing arsenic, therefore, becomes less attractive for sample preparation.

Another method which has been used is wet ashing; it employs the use of concentrated strong oxidizing mineral acids such as HNO_3, H_2SO_4, $HClO_4$, (HF), hydrogen peroxide and mixtures of them

(63,40,77,24,33) to bring about the oxidation of organics during sample preparation. This method appears to be the preferred one since trace element losses are minimal during the ashing (59). In this study an investigation into the wet ashing methods, HNO_3/H_2SO_4, $HNO_3/HClO_4$, $HNO_3/H_2SO_4/HClO_4$ and dry ashing with oxygen plasma has been carried out.

EXPERIMENTAL

Reagents and Materials

All the mineral acids used in this experiment were of analytical grade and were purchased from Fisher. Perchloric acid (70%) and sulphuric acid 18 M were used as purchased. Nitric acid was redistilled in a pyrex distilling kit. Potassium iodide (Fisher) was used in the solid form. Whatman #4 paper, which was pretreated with 1 molar nitric acid and sufficient deionized water to render it acid-free, was used in the dry ashing.

PROCEDURE

Dry Ashing: 0.3 ml of 100 ng/ml As(III) with 1 ml each of pyrrolidine and APDC added as organic matter solution were collected on a pretreated Whatman #4 filter paper. After drying it in air the paper was dry ashed in a Low Temperature Asher. At the end of the ashing, the ash residue was dissolved in 2 molar hydrochloric acid and the solution was made up to 25 ml with hydrochloric acid in a volumetric flask. Ten ml aliquots of this solution were analyzed for arsenic by atomic absorption-hydride generation technique.

Wet Ashing: Thirty ml of 1 ppb arsenic(III) solution with 1 ml each of pyrrolidine and APDC as organic matter were pipetted into a 250 ml erlenmeyer flask. A small short-stem funnel was placed in top. Ten ml of concentrated nitric acid and 10 ml of perchloric acid (70%) were added. This was evaporated to dense white fumes of perchloric acid. After cooling, 10 ml of deionized water was added and the sample was again evaporated to white dense fumes of perchloric acid. This solution was transferred quantitatively into a 25 ml volumetric flask. Ten ml aliquots of this solution were used for analysis. The results are shown in Table V.

RESULTS AND DISCUSSION

Table V gives the percent recovery for the various systems used in the ashing. It is seen from the table that there is a serious loss of arsenic during dry ashing. This is in agreement with reported values by Walsh et al. (76).

This table also indicate that destruction of organic matter before the detemination of arsenic can be achieved by wet ashing. These results agree with reported values (33).

TABLE V

DATA FOR THE STUDY OF DIFFERENT SYSTEMS FOR WET ASHING OF 30 ng OF As(III)

System	Percent recovery
Dry ashing with oxygen plasma	50±10
HNO_3/H_2SO_4	99± 0.5
$HNO_3/HClO_4$	100± 1
$HNO_3/H_2SO_4/HClO_4$	100± 0.5

Both perchloric acid and nitric acid are strong oxygen donors and it is the donated oxygen atom which destroy the organic matter. Perchloric acid releases oxygen according to the reaction equation

$$4HClO_4 + \Delta \rightarrow 2Cl_2 + 7O_2 + 2H_2O$$

Because of the oxidizing property of these acids, arsenic(III) is oxidized to arsenic(V) during the process of ashing. The following equation illustrates the oxidation of arsenic(III) to arsenic(V) by nitric acid

$$As_2O_3 + 4HNO_3 + H_2O \rightarrow 2H_3AsO_4 + 4NO_2 \uparrow$$

However, arsenic(V) is not reduced to arsine by borohydride solution. There is therefore the need to reduce arsenic(V) to arsenic(III) before analysis by the hydride generation technique. The best system for the reduction was found to be potassium iodide among other reducing systems tried and this method was used in this experiment. Appendix V discusses the various experiments concerning the reduction of arsenic(V) to arsenic(III).

CONCLUSIONS

In view of the results obtained, one can conclude that oxidation of organic matter from a sample matrix could be achieved by employing either of the following systems $HNO_3/HClO_4$, HNO_3/H_2SO_4, or $HNO_3/H_2SO_4/HClO_4$ with complete recovery of arsenic from the matrix.

APPENDIX V

REDUCTION OF ARSENIC(V) TO ARSENIC(III)

INTRODUCTION

Analysis of total arsenic in natural waters and arsenic(III) after ashing, by hydride generation using sodium borohydride solution requires that arsenic(V) be reduced to arsenic(III) before further reduction to arsine with the sodium borohydride solution.

Different types of reducing agents have been reported to be effective in reducing arsenic(V) to arsenic(III). These include the use of potassium iodide (59,53,35,27,52) sodium thiosulfate, sodium bisulfite and sodium metabisulfite (55,66,46,45). Different authors report different reducing agents to be the most effective. It is therefore necessary to investigate these reported reducing agents to find out which one is the most effective in reducing arsenic(V) to arsenic(III) after wet ashing. The work has also included the study of the time-dependence of the reduction of arsenic(V) to arsenic(III) using the most effective reducing agent.

EXPERIMENTAL

Reagents

Potassium iodide solid was used as purchased. 1% sodium thiosulphate ($Na_2S_2O_3$) was prepared by dissolving 1.0 g of $Na_2S_2O_3$ in 100 ml of deionized water. 3% sodium sulfite (Na_2SO_3) was prepared by dissolving 3.0 g of Na_2SO_3 in 100 ml of deionized water. 5% sodium metabisulfite ($Na_2S_2O_5$) was prepared by dissolving 5.0 g of $Na_2S_2O_5$ in 100 ml of deionized water.

Procedure

Five hundred ml of 0.2 ppb arsenic(V) solutions were prepared in 5 separate labelled polyethylene bottles. To each of these solutions was added about a gram of potassium iodide. Twenty ml of 1% sodium thiosulphate solution was then added to bottle 2, 20 ml of 3% sodium sulfite solution to bottle 3, 20 ml of 5% sodium metabisulfite solution to bottle 4, 20 ml of 3% sodium sulfite and 20 ml of 5% sodium metabisulfite to bottle 5. Reduction of arsenic(V) to arsenic(III) was monitored by atomic absorption spectrophotometer via the hydride generation method over a period of 1 1/4 hours.

RESULTS AND DISCUSSION

The results obtained, expressed as percent recovery for the various reducing systems used to reduce arsenic(V) to arsenic(III), is shown in Figure 6. The results indicate that KI produced the most complete reduction. In the absence of a reducing agent only 50% of arsenic(V) is reduced to arsine. The low percent recoveries for the other reducing systems might not be due to their inefficiency as reducing agents but might probably might be due to interferences from SO_2, SO_3 or H_2S produced when the borohydride reacted with the thiosulphate, sulfite or metabisulfite in acidic medium. It is known that these gaseous products interfere severely in hydride generation of arsenic.

Figure 7 shows the results obtained for the time dependent study for complete reduction of arsenic(V) to arsenic(III) by potassium iodide. The results show that arsenic(V) is completely reduced to arsenic(III) within the first 5 minutes.

FIGURE 6

Percent As(V) Recovered as As(III)

Versus Reducing System

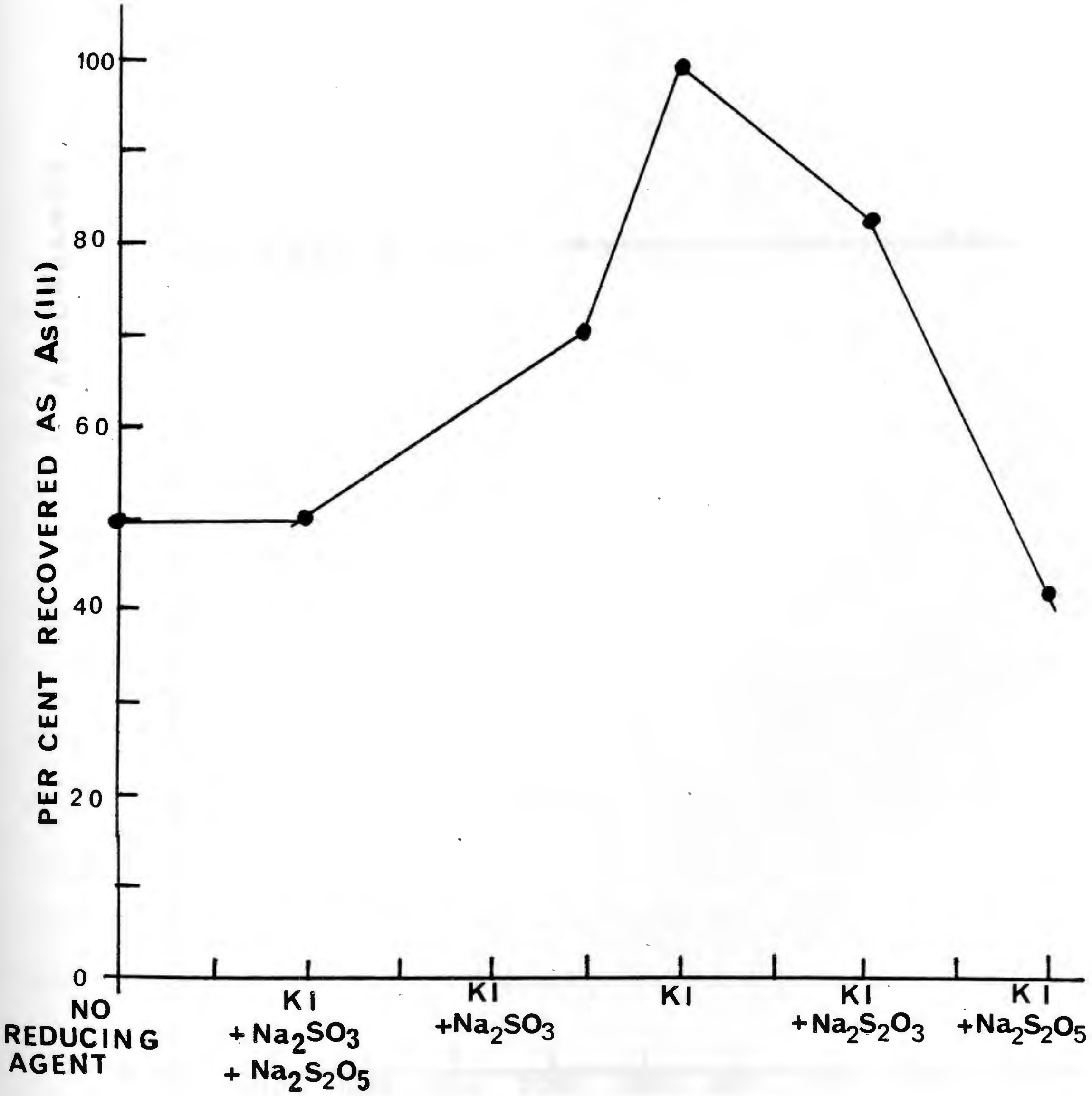
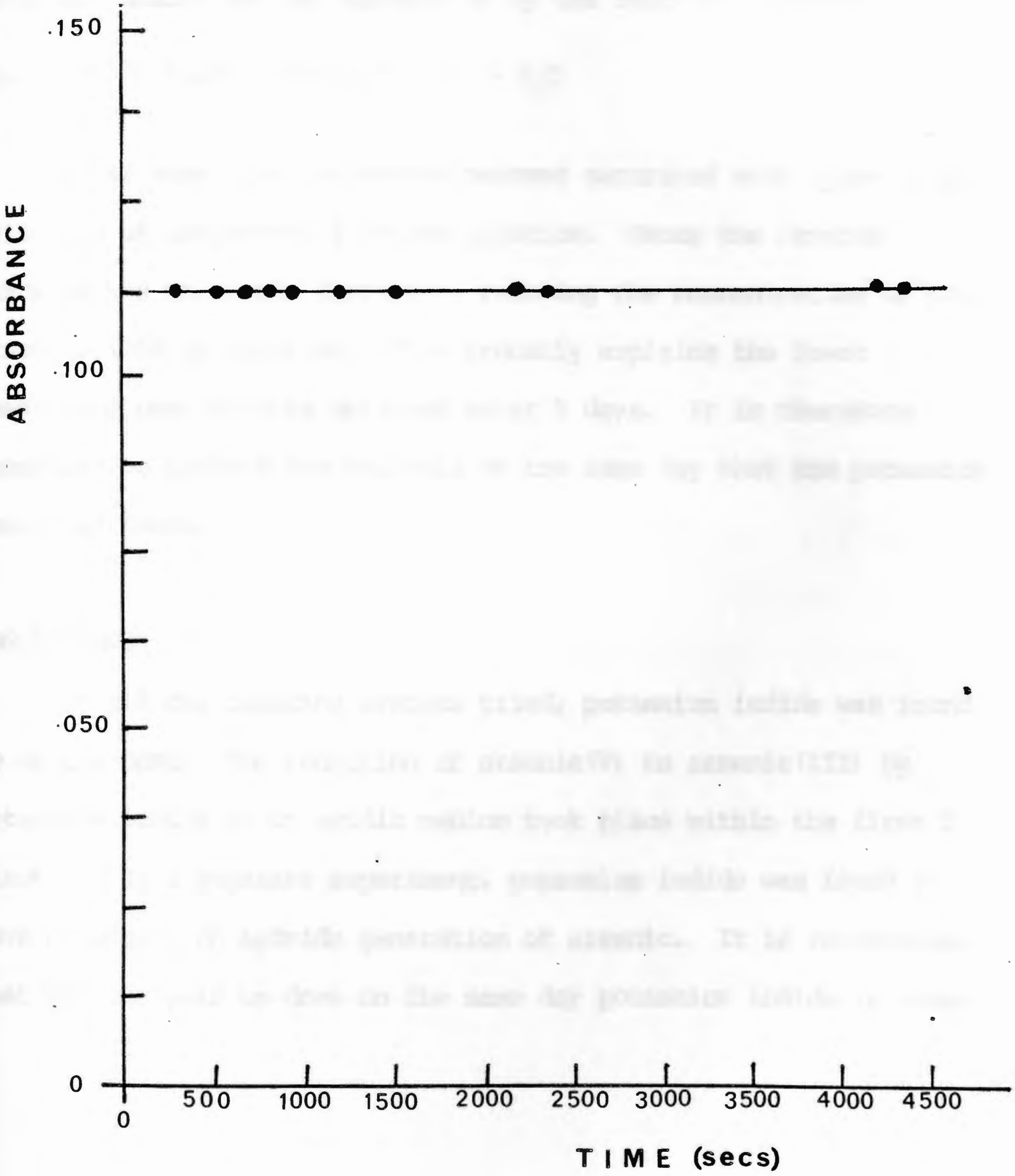


FIGURE 7

Absorbance Versus Time in Seconds for the Reduction of As(V) to As(III)



When determination was done 5 days later there was a decrease in absorbance peak heights. The reduction of As(V) to As(III) by potassium iodide can be represented by the reaction equation

$$2H^{+} + 3I^{-} + 3AsO_4^{3-} \rightleftharpoons AsO_3^{3-} + I_3^{-} + H_2O$$

After some time the system becomes saturated with I_2 due to air oxidation of the excess I^{-} in the solution. Hence the reverse reaction was enhanced, therefore, reducing the concentration of the arsenite ions in solution. This probably explains the lower absorbance peak heights obtained after 5 days. It is therefore necessary to perform the analysis on the same day that the potassium iodide is added.

CONCLUSIONS

Of all the reducing systems tried, potassium iodide was found to be the best. The reduction of arsenic(V) to arsenic(III) by potassium iodide in an acidic medium took place within the first 5 minutes. In a separate experiment, potassium iodide was found to have no effect on hydride generation of arsenic. It is recommended that the analysis be done on the same day potassium iodide is added.

APPENDIX VI

DATA TREATMENT

EQUATIONS AND FORMULAE UTILIZED IN THE THESIS:

A. Equations and formulae utilized in the statistical analysis of the data are those recommended by the Analytical Chemistry Division Commission on Analytical Nomenclature (22) and are listed below.

(1) Mean, $\bar{X} = 1/n\ \Sigma n$

(2) Deviation, $d = |X-\bar{X}|$

(3) Standard Deviation or Error, $S = \left(\frac{1}{n-1} \Sigma\ d^2 \right)^{\frac{1}{2}}$

(4) Relative Standard Deviation, $Sr = S/\bar{X}$

(5) Percent Relative Standard Deviation, $\%\ RSD = Sr \times 100$

B. The Detection Limit was calculated based on the formula, $D.L. = \bar{X} + K\sigma$ according to Zief and Mitchell (80) where D.L. is the Detection Limit, $\bar{X}$ is the average value of the blank, σ is the standard deviation of the blank, and the factor K has been assigned the value of 3.

C. The analytical sensitivity as has been defined by Price (54) is the concentration which will absorb 1% of the incident resonance radiation of that element. It may also be defined as the reciprocal of the slope of the calibration curve in the vicinity of the origin. Sensitivity for arsenic(III) quoted was obtained from the reciprocal of the slope of the plot of percent absorption versus concentration as shown in Figures 8, 9, and 10. The data for evaluating the detection limit and the sensitivity is shown in Table VI.

TABLE VI

DATE FOR DETECTION LIMIT AND SENSITIVITY CALCULATIONS

A. Detection Limit

Blank #	Absorbance	Deviation (d)	d^2
1	0.026	0	0
2	0.030	0.004	0.000016
3	0.030	0.004	0.000016
4	0.030	0.004	0.000016
5	0.022	-0.004	0.000016
6	0.022	-0.004	0.000016
7	0.022	-0.004	0.000016
8	0.022	-0.004	0.000016
9	0.030	0.004	0.000016
10	0.022	-0.004	0.000016

B. Sensitivity studies

	Percent absorption	Concentration (ng/ml)
I.	0.0	0.0
	16.2	2.4
	35.0	4.8
	66.0	9.5
II.	0.0	0.0
	10.9	1.2
	16.2	2.4
	35.0	4.8
	42.7	6.0
III.	0.0	0.0
	11.9	1.2
	18.3	2.4
	36.8	4.8

D. The standard working curves (calibration and standard addition) were based on the theoretical linear relationship between the concentration of the absorbing species in the light path and the absorbance as is expressed by Beer-Lambert's Law;

Absorbance = a b c

where a = molar absorptivity

b = path length

c = concentration in molarity

Absorbance (A) is defined by

$$A = \log \frac{1}{T} = \log I_0/I$$

where T = transmitted light

I_0 and I are the intensity of the resonance radiation entering and leaving the cell.

Typical standard addition curves are shown in Figures 11 and 12.

FIGURE 8

Sensitivity Curves: Percent Absorption Versus Concentration of Arsenic(III)

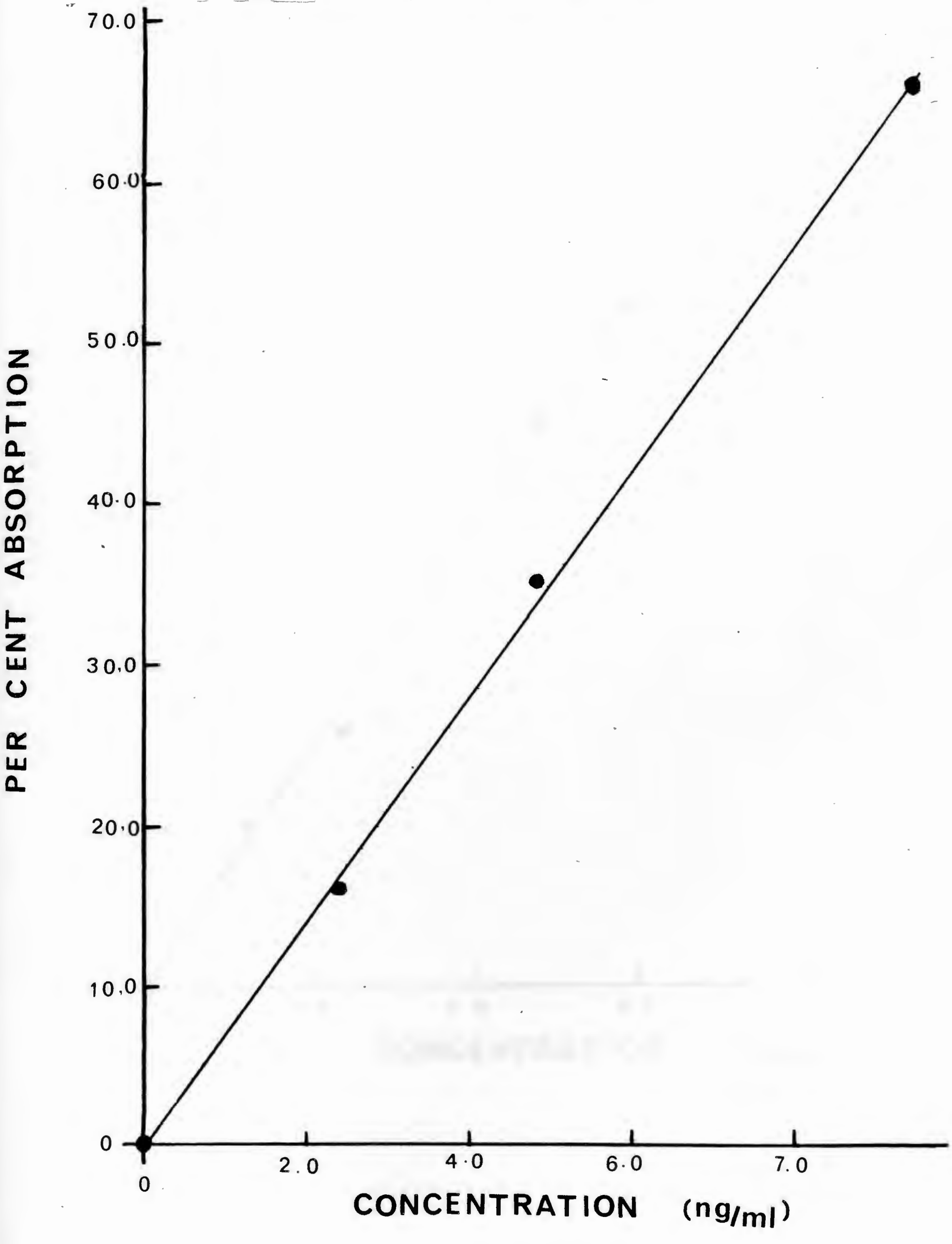


FIGURE 9

Sensitivity Curves: Percent Absorption Versus Concentration of Arsenic(III)

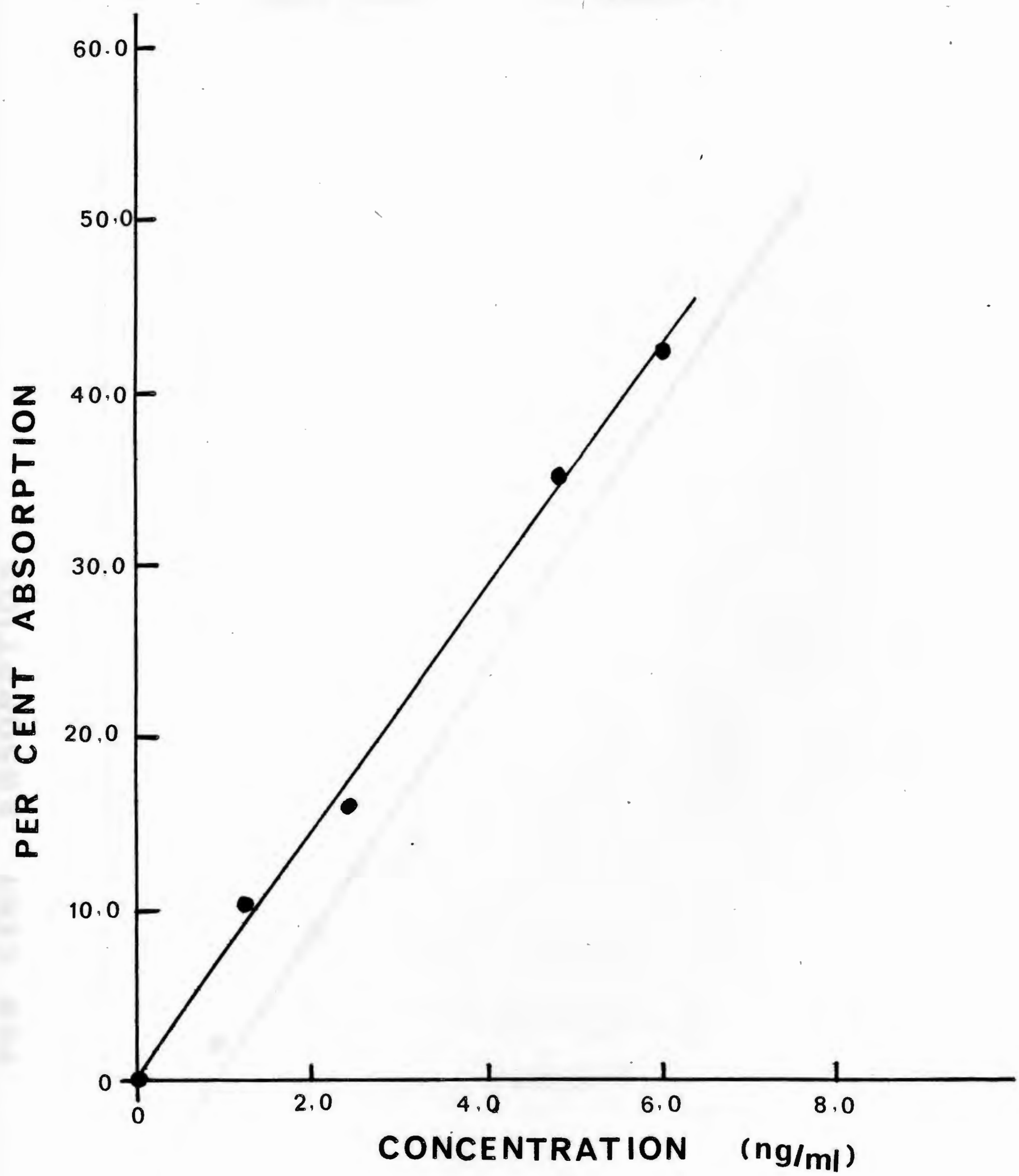


FIGURE 10

Sensitivity Curves: Percent Absorption Versus Concentration of Arsenic(III)

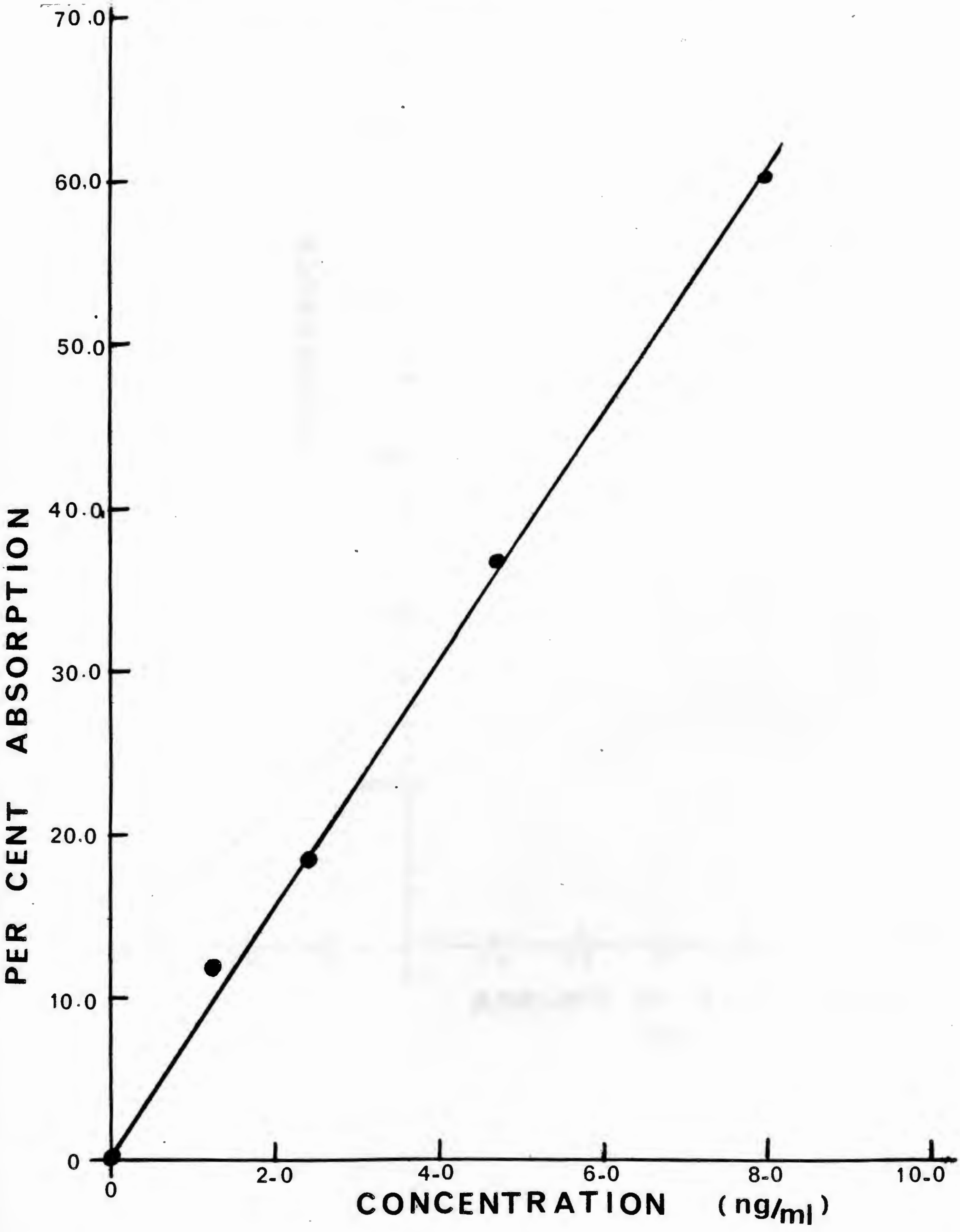


FIGURE 11

Standard Addition Curve for Total Arsenic

in Synthetic Sea Water

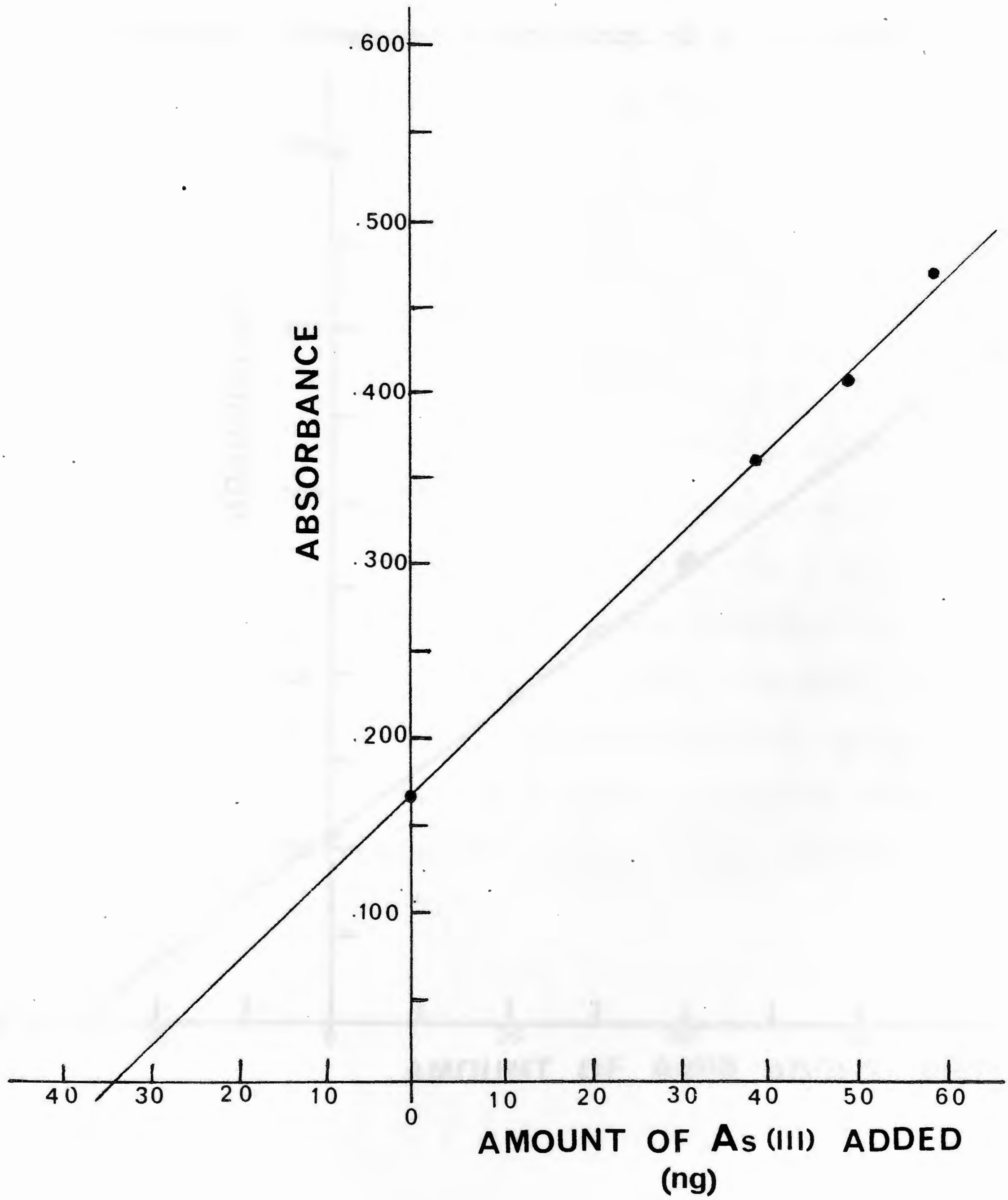
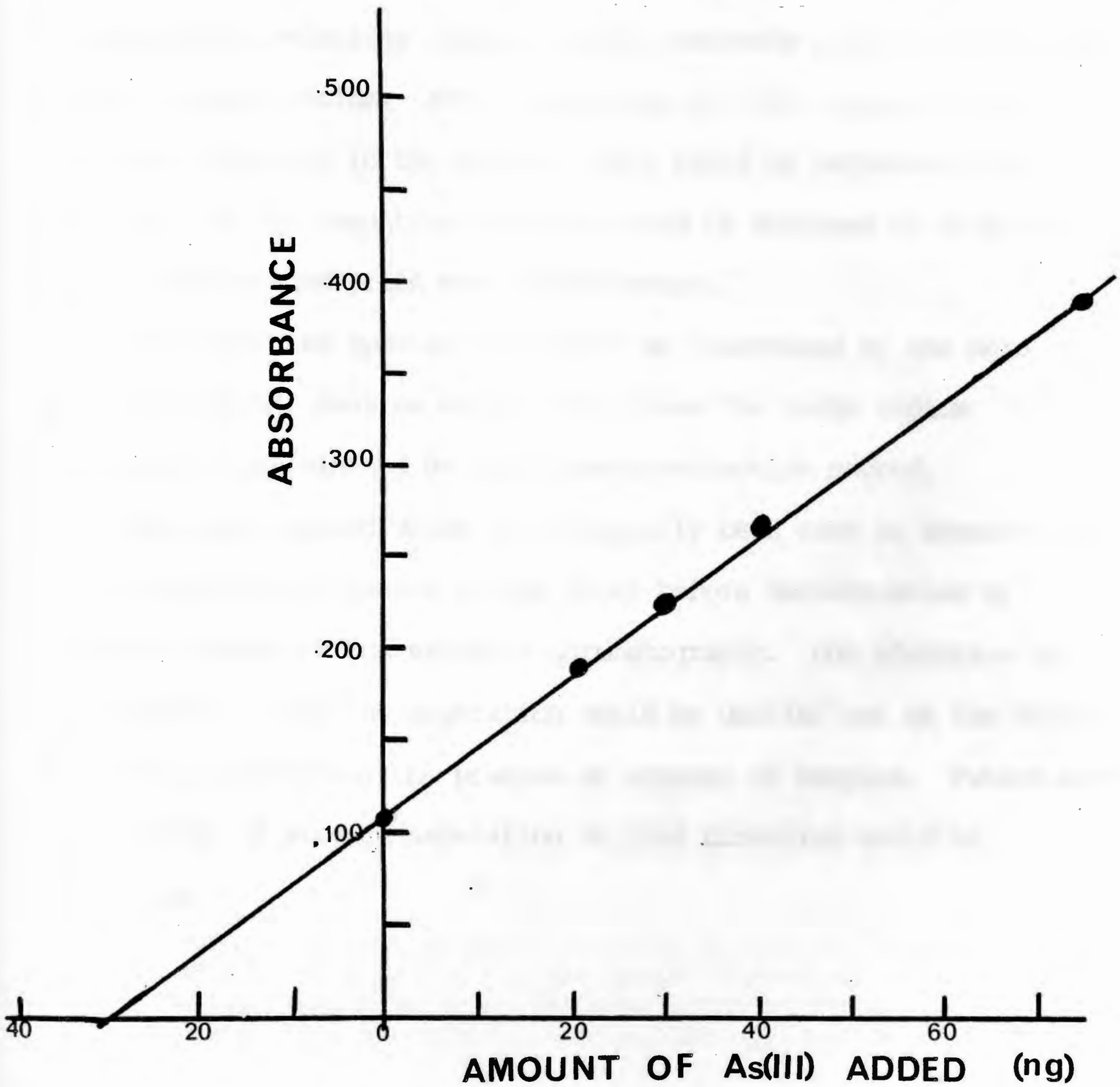


FIGURE 12

Standard Addition Curve for the Analysis of As(III) in Synthetic Sea Water. Absorbance Versus Amount of As(III) Added



SUGGESTIONS FOR FUTURE WORK

The proposed method offers a convenient way of determining traces of arsenic(III) and arsenic(V) in sea water. The method could be extended to determine organo-arsenic compounds such as methyl and dimethyl arsenic acids. After separation by APDC, organo-arsenic compounds remaining in the aqueous layer could be separated with molybdate and the resulting solution could be analyzed by graphite furnace-atomic absorption spectrophotometry.

The separated species could also be determined by the more sensitive method, neutron activation, since the large sodium background is eliminated by the solvent extraction method.

The other method which has frequently been used to separate the various species of arsenic in sea water before determination by graphite-furnace is ion-exchange chromatography. One advantage of this method is that the separation could be carried out at the site, therefore, eliminating the problem of storage of samples. Future work on the study of arsenic separation in this direction would be worthwhile.

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