

ED 020-100724

THE DEVELOPMENT OF A METHOD FOR THE DETERMINATION OF ORGANOARSENICALS IN AIR

George Colovos, Ph.D.

Norman Hester, Ph.D.

Greg R. Ricci

Lloyd S. Shepard

ROCKWELL INTERNATIONAL

Environmental Monitoring & Services Center

Environmental & Energy Systems Division

2421 West Hillcrest Drive

Newbury Park, CA 91320

Contract No. 210-77-0134

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health
Division of Physical Science and Engineering
Cincinnati, Ohio 45226

September 1980

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

DISCLAIMER

Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

ABSTRACT

A sampling and analytical method for the determination of organoarsenicals found in the air of workplaces is described.

The requirements for an effective sample collection method for methylarsonic acid (MMA), dimethylarsenic acid (DMA) and para-aminophenylarsonic acid (p-APA) have been studied. Sampling for both particulate and vapor forms was addressed and it was found that under the laboratory conditions studied none of the compounds existed in the vapor form. Three filter types were evaluated: mixed cellulose ester (0.8 μm pore size), Fluoropore (1.0 μm) and Mitex (5.0 μm). It was found that only the cellulose ester and Fluoropore filters could quantitatively collect particulates of these compounds. However, the chemical stability of the organoarsenical species on cellulose ester was found to be poor. The experimental results indicated that these compounds are stable on the Fluoropore filters but not on the cellulose ester matrix. On this basis, it was concluded that Fluoropore is the preferred medium for sampling organoarsenicals in air.

The analysis was performed by a novel technique utilizing automated ion chromatography coupled with an arsine generation-AAS detection system. The separation of arsenic (III), arsenic (V), MMA, DMA, and p-APA is achieved by utilizing a standard Dionex 3 x 500 mm anion separator column. When this column is used with 0.0024 M NaHCO_3 /0.0019 M Na_2CO_3 /0.001 M $\text{Na}_2\text{B}_4\text{O}_7$ eluent, all the compounds except As(III) and DMA are separated effectively. To separate DMA from As(III), a lower ionic strength eluent (0.005 M $\text{Na}_2\text{B}_4\text{O}_7$) can be used in a separate analysis. The detection system utilizes a continuous hydride generation system followed by heated quartz furnace atomization and atomic absorption spectrometry. The detection limits for As(III), As(V), MMA, DMA, and p-APA were less than 10 ng/mL in solution.

The complete sampling and analysis procedure was tested for precision and accuracy using filter samples loaded in a dynamic aerosol generation and sampling system to simulate workplace atmospheres. The results have shown the developed method to be very precise and accurate for concentrations ranging from 5-20 $\mu\text{g}/\text{m}^3$. Depending on the concentration and species, the relative standard deviation ranged from $\pm 4.4\%$ at the lowest level to $\pm 4.7\%$ at the highest level. The accuracy ranged from 90-120% of the values obtained by Neutron Activation (NAA) and X-Ray Fluorescence (XRF) analyses.

CONTENTS

Abstract	iii
Acknowledgements	vii
Introduction	1
Separation and Determination of Organoarsenicals	3
The Atomic Absorption Detection System	3
Separation of Arsine Derivatives by Gas Chromatography or by Fractional Distillation	6
Ion Chromatographic Separation of Organoarsenicals	10
Optimization of Detection and Resolution of p-Aminophenylarsonic Acid	12
Chromatographic Resolution of DMA from AsO_3^{3-}	16
Interferences in the Analysis of Organoarsenicals	23
Precision of Analysis Using Synthetic Standard Solutions	23
Sampling Methods	25
Organoarsenical Vapors in Air	25
Filtering Media for the Collection of Particulate Organoarsenicals	26
Stability of Organoarsenicals in Aqueous Extracts of Cellulose Ester Filters	26
Stability of Filter Extracts as a Function of Storage Time and Temperature	28
Effect of Sample Preparation and Storage Conditions on Recovery of Organoarsenicals from Cellulose Ester, Fluoropore, and Mitex Membrane Filters	30
Collection Efficiency of Various Filters	33
Effects of Temperature, Humidity, and SO_2 on Exposed Filter Samples	36
Evaluation of Developed Sampling and Analysis Procedure for Determination of Organoarsenicals in Air	38
Proposed Procedure for Determination of Airborne Organoarsenicals	38
Sampling Procedure	38
Analytical Procedure	38
Ruggedness Testing of Proposed Procedure	40
Precision and Accuracy of Proposed Method	43
Summary and Conclusions	46
References	47

FIGURES

1. The automated arsine generation/AAS detection system	4
2. Instrumental response of MMA, DMA and inorganic arsenic (III) as a function of HNO_3 acid concentration	8
3. Analytical scheme involving cold trapping and chromatographic separation of arsines	9

FIGURES (Continued)

4. Typical chromatograms of a) the NaBH_4 (pellet) reagent blank, and b) a mixture of MMA and DMA utilizing cold trapping followed by thermal distillation 11
5. Automated ion chromatograph coupled with arsine generation/AAS detection system 13
6. IC-AAS chromatogram of 20 ng/mL DMA, AsO_3^{3-} , MMA, AsO_4^{3-} , and 4 $\mu\text{g/mL}$ p-APA.... . 14
7. In-line persulfate oxidation of organoarsenicals at 90°C using the IC-AAS detection system 15
8. IC-AAS chromatogram of 20 ng/mL as arsenic of DMA, MMA, and p-APA obtained by utilizing persulfate oxidation at 90°C 17
9. Diagram of the final configuration for the automated IC-AAS analytical system 18
10. IC-AAS chromatogram of unresolved DMA (16 ng/mL) and AsO_3^{3-} (100 ng/mL), MMA (20 ng/mL), p-APA (80 ng/mL) and AsO_4^{3-} (120 ng/mL).... . 19
11. IC-AAS chromatogram of 20 ng/mL DMA, AsO_3^{3-} obtained by using a weak eluent (0.005 M $\text{Na}_2\text{B}_4\text{O}_7$).... . 20
12. IC-AAS chromatogram of DMA and AsO_3^{3-} using two 3 x 500 mm IC columns and weak eluent (0.005 M $\text{Na}_2\text{B}_4\text{O}_7$) 21
13. Separation of five-component aqueous solution of trace inorganic and organic arsenic species by gradient elution..... 22
14. Experimental design used to test and compare the stability of organoarsenicals on cellulose ester, Fluoropore, and Mitex filters.... . 31

TABLES

1.	Relative response of various organoarsenical compounds analyzed by the automated flameless hydride generation technique.	5
2.	Elemental analysis (C,H,N) of organoarsenical compounds obtained from various commercial sources	7
3.	Precision of analysis of synthetic solutions	24
4.	Stability at room temperature of aqueous extracts of spiked cellulose ester filters as a function of time	27
5.	Extraction solutions used in the stability studies	28
6.	Stability of aqueous extracts of spiked cellulose ester filters as a function of extraction solution, storage temperature, and storage time	29
7.	Average percent recoveries ($\pm$ Std. Dev.) of organoarsenicals from spiked cellulose ester, Fluoropore, and Mitex filters . . .	32
8.	Collection efficiency of cellulose ester membrane filters determined by using the tracer technique.....	34
9.	Collection efficiency of Fluoropore and Mitex filters for sampling organoarsenicals in air	35
10.	Effect of temperature (50°C) and humidity (95% RH) on particulate organoarsenicals collected on Fluoropore filters	36
11.	Effect of SO ₂ on particulate organoarsenicals collected on Fluoropore filters	37

TABLES (Continued)

12.	Instrumental conditions for the analysis of organoarsenicals in air particulate samples	39
13.	Youden-Steiner ruggedization experimental design	42
14.	Precision of combined sampling and analytical method using Fluoropore filters loaded in the aerosol generation/sampling system.....	44
15.	Comparison of total arsenic concentrations on generated filters determined by IC-AAS, NAA, and XRF analysis techniques	45

ACKNOWLEDGMENTS

The authors wish to express sincere appreciation to Dr. Janet Haartz, Project Officer, for her assistance in this study. They also gratefully acknowledge the National Institute of Occupational Safety and Health for their financial support of this work through Contract No. 210-77-0134.

The authors would also like to express their sincere thanks to Daniel Garland for his assistance in the laboratory and Marian Dempsey for her enormous effort in typing and formatting this text.

INTRODUCTION

The use of arsenic and its organic derivatives as pesticides, herbicides and wood preservatives has been increasing steadily each year. As a result, large quantities of these compounds are manufactured by the chemical industry and eventually find their way into the environment (1). About seventy percent of these chemicals are inorganic in form and the rest are organoarsenicals (2). Of the organoarsenicals, the most important species from the point of view of use and health effects, are monomethylarsonic acid (MMA), dimethylarsenic acid (DMA), and p-aminophenylarsonic acid (p-APA). In order to define fully their varying toxicities and effects on health, sampling and analysis of individual arsenicals in workplaces and other environmentally sensitive areas is of extreme importance. For this reason considerable activity has been generated in developing methods for analyzing mixtures of various arsenicals (3-11). Most of the developed procedures are based on the formation of volatile arsine derivatives which can be collected in a cold trap and then separated either by gas chromatography (4) or thermal distillation (3,5), followed by current discharge (3,5) or microwave emission detection (4). The sensitivity of these methods is excellent but problems with molecular rearrangements (4), imprecision and incomplete recoveries (6-7) make them unsuitable to use for routine application. Most recently the use of conventional ion chromatograph separation (8), followed by either differential pulse polarographic analysis or flameless atomic absorption analysis of collection fractions has eliminated many of the problems (9-11), but the methods remain very tedious and time-consuming.

The objective of the effort reported here was to develop a measurement method for estimating worker exposure to organoarsenicals in the air of workplace environments. The Occupational Safety and Health Standards of the U.S. Department of Labor specify that employee exposure to organoarsenicals shall not exceed $500 \mu\text{g}/\text{m}^3$ (as arsenic) taken as an eight hour, time-weighted average (12). The corresponding permissible exposure limit (OSHPPEL) for inorganic arsenic is $10 \mu\text{g}/\text{m}^3$. In order to develop a method capable of distinguishing organoarsenicals from both elemental and inorganic arsenic compounds, the following four tasks were performed. The first task was to develop an analytical technique and detection system which could distinguish the organic arsenic forms from the inorganic. The second task was to develop an appropriate sampling device for quantitative collection of the sample. The third task was to "ruggedize" the analytical procedure so that all the parameters affecting the performance were recognized and controlled. The fourth task was to test the combined sampling and analysis procedure for precision and accuracy.

The analytical technique which was developed makes use of automated ion chromatography for the separation of MMA, DMA and p-APA from each other, as well as from AsO_3^{3-} and AsO_4^{3-} , and is coupled with a continuous hydride generation-AAS detection system. The developed system proved to be a very sensitive, selective and efficient means of analyzing these species. Detection limits of less than 10 ng/mL of As in solution were obtained and the analysis

can be performed at the rate of about seven samples per hour.

The sampling of both particulate and vapor forms of MMA, DMA and p-APA was studied and it was found that vapors of the organoarsenicals were practically nonexistent and therefore only the particulate form had to be considered. Fluoropore® (PTFE/polyolefin) membrane filters were found to be the most effective collection media for particulate arsenicals. The cellulose ester filter was found to react with certain species and Mitex® (PTFE) membranes were found not to collect the particulates effectively. Quantitative recovery of collected arsenicals from the filter was obtained by ultrasonic extraction with eluent buffer.

The above efforts were the cornerstones in the development of the method. The Youden-Steiner statistical screening technique was used to ruggedize the analytical method. After ruggedization, the combined sampling and analysis procedure was tested for precision and accuracy using filter samples loaded in a dynamic aerosol generation and sampling system to simulate workplace atmospheres (13). The results have shown the developed method to be very precise and accurate for concentrations ranging from 5-20 $\mu\text{g As/m}^3$. Depending on the concentration and species, the relative standard deviation ranged from $\pm 14.4\%$ at the lowest level to $\pm 4.7\%$ at the highest level. The accuracy ranged from 90-120% of the values obtained by Neutron Activation (NAA) and X-Ray Fluorescence (XRF) analyses.

Details of the experimental efforts which were made for the development of this measurement technique are presented in this report.

IMAGE AREA

COPIES OF
THIS REPORT
ARE AVAILABLE
FOR
REPRODUCTION
AND
TRANSMISSION

SEPARATION AND DETERMINATION OF ORGANOARSENICALS

The separation of the individual components of a mixture of very closely related organoarsenical compounds and their subsequent quantitation using an appropriate detection system were the primary analytical problems associated with this study. Assuming that separation of the organoarsenical compounds from each other as well as from their inorganic counterparts is feasible, then the problem is mainly in the detection system. If a system specific to arsenic were available, other chemical species present in the samples would not be detected and therefore extensive clean-up of the samples or further separations would not be necessary. Such a detection system can become available by adapting the hydride generation technique which separates the various forms of arsenic from the sample matrix via the formation of their corresponding arsine derivatives. Gas chromatography and fractional distillation of the arsine derivatives have been examined in addition to ion chromatographic separation of the original species. The ion chromatographic technique followed by hydride generation and atomic absorption detection was determined to be the most effective.

The studies which were conducted for the separation of the organoarsenicals and the efforts to develop a detection system will be discussed in detail in the following sections.

THE ATOMIC ABSORPTION DETECTION SYSTEM

The flameless atomic absorption method of analysis for total arsenic, which is based on the formation of arsine by reaction with sodium borohydride, is very well known (14). Figure 1 presents the flow diagram of an automated version of this method. Using this technique, arsenic in the sample reacts with borohydride in acidic solution in the mixing coil and is reduced to arsine. The arsine is then directed through a gas-liquid separator and carried to a heated ($\sim 800^{\circ}\text{C}$) quartz cell which is aligned in the light path of the atomic absorption spectrometer. At the high temperature of the cell the arsine is decomposed to elemental arsenic which can be determined using flameless atomic absorption. Thus, this system is a specific detector for arsenic which can be adapted for the determination of organoarsenicals since, under the same conditions, the organoarsenicals are reduced to produce the corresponding organic arsines. MMA produces methylarsine, DMA produces dimethylarsine, and p-APA produces p-aminophenylarsine. To utilize this concept fully as a detector, it is important to know the behavior of each organoarsenical compound in this system. Table 1 presents the response of the compounds MMA and DMA relative to that of inorganic arsenic (III) using this technique. The compound p-APA could not be detected using this configuration of Figure 1 and therefore data are not given. As will be discussed later, detection of p-APA required further refinement of the analytical technique. Several commercial sources of the compounds MMA and DMA were studied. The data show that the responses of the organoarsenicals are not equivalent and suggest that the purity of these

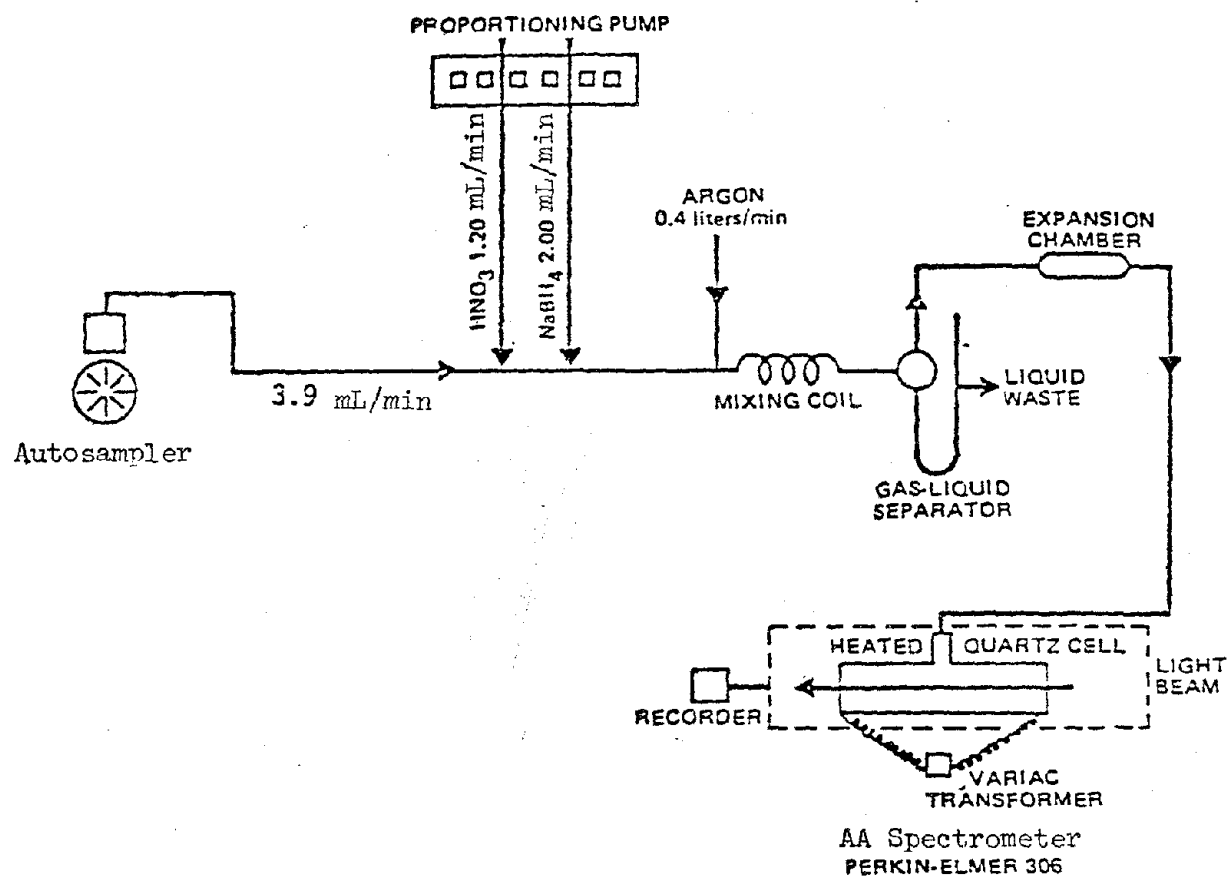


Figure 1. The automated arsine generation/AAS detection system.

Table 1. Relative response of various organoarsenical compounds analyzed by the automated flameless hydride generation technique.

Compound	Source	Relative Response
As ₂ O ₃	BANCO	1.00
MMA	K&K	0.90
MMA	Ansul	1.34
MMA	Vineland	1.57
DMA	K&K	1.08
DMA	K&K Recrystallized	1.19
DMA	Ansul	1.46
DMA	MCB	1.32

In all cases nominal concentrations of 20 µg/mL (As) were analyzed. Responses are reported as relative to that of the As₂O₃. Under the experimental conditions p-APA showed no significant response.

compounds varies from supplier to supplier. Elemental analysis of organoarsenical compounds received from the various vendors showed that the MMA purchased from K&K, and the DMA purchased from K&K and MCB were very impure and therefore they were not used further in the study. The results of the elemental analyses are given in Table 2. Only materials obtained from the Ansul Company were considered to have the desired purity to be used throughout the study.

The varying instrumental responses of the organoarsenicals were investigated by studying two of the parameters which can affect the analytical response. The first parameter studied was that of the concentration of the acid used in the borohydride reduction system. The responses of equivalent arsenic concentrations of arsenic (III), MMA, and DMA were studied as a function of nitric acid concentrations (1-10%). The response for inorganic arsenic increased only a few percent with increasing acid concentration. For MMA the effect of acid concentration on the instrumental response was rather insignificant but for DMA the effect was very significant. As the acid concentration increased from 1% to 10%, the response dropped by over 50%. However, the most significant result was that at no point did the response for inorganic arsenic (III), MMA and DMA become equivalent. Figure 2 presents graphically the effect of HNO_3 acid concentration on the relative response of organoarsenicals in the detection system.

The second parameter studied was the temperature of the quartz furnace because the difference in response between arsine and organoarsines may have been the result of incomplete decomposition of the organic species in the quartz tube. This may occur if the residence time in the furnace is too short or if the atomization temperature is not optimum. The residence time of atomic arsenic was increased by additionally heating the inlet tube of the furnace. This experiment showed no normalization of the relative response of the organoarsenicals. Instead, a significant decrease in response for all species was observed which probably was due to losses of arsenic to the walls. Increasing the temperature of the absorption cell from 700° to 1000°C resulted in an increased response for all species, but again no normalization of the responses was obtained. These differences in response of the organoarsenicals are most likely due to differences in the rate or extent of reduction of each species. Although equivalent responses for each species was not obtained, this system can still be used as a detector provided that complete separation of each species is feasible. Two approaches were investigated for the separation and detection of the species. In the first, separation of the arsine derivatives by both gas chromatography and fractional distillation was examined. In the second, ion chromatographic separation of the original species followed by continuous generation of the arsine derivatives and atomic absorption detection was studied.

SEPARATION OF ARSINE DERIVATIVES BY GAS CHROMATOGRAPHY OR BY FRACTIONAL DISTILLATION

Arsine, methylarsine and dimethylarsine are quite volatile and can be purged from the reduction solution and collected in a cold trap. The reduction of p-APA produces the salt of the amine, and therefore the solution has to be neutralized to recover the p-aminophenylarsine. Based on these properties an analytical scheme such as that depicted in the flow chart of Figure 3 is

Table 2. Elemental analysis (C,H,N) of organoarsenical compounds obtained from various commercial sources.

Compound	Source	CARBON			HYDROGEN			NITROGEN		
		% Expected	% Found	% Δ	% Expected	% Found	% Δ	% Expected	% Found	% Δ
MMA	Vineland K&K Ansul	8.45	8.62	+ 2.0	3.57	3.56	- 0.3		NOT	
		6.54	4.29	-34.0	2.72	4.95	+82.0			
		8.57	8.65	+ 0.9	3.57	3.70	+ 3.6		APPLICABLE	
DMA	Ansul MCB K&K K&K Recrystallized	17.39	16.80	- 3.4	5.07	5.11	+ 0.8		NOT	
		15.00	11.71	-21.9	4.38	5.44	+24.2			
		17.39	19.60	+12.7	5.07	5.64	+11.2		APPLICABLE	
		17.39	18.77	+ 7.9	5.07	5.77	+13.8			
p-APA	MCB K&K	33.18	33.24	+ 0.2	3.69	3.80	+ 3.0	6.45	6.39	-0.9
		33.18	33.53	+ 1.1	3.69	3.92	+ 6.2	6.45	6.33	-1.9

RECEIVED
FEB 11 1964
FBI - NEW YORK
FBI - NEW YORK
FBI - NEW YORK

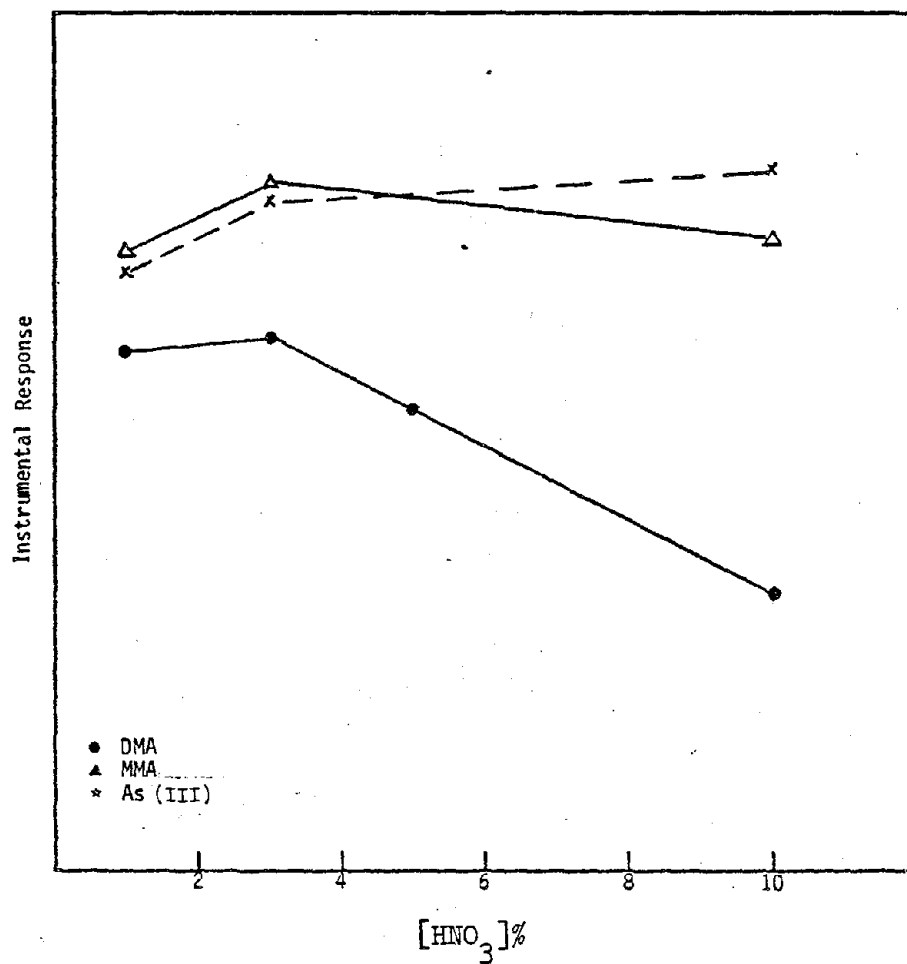


Figure 2. Instrumental response of MMA, DMA and inorganic arsenic (III) as a function of HNO_3 acid concentration.

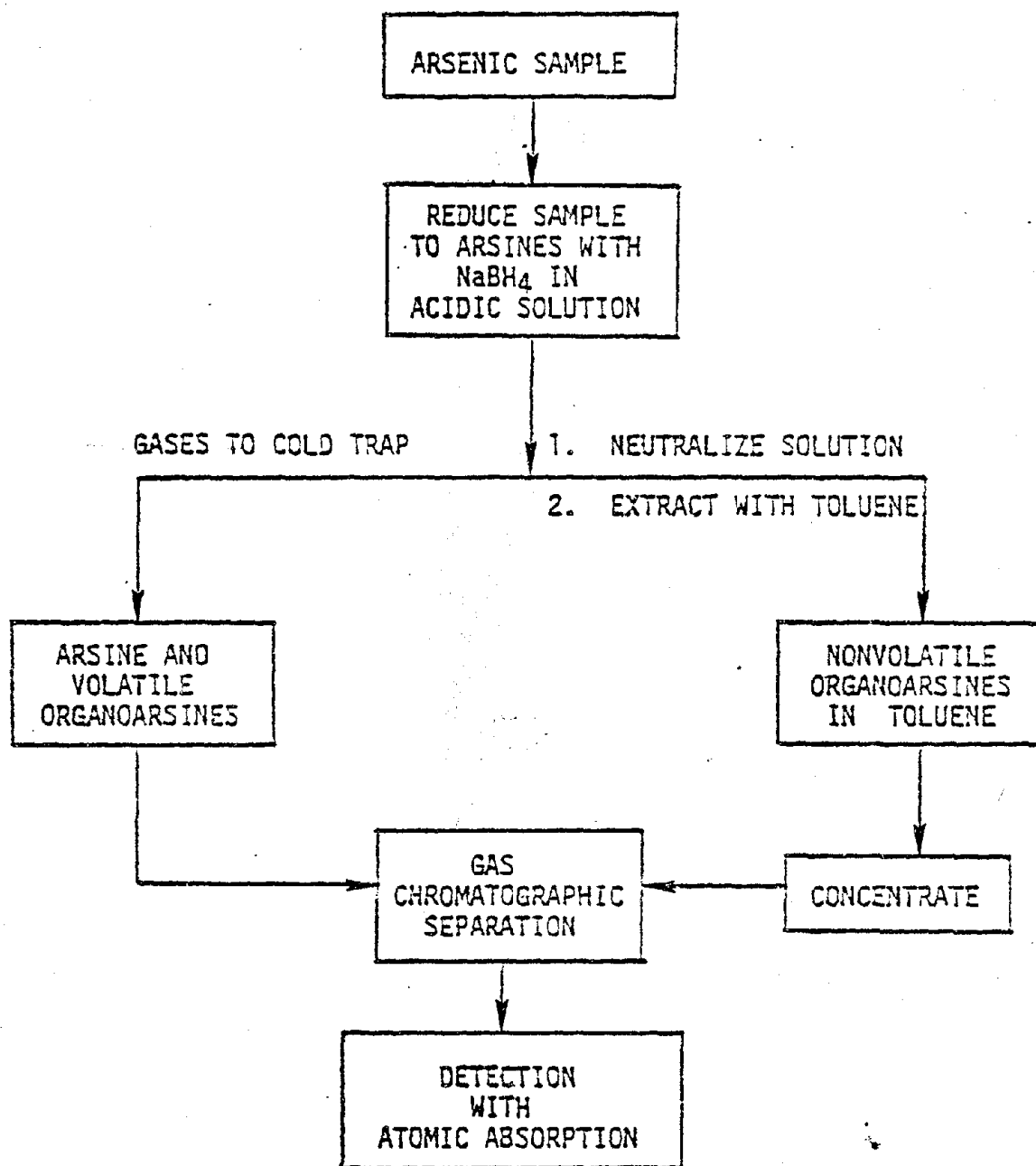


Figure 3. Analytical scheme involving cold trapping and chromatographic separation of arsines.

possible. Following this approach the condensate in the cold trap can be brought up to room temperature and injected into a gas chromatograph, and the toluene extract can be concentrated and an aliquot similarly injected into a gas chromatograph. Talmi and Bostic have used this technique for the chromatographic separation of arsine and a series of aliphatic organoarsines (4). They used a microwave emission detector with their gas chromatograph for arsine detection, and a 6% Carbowax 20M on 60/80 mesh Chromosorb 101 column. In the present study the previously discussed flameless atomic absorption technique was used as a detector. In the initial experiments the expected sensitivity of the AAS detector was not obtained. This was due to the absence of hydrogen from the system. It was shown that approximately 5% hydrogen was necessary for obtaining a good signal.

The developed system was tested thoroughly for the separation and determination of organoarsenicals but the resolution and reproducibility were very poor. Use of silica gel or glass beads in the trapping system and careful thermal distillation using constant temperature baths improved the resolution of the species but the reproducibility was still poor. For example, the standard deviation obtained for five chromatograms of a sample of MMA containing 60 ng of arsenic was $\pm 10\%$. For four chromatograms of a sample of DMA containing 100 ng of arsenic, a standard deviation of $\pm 25\%$ was found. Figure 4 presents typical chromatograms of: 1) a reagent blank, and 2) a mixture of MMA and DMA. The reagent blank was identified as inorganic arsenic contamination present in the NaBH_4 pellets which were being used.

A major problem encountered with the cold trapping technique was water vapor freezing out in the tubing, causing changes in the gas flow rate through the system. Efforts were made to remove the water from the system as recommended in the literature (5) by adding a water vapor trap between the sample reaction chamber and the arsine trap. Various other approaches utilizing diverse drying media such as anhydrous CaCl_2 , Na_2SO_4 , $\text{Mg}(\text{ClO}_4)_2$, and CaSO_4 were tested. None of these were found to improve the system.

Finally, some efforts were made to improve the system by conditioning the surfaces in contact with the arsines in a fashion similar to that proposed by Crecelius (5). This involved treatment of the surfaces with high concentrations of arsines (AsH_3 or R_2AsH) to eliminate active arsine absorption sites in the system. However, this did not improve the analysis, and calibration curves remained irreproducible.

In summary, the separation of arsine, methylarsine, and dimethylarsine by either gas chromatography or fractional distillation, in our laboratory, proved to be somewhat cumbersome. In addition, the method cannot be applied for the determination of p-APA for which a different approach, involving toluene extraction of the nonvolatile p-APA had to be investigated. Attempts were made to extract nonvolatile arsine with toluene from a basic solution followed by GC analysis of the toluene extract. No response was obtained for the p-APA.

ION CHROMATOGRAPHIC SEPARATION OF ORGANOARSENICALS

Since neither gas chromatography nor thermal distillation of the arsine derivatives of the organoarsenicals provided a satisfactory analytical method,

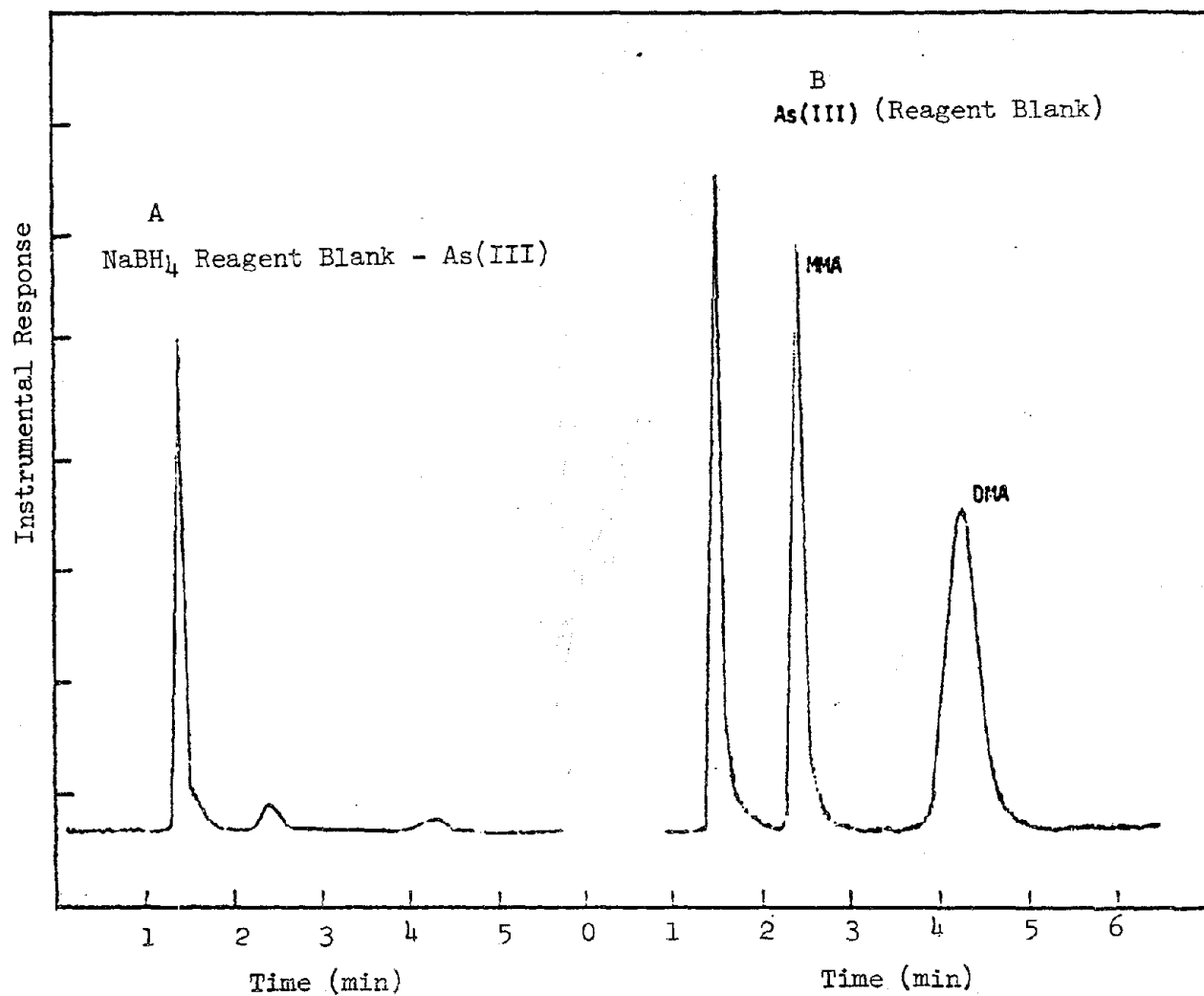


Figure 4. Typical chromatograms of a) the NaBH₄ (pellet) reagent blank, and b) a mixture of MMA and DMA utilizing cold trapping followed by thermal distillation.

ion chromatography (IC) was used as an alternate approach. The feasibility of using ion exchange chromatography for the separation of the various arsenic species was realized in initial experiments using a Dionex Model 10 Ion Chromatograph. Separation of MMA and DMA was observed upon analysis of aqueous standard solutions containing high concentrations of these species, using the normal anion system with 0.003 M NaHCO_3 /0.0024 M Na_2CO_3 eluent. However, the sensitivity of analysis using the Dionex conductivity detection system was very poor because of the low specific conductivities of the arsenic species in solution. In addition, the arsenic species eluted unresolved in the presence of the common anions Cl^- , PO_4^{3-} , Br^- , NO_3^- , and SO_4^{2-} . Element specific detection of trace concentrations was possible by eliminating the conductivity detector and interfacing the ion chromatograph directly to an arsine generation/AAS detection system. The diagram of the IC-AAS analytical system is shown in Figure 5. An automated ion chromatograph was utilized so that the sampling and injection were controlled by an autosampler. The eluent which is exiting continuously from the anion separator column is fed into a hydride generation system similar to that used in the determination of total inorganic arsenic (14). In this the effluent which contains the separated arsenic species is first mixed with acid and then it reacts with the sodium borohydride (NaBH_4) reagent to form the corresponding arsine derivatives. The generated arsines are transferred with argon carrier gas to the heated quartz furnace aligned in the light path of the AAS where thermal decomposition into free As and H atoms takes place. A chromatograph is obtained by continuous AAS monitoring of the various arsine derivatives.

This approach was tested by analyzing single and mixed component aqueous standard solutions of AsO_3^{3-} , AsO_4^{3-} , MMA, DMA and p-APA. A 500 mm anion separator column and 0.003 M NaHCO_3 /0.0024 M Na_2CO_3 eluent was utilized. Figure 6 presents a chromatogram of a five component standard solution which demonstrates that the ion chromatographic separation procedure for the arsenicals, combined with the atomic absorption detection technique, is superior to the previously tested approaches. The order of elution is: unresolved DMA and AsO_3^{3-} < MMA < p-APA < AsO_4^{3-} . As can be seen in this chromatogram, two problems had to be resolved for the optimization of this analytical technique. First, the sensitivity of analysis for p-APA had to be increased. The concentration of p-APA in Figure 6 is 4 $\mu\text{g/mL}$, a factor of 200x more concentrated than the other species. Second, an appropriate eluent had to be selected which could resolve DMA from AsO_3^{3-} .

Optimization of Detection and Resolution of p-Aminophenylarsonic Acid

As was mentioned above, the sensitivity of p-APA using either the automated flameless/total arsenic analytical system or the IC-AAS speciation system was very poor. Efforts, therefore, were directed toward improving the sensitivity of the method for this compound. Oxidation of p-APA to its inorganic form using saturated persulfate solution is feasible. This oxidation can be performed in the automated hydride generation system as shown in Figure 7 by introducing a new reagent line and mixing coil. The sample is injected onto the column, separated, eluted, oxidized with the persulfate to the inorganic form, and then reduced with NaBH_4 . At first it was thought that in order to utilize successfully the in-line persulfate oxidation for detection of p-APA, a heated mixing coil must be used at 90°C. The chromatogram obtained at this

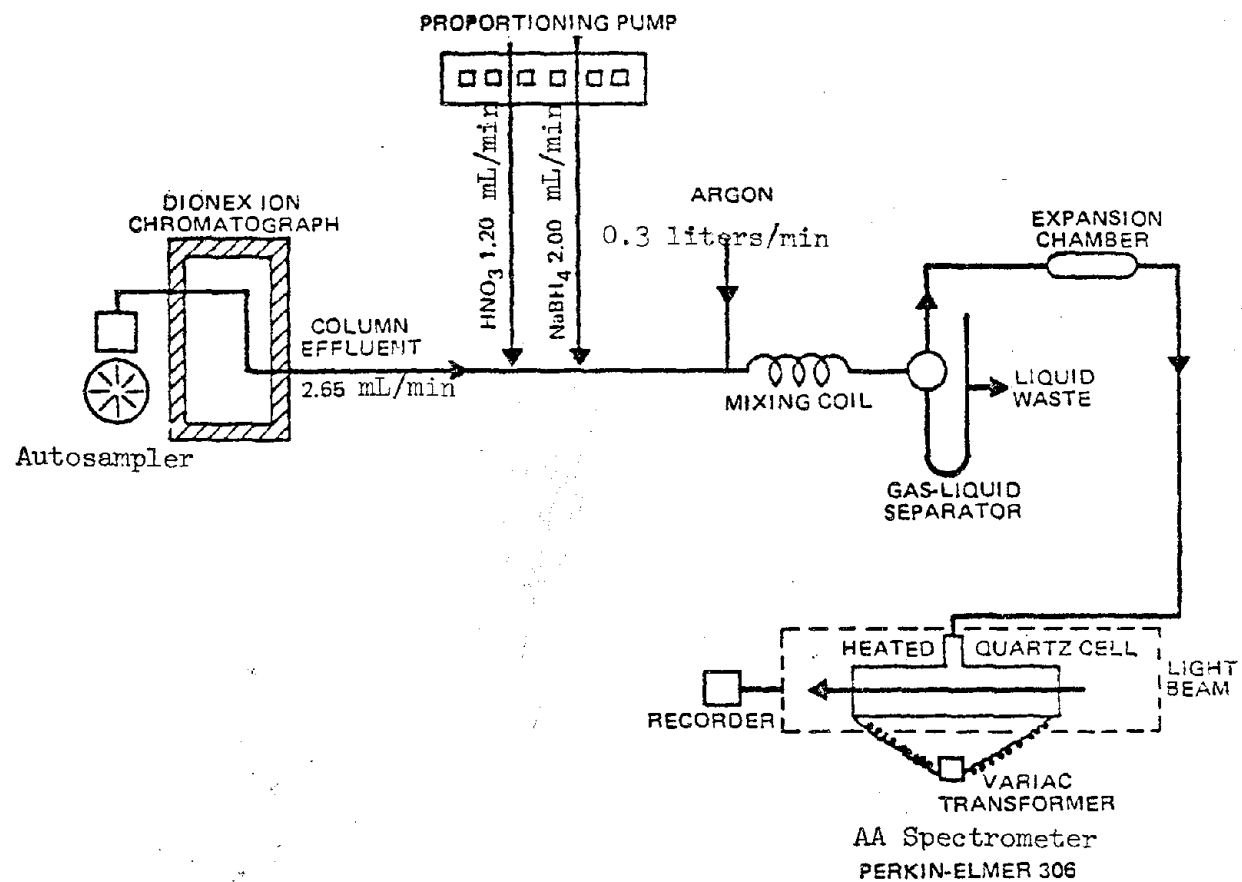


Figure 5. Automated ion chromatograph coupled with arsine generation/AAS detection system.

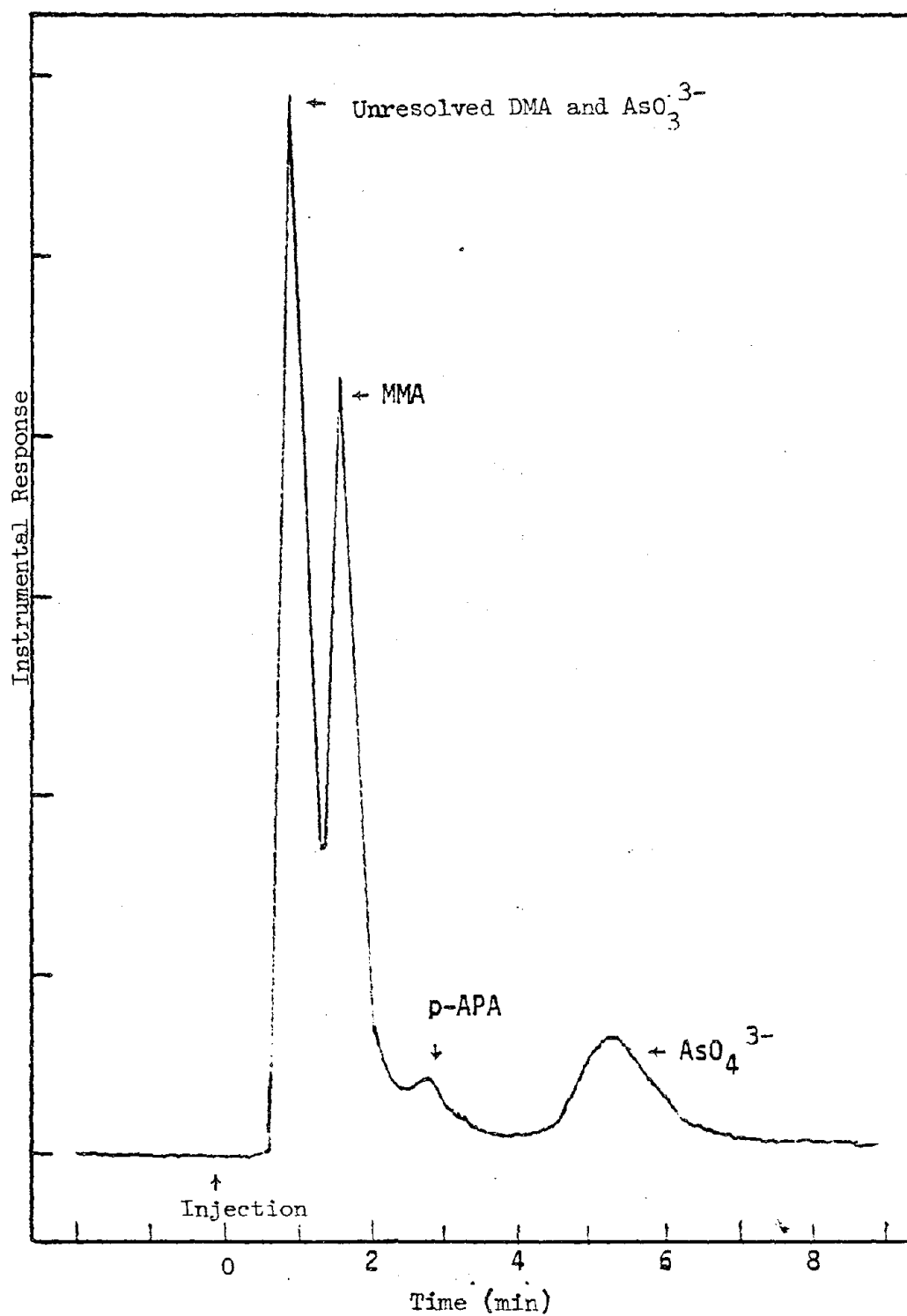


Figure 6. IC-AAS chromatogram of 20 ng/mL DMA, AsO_3^{3-} , MMA, AsO_4^{3-} , and 4 $\mu\text{g/mL}$ p-APA. The experimental conditions were: 3x500 mm anion separator column, 0.003 M NaHCO_3 /0.0024 M Na_2CO_3 eluent; flow rate 2.60 mL/min; 500 psi pressure; 1 cm/min chart speed; scale expansion 3x.

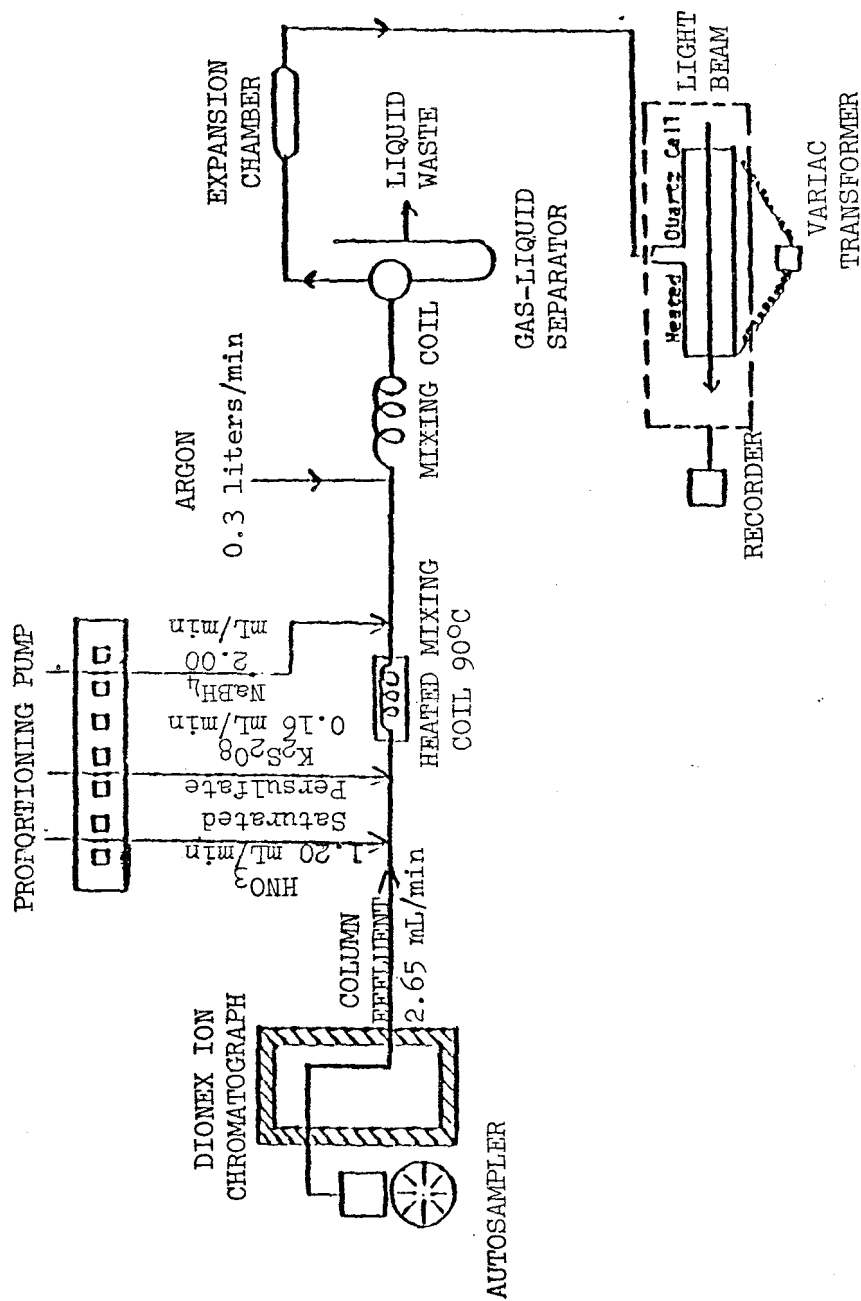


Figure 7. In-line persulfate oxidation of organoarsenicals at 90°C using the IC-AAS detection system.

temperature is presented in Figure 8 and shows increased sensitivity for the p-APA but poor overall resolution. This poor resolution is probably caused by diffusion of the separated species in the heated mixing coil. In later experiments it was found that the sensitivity of the p-APA depends much more on the nature and concentration of the acid present during the reduction with NaBH_4 than on the temperature. It was found that by changing the dilution acid from 10% HNO_3 to a 15% HCl solution saturated with potassium persulfate, the sensitivity of p-APA increased such that its relative response became equivalent to that of AsO_4^{3-} . The final configuration of the developed analytical system is depicted in Figure 9. Resolution of the species was further improved by more appropriate selection of eluents. Experimentally it was found that resolution of MMA and p-APA is further improved by using as the eluent 0.0024 M NaHCO_3 /0.0019 M Na_2CO_3 /0.001 M $\text{Na}_2\text{B}_4\text{O}_7$. In Figure 10 a chromatogram of the components is shown. Using this eluent, MMA elutes in ~ 3 minutes, p-APA elutes in ~ 6 minutes, and AsO_4^{3-} elutes in ~ 10 minutes.

Chromatographic Resolution of DMA from AsO_3^{3-}

As was shown above, DMA is not separated from AsO_3^{3-} using the standard eluent (0.003 M NaHCO_3 /0.0024 M Na_2CO_3). This problem was solved in two ways: first, by utilizing lower ionic strength eluent for the isocratic elution; and second, by performing gradient elution. Presented in Figure 11 is a chromatogram obtained with the weak eluent (0.005 M $\text{Na}_2\text{B}_4\text{O}_7$) demonstrating the separation of DMA from AsO_3^{3-} . To further improve the separation of DMA and AsO_3^{3-} , a second 3x500 mm anion separator column can be added as shown in the chromatogram of Figure 12.

Separation can also be obtained by gradient elution. An Altex dual pump gradient elution HPLC with solvent programmer was used with 0.0025 M $\text{Na}_2\text{B}_4\text{O}_7$ and 0.003 M NaHCO_3 /0.0024 M Na_2CO_3 as eluents to demonstrate the feasibility of this technique. The solvent programmer allows optimum resolution by selecting a) initial and final percentages of the eluents; b) exponent of the desired gradient curve; c) gradient time; and d) flow rate through the column. Figure 13 shows the ion chromatographic separation achieved by using gradient elution.

These experiments have shown clearly that two approaches can be applied for the complete characterization of a sample by the IC-AAS technique. The first is to perform two separate analyses on each sample using isocratic elution: one analysis to determine MMA, p-APA and AsO_4^{3-} , and a second analysis to determine AsO_3^{3-} and DMA. The second approach is gradient elution using 0.0025 M $\text{Na}_2\text{B}_4\text{O}_7$ as starting, and 0.003 M NaHCO_3 /0.0024 M Na_2CO_3 as ending eluent. Although the gradient elution technique is more effective and separates all the species in one run, the column must be restabilized after each run for approximately one hour, and this makes the analysis very time-consuming. For this reason, two separate analyses by the isocratic approach is the preferred method. Of course with this approach the species MMA, p-APA, and AsO_4^{3-} are retained on the column when using the weak eluent for the determination of DMA and AsO_3^{3-} , tying up active resin sites, and the column must be flushed with the stronger eluent after 10-15 samples have been analyzed.

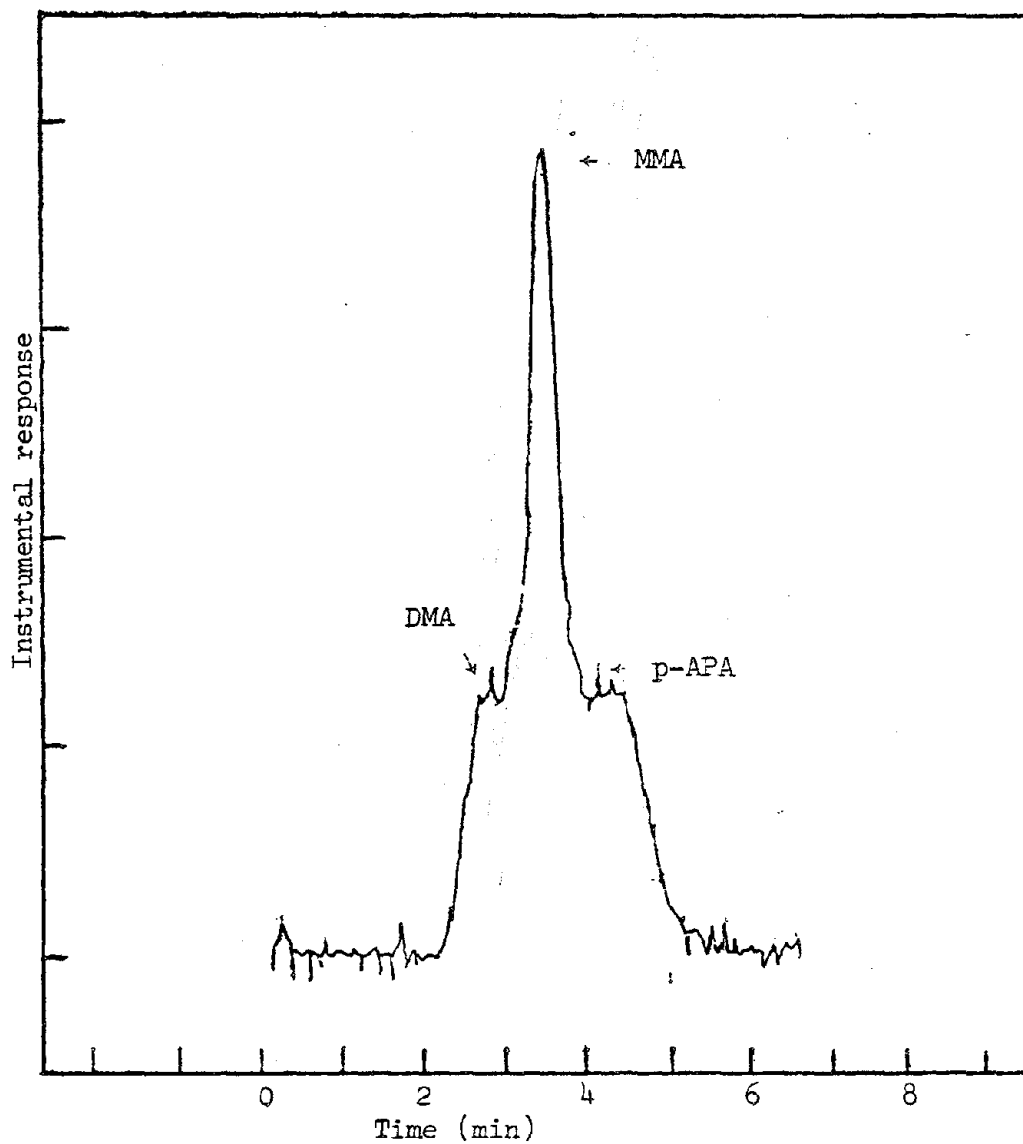
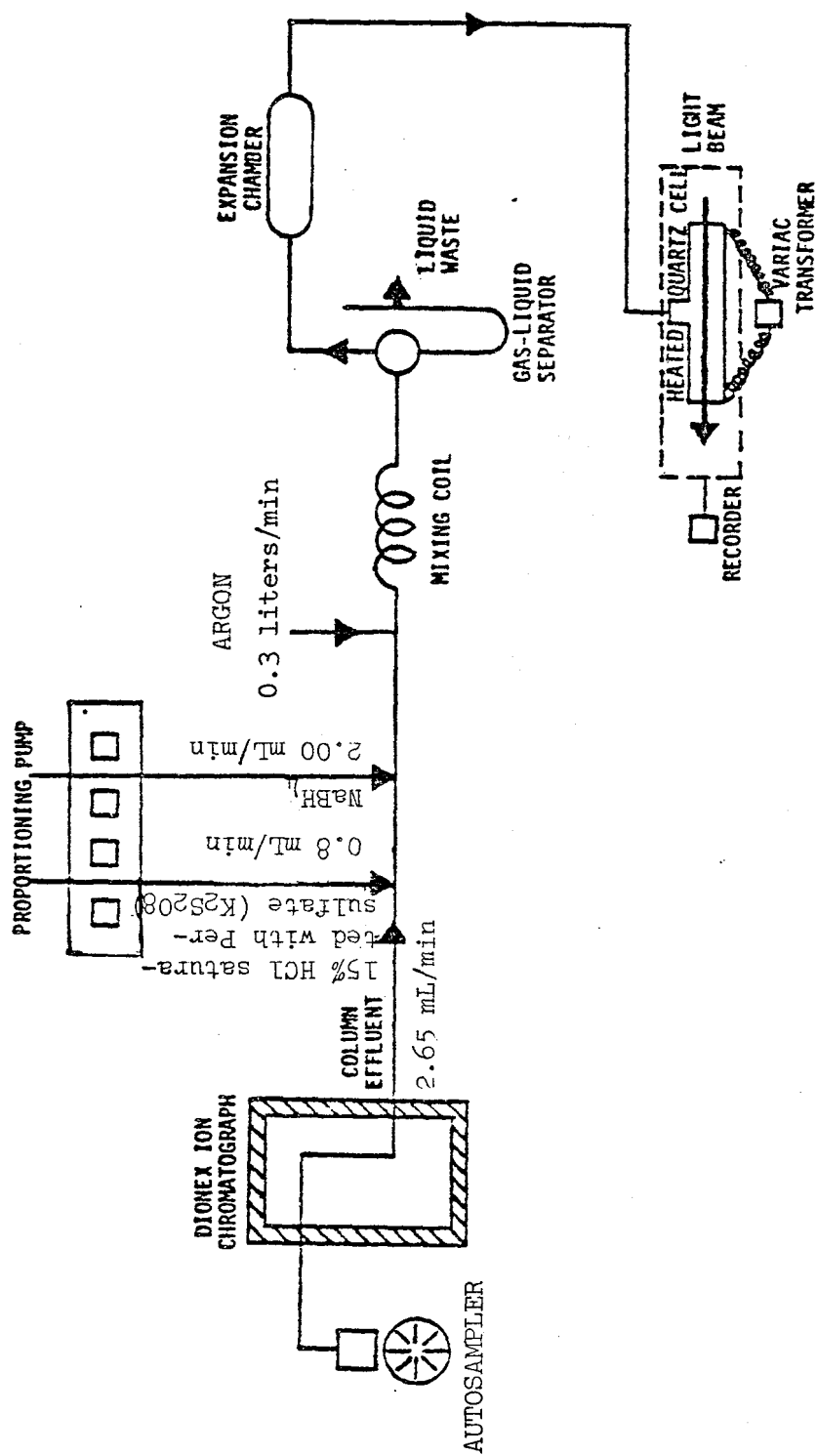


Figure 8. IC-AAS chromatogram of 20 ng/mL as arsenic of DMA, MMA, and p-APA obtained by utilizing persulfate oxidation at 90°C. Instrumental conditions were: 3x500 mm anion separator column; 0.003 M NaHCO_3 /0.0024 M Na_2CO_3 eluent, 500 psi, 1 cm/min chart speed.



AA SPECTROMETER
PERKIN-ELMER 306

Figure 9. Diagram of the final configuration for the automated IC-AAAS analytical system.

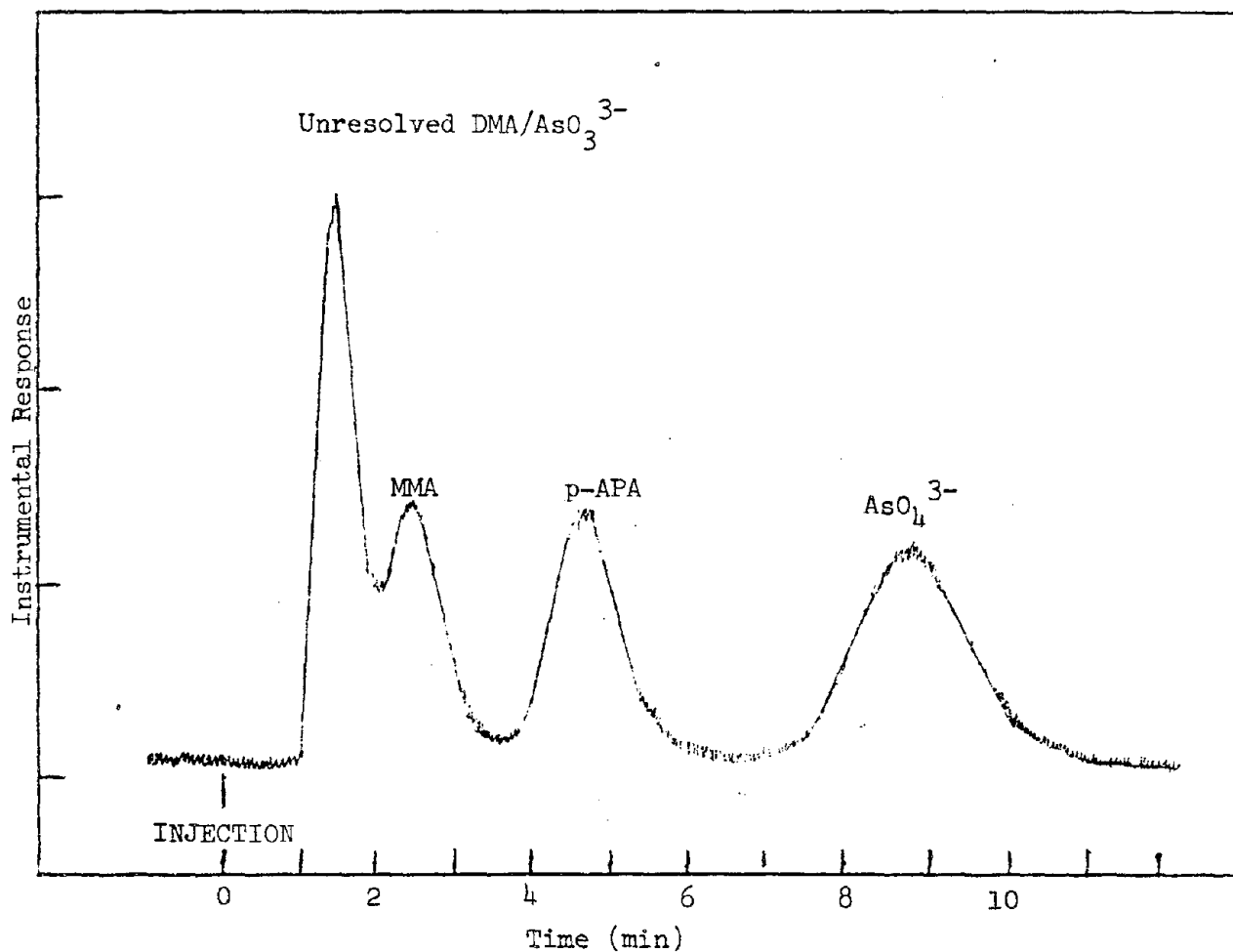


Figure 10. IC-AAS chromatogram of unresolved DMA (16 ng/mL) and AsO_3^{3-} (100 ng/mL), MMA (20 ng/mL), p-APA (80 ng/mL) and AsO_4^{3-} (120 ng/mL). The chromatogram was obtained with the following conditions: sample volume 0.80 mL; 3x500 mm Dionex anion separator column; eluent 0.0024 M NaHCO_3 /0.0019 M Na_2CO_3 /0.001 M $\text{Na}_2\text{B}_4\text{O}_7$; flow rate 2.60 mL/min; chart speed 1 cm/min and AAS scale expansion 3x.

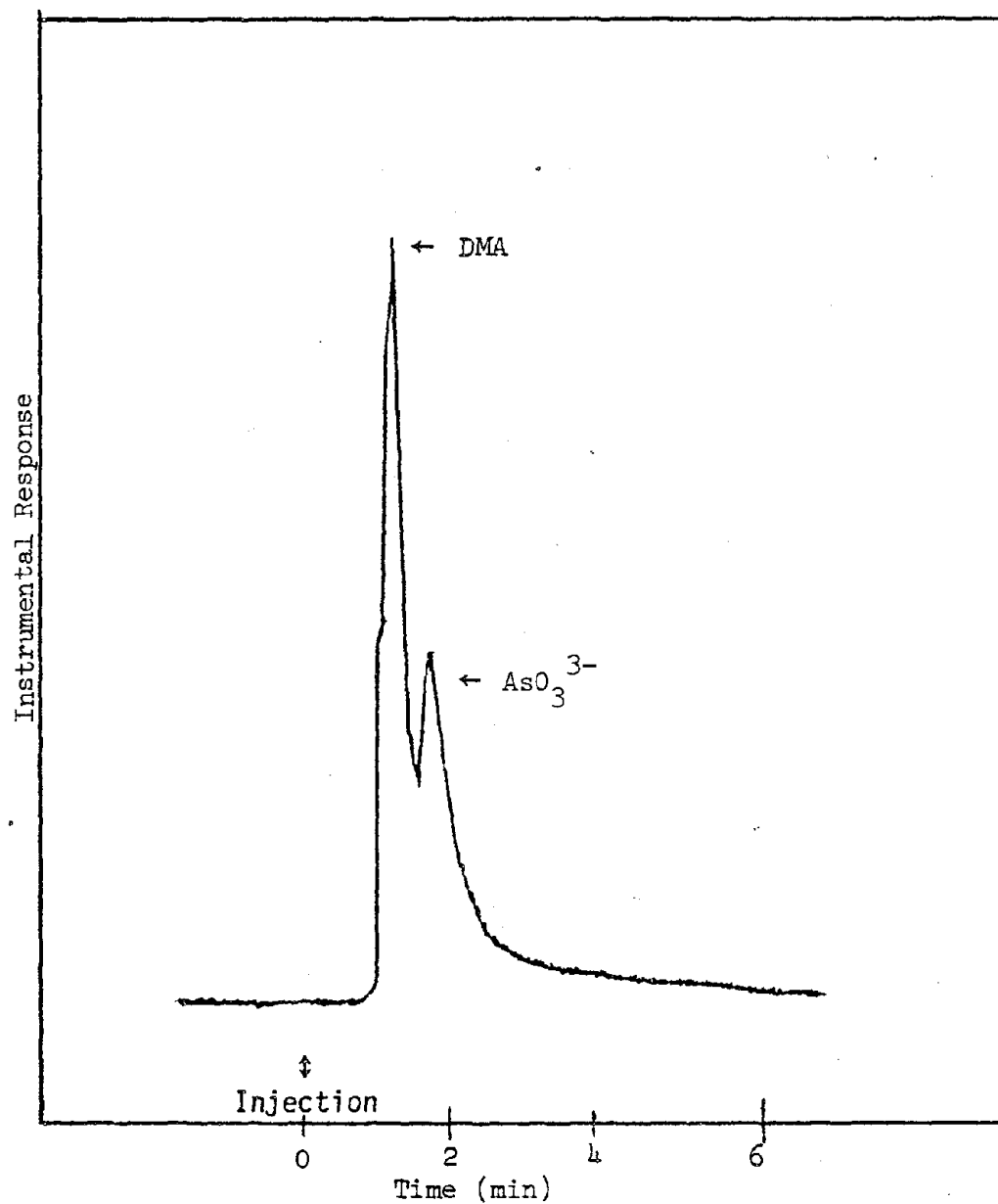


Figure 11. IC-AAS chromatogram of 20 ng/mL DMA, AsO_3^{3-} obtained by using a weak eluent (0.005 M $\text{Na}_2\text{B}_4\text{O}_7$). Instrumental conditions were: 3x500 mm anion separator column; 500 psi; 1 cm/min chart speed.

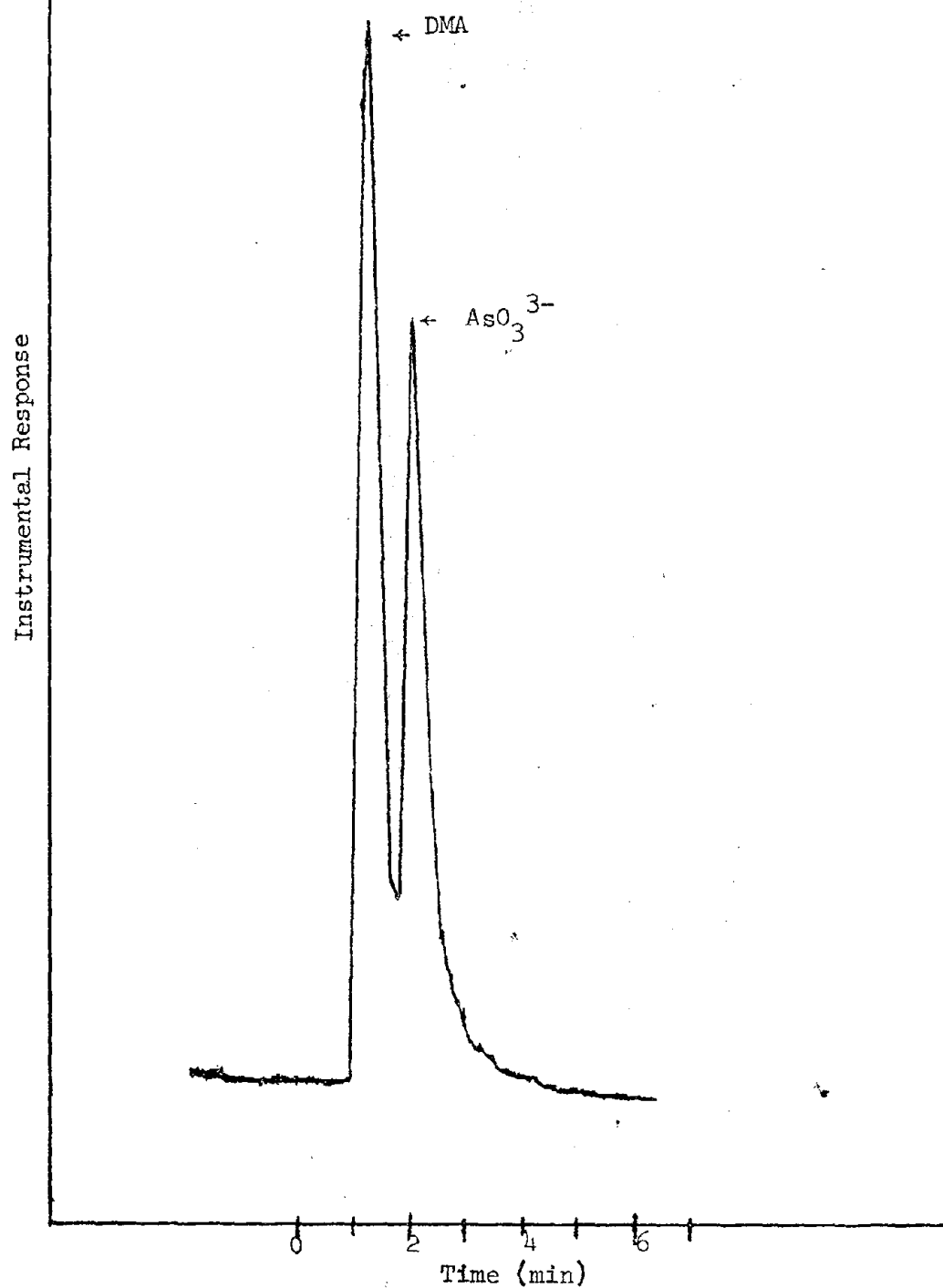


Figure 12. IC-AAS chromatogram of DMA and AsO_3^{3-} using two 3 x 500 mm IC columns and weak eluent (0.005 M $\text{Na}_2\text{B}_4\text{O}_7$).

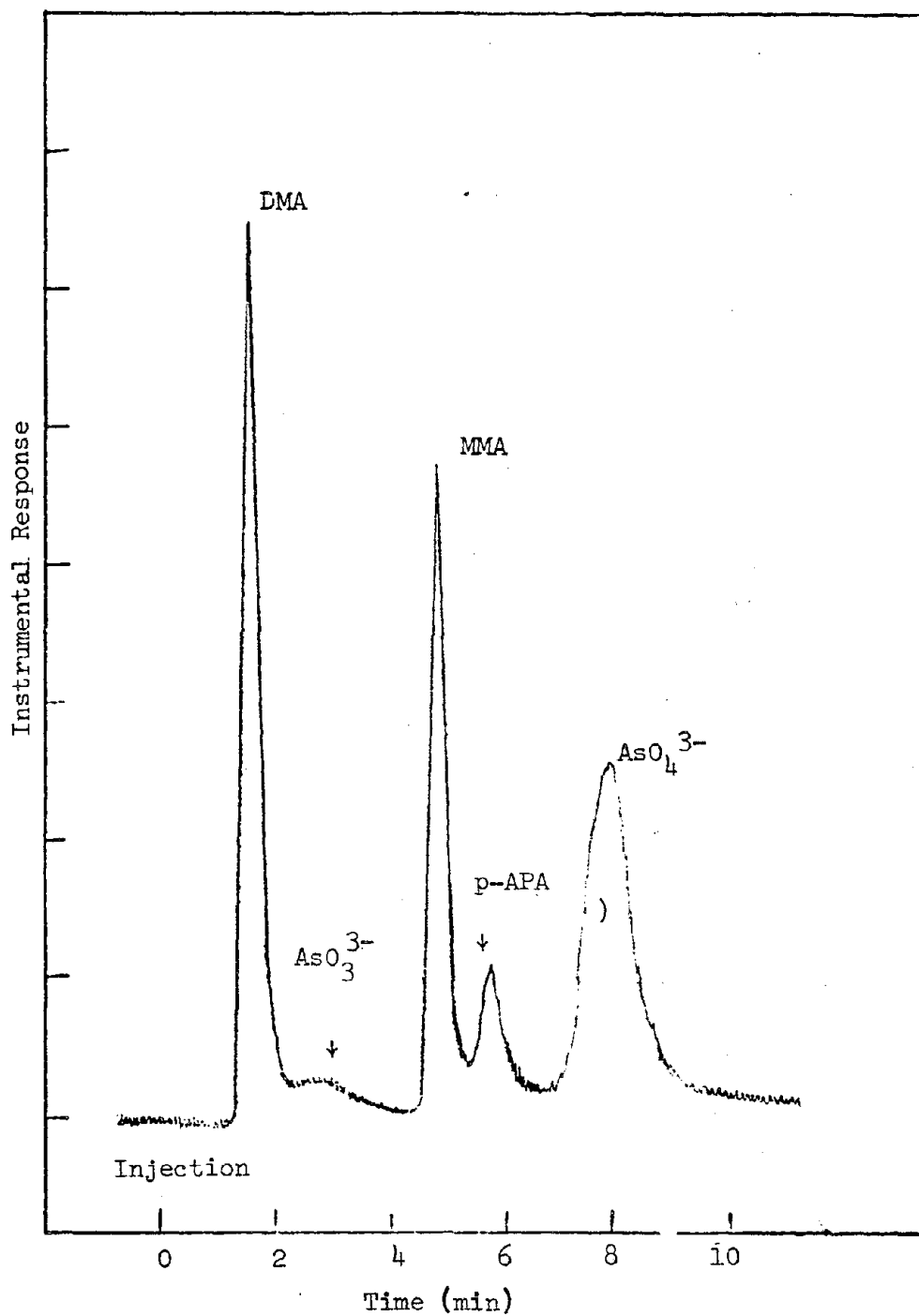


Figure 13. Separation of five-component aqueous solution of trace inorganic and organic arsenic species by gradient elution. The experimental conditions were: sample volume 0.80 mL; 3x500 mm Dionex anion separator column; 0.0025 M $\text{Na}_2\text{B}_4\text{O}_7$ and 0.003 M NaHCO_3 /0.0024 M Na_2CO_3 eluents; 3.5 min time gradient; flow rate 2.60 mL/min; chart speed 1 cm/min and scale expansion 3x.

Interferences in the Analysis of Organoarsenicals

The ion chromatographic technique, like other chromatographic techniques, is subject to interference from species within elute unresolved from the species of interest. The only interference which has been identified is AsO_3^{3-} , which elutes unresolved from DMA when $0.0024 \text{ M NaHCO}_3/0.0019 \text{ M Na}_2\text{CO}_3/0.001 \text{ M Na}_2\text{B}_4\text{O}_7$ is used as eluent. Resolution can, however, be achieved using $0.005 \text{ M Na}_2\text{B}_4\text{O}_7$ eluent as described above. All other species tested as potential interferences (NaAsO_3 , Na_3AsO_4 and H_3AsO_4) exist in solution as AsO_4^{3-} and therefore do not interfere. Under the pH conditions of this analysis the cationic arsenic halides will be hydrolyzed in aqueous solution forming As(III) species which will be observed to interfere as the AsO_3^{3-} .

Precision of Analysis Using Synthetic Standard Solutions

The precision of analysis as a function of concentration was studied. Synthetic aqueous standard solutions containing DMA, AsO_3^{3-} , MMA, p-APA and AsO_4^{3-} were prepared at four concentration levels in buffer matrix (Eluent 1), and analyzed consecutively five times using the automated chromatographic technique. An overall linear least squares fit of concentration versus peak height was calculated for each species, the slope and intercept parameters were then used to calculate a regression concentration for each data point. Finally, the average regression concentrations and percent relative standard deviations were calculated. The data presented in Table 3 demonstrate a precision of analysis better than 8.0 percent for most species in the concentration range of 20-80 ng/mL. The precision of analysis of AsO_3^{3-} , DMA, and AsO_4^{3-} is approximately 11 percent at the 20 ng/mL concentration level.

Table 3. Precision of analysis of synthetic solutions.

Species	Concentration arsenic (ng/mL) $\pm$ % RSD (N = 5)		
	20	40	80
DMA	19.58 $\pm$ 11.2%	40.84 $\pm$ 7.3%	60.40 $\pm$ 3.0%
AsO ₃ ⁻³	20.28 $\pm$ 11.2%	40.26 $\pm$ 7.4%	59.74 $\pm$ 5.8%
MMA	19.99 $\pm$ 8.1%	40.98 $\pm$ 5.3%	59.20 $\pm$ 4.5%
p-APA	20.14 $\pm$ 6.0%	40.06 $\pm$ 4.1%	60.39 $\pm$ 5.8%
AsO ₄ ⁻³	20.03 $\pm$ 10.8%	40.32 $\pm$ 3.5%	59.73 $\pm$ 3.6%

SAMPLING METHODS

The development of an effective sample collection technique for the determination of organoarsenicals in air requires adherence to the following important criteria: 1) the sampling device must be compatible with personal sampling pumps; 2) the collection medium must quantitatively collect particulates as well as any vapor forms of the organoarsenical compounds; 3) the method must be efficient at temperatures up to 50°C and a relative humidity of 95%; 4) the collection medium must be capable of retaining the compounds without loss or chemical change before analysis; and 5) the collected species must be extracted quantitatively from the collection medium for analysis.

The organoarsenical compounds studied were assumed to exist in air both as particulates and vapors. Collection of airborne particulates can be achieved effectively by a variety of filtering media which are amenable to use with personal sampling pumps. The selection of a medium for the collection of vapors is somewhat more involved. Filters chemically treated with common bases such as organic amines, NaHCO_3 , or Na_2CO_3 were proposed as a means of trapping the vapors. However, as discussed below, experiments designed to estimate the contribution of vapor forms to the total atmospheric contamination showed the concentrations of such vapors to be insignificant over the temperature range tested. The problem then became simply to evaluate and select a filtering medium which could satisfy the remaining criteria for the collection of particulate organoarsenicals. Although this appears to be a straightforward task, studies conducted with cellulose ester, Mitex, and Fluoropore filters have shown this not to be the case. Although the cellulose ester filter medium quantitatively collected total arsenic, it was found to be incompatible with the compounds. The Mitex filter, on the other hand, could not collect the particulates quantitatively, even though it was found to be compatible with the compounds. The experimental studies performed to evaluate and select a suitable filtering medium for the collection of particulate organoarsenicals are presented in detail below.

ORGANOARSENICAL VAPORS IN AIR

The contribution of vapor forms of organoarsenicals to the total atmospheric concentration depends on the vapor pressure of each compound and on the temperature conditions. Data on the vapor pressures of the compounds studied were not available and therefore the following experiment was designed to estimate the contribution of vapor forms expected to exist in a workplace atmosphere.

An enclosed sampling train for generation and quantitative collection of vapors was assembled with the following components: 1) a glass impinger wrapped with heating tape to serve as a vapor generator and modified so that the air inlet tube was 4 cm above the bottom; 2) a 47 mm cellulose ester membrane filter in line to collect particulates; 3) three bubblers in series to collect any

Table 4. Stability at room temperature of aqueous extracts of spiked cellulose ester filters as a function of time.

Species	Percent Recoveries $\pm$ Standard Deviation		
	1st Day	5th Day	7th Day
DMA/AsO ₃ ³⁻ *	100.4 $\pm$ 1.5	124.7 $\pm$ 11.9	150.6 $\pm$ 5.6
MMA	106.7 $\pm$ 1.0	58.2 $\pm$ 4.1	23.2 $\pm$ 2.5
p-APA	95.5 $\pm$ 5.3	91.6 $\pm$ 6.6	85.1 $\pm$ 6.0
AsO ₄ ³⁻	143.6 $\pm$ 24.5	118.4 $\pm$ 16.1	119.8 $\pm$ 18.3
	N = 2 **	N = 5	N = 4

* The percent recoveries shown are for unresolved DMA/AsO₃³⁻. The filter samples were not analyzed a second time using the weaker eluent³ to quantitate these two species individually.

Stability of Filter Extracts as a Function of Storage Time and Temperature --

An experiment was performed to determine if the organoarsenicals would be more stable if stored in an acidic or basic solution, and if refrigeration of the extracts would lead to increased stability. Fifteen cellulose ester filters were spiked with the equivalent of 1.5 μg of arsenic from each of the five species. The filters were allowed to dry before extraction for 30 minutes with 25 mL of one of the extraction solutions shown in Table 5. After sample preparation, extracts were either stored at room temperature or refrigerated. Each experiment was run in triplicate and the nonrefrigerated extracts were analyzed four days and six days after extraction, whereas the refrigerated extracts were analyzed six days after extraction. Table 6 presents the results of this experiment. The data show that chemical changes are still occurring, but that acetate and borate buffers, as well as refrigeration, improve the stability of MMA. No effort was made to explain the high recoveries for p-APA and AsO_4^{3-} or the low recoveries for DMA and AsO_3^{3-} .

Table 5. Extraction solutions used in the stability studies.

Extraction Solution	Description
A	H ₂ O
B	0.0021 M NaHCO ₃ /0.017 M Na ₂ CO ₃ /0.0015 M Na ₂ B ₄ O ₇
C	0.005 M Na ₂ B ₄ O ₇
D	0.001 M CH ₃ COONa

ADDITION OF
THERMAL AGING
EFFECTS
ON THE
STRENGTH OF
STEEL
AND
CONCRETE
STRUCTURES

Table 6. Stability of aqueous extracts of spiked cellulose ester filters as a function of extraction solution, storage temperature, and storage time.

Experimental Conditions	Percent Recovery $\pm$ Standard Deviation N = 3				
	Species				
Extraction Solution Storage Temperature Storage Time	DMA	AsO ₃ ³⁻	MMA	p-APA	AsO ₄ ³⁻
A Refrigerate 6 Days	99.6 $\pm$ 0.75	79.0 $\pm$ 7.9	88.7 $\pm$ 10.6	111.0 $\pm$ 1.4	93.5 $\pm$ 10.2
A Room Temperature 6 Days	114.7 **	171.4 **	28.6 $\pm$ 8.1	112.6 $\pm$ 4.0	80.7 $\pm$ 45.2 106.8 $\pm$ 3.2*
B Room Temperature 4 Days	72.0 **	40.0 **	79.8 $\pm$ 16.1	106.1 $\pm$ 5.2	123.7 $\pm$ 7.4
C Room Temperature 4 Days	73.3 **	45.7 **	93.6 $\pm$ 9.6	117.5 $\pm$ 7.3	112.4 $\pm$ 5.7
D Room Temperature 4 Days	88.0 **	65.7 **	106.1 $\pm$ 5.0	110.0 $\pm$ 1.8	113.9 $\pm$ 4.6

* Two data points

** One data point

On the basis of the results (Table 6), it was decided to extract the samples with buffer B because: 1) this extraction medium yields greater stability of MMA at room temperature, and with refrigeration recoveries might be even more improved; and 2) this extraction medium is the eluent used for separation and analysis of MMA, p-APA, and AsO_4^{3-} . In later work the concentration of this eluent buffer was changed slightly to $0.0024 \text{ M NaHCO}_3/0.0019 \text{ M Na}_2\text{CO}_3/0.001 \text{ M Na}_2\text{B}_4\text{O}_7$ to optimize further the chromatographic resolution of the compounds.

Effect of Sample Preparation and Storage Conditions on Recovery of Organo-arsenicals from Cellulose Ester, Fluoropore, and Mitex Membrane Filters.

As shown in the previous experiments, extracts of organoarsenicals obtained from cellulose ester filters and analyzed by the developed IC-AAS method suffer severely from lack of stability. To evaluate conclusively and also to find an appropriate filtering medium, experiments were performed to test the stability of organoarsenicals simultaneously on cellulose ester, Fluoropore, and Mitex filters. The experimental design is outlined in Figure 14. This design was developed to test the variables associated with the sample preparation and storage for each of the three filtering media. Triplicate spiked filters were used for each parameter tested. A mixed standard solution containing MMA, DMA, and p-APA was used for spiking. Each filter was spiked with the equivalent of 1.5 μg of arsenic from each species. The inorganic species As(III) and As(V) were not included on the filter spikes in anticipation that if any instability of the organoarsenical species was encountered, conversion to either of the inorganic species could be expected and interpretation of the analytical results would be simplified. A total of 30 filters were spiked in individual 50 mL beakers and extracted ultrasonically in 25 mL of buffer B for 30 minutes. The filter extracts were analyzed against calibration standards prepared in the same buffer matrix. The average percent recoveries and standard deviation of the triplicate filter spikes for each species are presented in Table 7. From the results presented there, the following conclusions can be made:

1. The percent recoveries of DMA from each filter type are excellent in all cases (94.4-104.0%) and therefore no stability problem is seen for this species.
2. The percent recoveries of MMA and p-APA from cellulose ester filters which were stored three days before extraction and analysis are poor (62-78%), whereas the percent recoveries obtained for the same species from Fluoropore and Mitex filters stored for three days are excellent (better than 90%).
3. The percent recoveries of MMA and p-APA from cellulose ester filters are significantly better if the filter samples are extracted the same day as they are spiked rather than storing the spiked filters for three days.
4. Removal of the undissolved cellulose ester filter material from aqueous extracts did not appear to improve the stability of the organoarsenicals.

On the basis of these results, it is clear that a more inert filter material (Mitex or Fluoropore) should be used. As will be discussed below, the collection efficiency of the Fluoropore filters is better than that of the Mitex filters, and for this reason it was finally decided to use Fluoropore filters

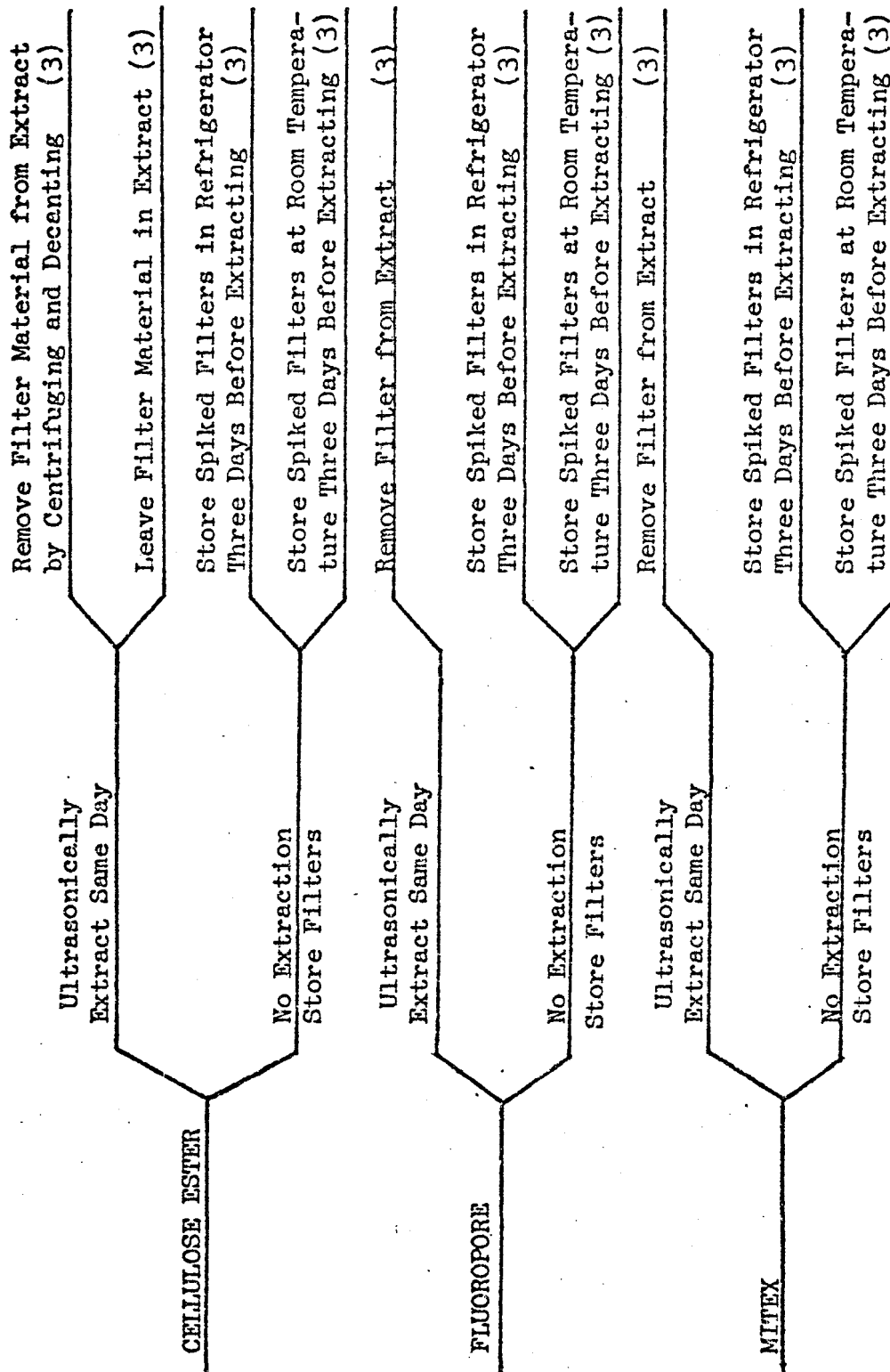


Figure 14. Experimental design used to test and compare the stability of organoarsenicals on cellulose ester, Fluoropore, and Mitex filters. Triplicate spiked filters were used for each experiment.

for the combined sampling and analysis procedure.

Collection Efficiency of Various Filters

Experiments to test the collection efficiency of the cellulose ester, Mitex, and Fluoropore filters were performed by generating and collecting aerosols of each of the organoarsenical species under controlled conditions. The aerosol generation/sampling system which was used for this was built and characterized in a previous study (13). The system was found to produce 90% of the particle mass in the size range of 0.1 to 10 μm .

Cellulose ester filters -- As mentioned previously, cellulose ester membrane filters were selected as a first choice for sampling the organoarsenical particulates in air because they are the standard Millipore filter used for aerosol sampling. The collection efficiency of this filter medium was established early in the project before the proposed IC-AAS analytical technique was developed. This was done by generating and collecting single component aerosol samples of each of the organoarsenicals (monosodium methylarsonate (MSMA), disodium methylarsonate (DSMA), DMA and p-APA) simultaneously with a tracer aerosol (Cd or Mo). The resulting filter samples were then extracted and analyzed for both total arsenic and the tracer metal. Collection efficiency was determined by comparison of the known ratio of tracer (Cd or Mo) to arsenic in the aerosol generation solution, to the ratios found on the filters. In addition, each aerosol cassette monitor was assembled with a double stage filtering arrangement to test for "breakthrough". The first collection stage was comprised of two untreated filters - a Millipore mixed cellulose ester membrane and a cellulose support pad. The second collection stage was comprised of two chemically treated filters to enhance the collection of volatile and particulate arsenic if breakthrough occurred - a Whatman 41 and a cellulose support pad. A 10% (v/v) tetrabutylammonium hydroxide and 10% (v/v) glycerol solution in deionized water was used for impregnating the second stage filters, as recommended in the literature by Walsh et al (16).

Finally, two sets of five replicate filters were generated during the same run for each compound to compare the results from two extraction procedures which were also studied. The first extraction procedure was simply an ultrasonic extraction of each of the filters from one set, in 10% HNO_3 for 30 minutes, and diluting to volume. The second extraction procedure involved total digestion of the cellulose ester membrane filters from the remaining set, using concentrated HNO_3 acid, taking to dryness on a steam bath, and diluting to volume with 10% HNO_3 . This procedure followed closely the ruggedized procedure for NIOSH P&CAM 173 (13). The additional filters from the same set (cellulose support pads and Whatman 41) could not be totally dissolved, however, and were refluxed in 10% HNO_3 for 30 minutes, filtered through glass wool, and then diluted to volume. All samples containing p-APA were treated with saturated potassium persulfate to oxidize the p-APA to inorganic arsenic.

Analysis of the samples showed that collection of each organoarsenical compound and its tracer was effected only on the first filter of the in-line series, i.e. on the mixed cellulose ester membrane. No detectable levels were found on the other filters. Table 8 summarizes the collection efficiencies determined for each of the organoarsenical compounds, using those two extraction techniques.

Table 7. Average percent recoveries ($\pm$ Std. Dev.) of organoarsenicals from spiked cellulose ester, Fluoropore, and Mitex filters (N = 3).

Species	Millipore Cellulose Ester Membrane Filters				Fluoropore Polyethylene Backed Teflon Filters			Mitex Unbacked Teflon Filters		
	Extract Filters Same Day/ Remove Filter Material	Extract Filters Same Day/ Leave Filter Material	Store Filters 3 Days in Refrigerator	Store Filters 3 Days at Room Temperature	Extract Filters Same Day/ Remove Filter Material	Store Filters 3 Days in Refrigerator	Store Filters 3 Days at Room Temperature	Extract Filters Same Day/ Remove Filter Material	Store Filters 3 Days in Refrigerator	Store Filters 3 Days at Room Temperature
DMA	100.6 $\pm$ 6.4	100.7 $\pm$ 8.4	94.4 $\pm$ 2.1	101.8 $\pm$ 4.4	104.0 $\pm$ 7.4	104.0 $\pm$ 6.4	100.6 $\pm$ 6.4	102.2 $\pm$ 8.2	102.9 $\pm$ 5.2	102.2 $\pm$ 5.0
MMA	100.9 $\pm$ 0.8	103.3 $\pm$ 6.5	75.1 $\pm$ 9.6	77.6 $\pm$ 6.4	106.4 $\pm$ 4.3	102.2 $\pm$ 2.0	103.3 $\pm$ 4.4	110.9 $\pm$ 3.1	104.9 $\pm$ 3.0	110.0 $\pm$ 5.3
p-APA	83.3 $\pm$ 1.0	76.7 $\pm$ 7.7	61.7 $\pm$ 11.5	64.6 $\pm$ 7.3	98.3* $\pm$ 7.2	98.0* $\pm$ 4.8	95.6 $\pm$ 2.1	100.5 $\pm$ 8.2	94.0 $\pm$ 6.8	90.7 $\pm$ 11.4

*Calculated with the exclusion of one outlying data point

Table 8. Collection efficiency of cellulose ester membrane filters determined by using the tracer technique. Two extraction procedures were also studied: total digestion vs ultrasonic extraction. Samples containing p-APA were treated with saturated potassium persulfate. N = 5 for each experiment.

Compound	Collection Efficiency, %	
	<u>Ultrasonically Extracted</u>	<u>Total Digestion</u>
MSMA	94.9	97.2
DSMA	95.2	97.1
DMA	100.1	89.6
p-APA	43.4	89.2

For p-APA extracted ultrasonically, a low recovery of 43.4% was obtained, indicating that the persulfate oxidation was incomplete and that heating is necessary.

Fluoropore and Mitex filters -- After experimental studies revealed that the organoarsenicals were incompatible with the cellulose ester filter material, Fluoropore and Mitex filters were evaluated for sampling organoarsenicals in air. The approach taken to test the collection efficiency of these alternative filter media was simpler in that it did not involve the use of a tracer aerosol. Rather than performing separate sample generations and analyses for each compound, three component samples (MMA, DMA, and p-APA) were generated and then analyzed by the developed IC-AAS speciation technique.

To determine collection efficiency, each aerosol cassette monitor was assembled with a double stage filtering arrangement to test for "breakthrough". The aerosol cassettes were assembled in the following manner using two of either the 5 μ m Mitex unbacked Teflon filters or two of the 1.0 μ m Fluoropore polyethylene-backed Teflon filters: Teflon filter #1 (upstream), supported by a cellulose pad and isolated from Teflon filter #2 (downstream), also supported by a cellulose pad. Both the Mitex and Fluoropore filters were used for simultaneous sampling of an atmosphere of $\sim 60 \mu\text{g}/\text{m}^3$ as arsenic of each of the three organoarsenical species in the aerosol generation/sampling system. After sample collection, the four filters from each cassette (both Teflon filters and both cellulose support pads) were extracted and analyzed. The results are presented in Table 9, and are expressed in $\mu\text{g As}/\text{m}^3$ and an average and standard deviation were calculated for each species. The data show that no breakthrough is seen past the first Fluoropore filter, whereas significant breakthrough is seen on the cellulose support pad behind the first Mitex filter. The 5 μ m pore size of the Mitex filter is simply too large to collect the particulates quantitatively. The collection efficiency of the Fluoropore 1 μ m filters is better than 99%, whereas the collection efficiency of the Mitex 5 μ m filters relative to the Fluoropore filters is only $\sim 65\%$. On the basis of these results, Fluoropore filters were selected for the collection of organoarsenical particulates in air. Their collection efficiency is as good as the traditionally used cellulose ester filters and in addition are inert

Table 9. Collection efficiency of Fluoropore and Mitex filters for sampling organoarsenicals in air (N = 5).

Organoarsenical Species	Filter Stage	Concentration Arsenic ($\mu\text{g}/\text{m}^3$) $\pm$ Std. Deviation	
		Fluoropore 1.0 μm	Mitex 5.0 μm
MMA	Membrane Filter 1	57.04 $\pm$ 5.32	37.11 $\pm$ 3.28
	Support Pad 1	< DL	3.26 $\pm$ 0.48
	Membrane Filter 2	< DL	< DL
	Support Pad 2	< DL	< DL
DMA	Membrane Filter 1	54.29 $\pm$ 2.67	36.67 $\pm$ 3.21
	Support Pad 1	< DL	3.42 $\pm$ 0.54
	Membrane Filter 2	< DL	< DL
	Support Pad 2	< DL	< DL
p-APA	Membrane Filter 1	50.77 $\pm$ 2.99	32.67 $\pm$ 3.62
	Support Pad 1	< DL	3.06 $\pm$ 0.76
	Membrane Filter 2	< DL	< DL
	Support Pad 2	< DL	< DL
Estimated Collection Efficiency		> 99%	$\sim$ 65%

DL = $\sim 0.5 \mu\text{g}/\text{m}^3$

towards the various organoarsenical species.

Effects of Temperature, Humidity, and SO₂ on Exposed Filter Samples

The effectiveness of the proposed sampling procedure using 1 μ m Fluoropore filters was further tested under conditions of high temperature (50°C) and high humidity ($\sim$ 95% RH) as well as in the presence of high SO₂ concentrations. This was done by subjecting filters which previously had been loaded with organoarsenical aerosols to these conditions as follows. In one experiment, arsenic-free air of 50°C and 95% relative humidity was passed through pre-loaded filters for the same period of time as the initial sample collection time. In a second experiment, air containing 1 ppm SO₂ was passed through the preloaded filters. These filters were then analyzed along with control filters which had not been subjected to these conditions. The results of these experiments are presented in Tables 10 and 11, and show clearly that there is no significant effect of temperature, humidity or SO₂ on the samples.

Table 10. Effect of temperature (50°C) and humidity (95% RH) on particulate organoarsenicals collected on Fluoropore filters (N = 5).

Species	Arsenic ($\mu\text{g}/\text{m}^3 \pm$ Standard Deviation)	
	Control Samples	Samples Exposed to 50°C/95% RH
MMA	24.36 $\pm$ 0.63	24.92 $\pm$ 0.70
DMA	23.97 $\pm$ 0.88	23.86 $\pm$ 0.27
p-APA	21.41 $\pm$ 1.79	19.24 $\pm$ 1.08

RECEIVED
JAN 10 1968
U.S. ARMY
CORPS OF
ENGINEERS
FORT MONROE
VA 23046

Table 11. Effect of SO₂ on particulate organoarsenicals collected on Fluoropore filters (N = 5).

Organoarsenical Species	Filter Stage	Arsenic (ug/m ³) ± Standard Deviation	
		Control Samples	Samples Exposed to 1 ppm SO ₂
MMA	Fluoropore Filter 1	55.76 ± 0.33	55.38 ± 3.84
	Support Pad 1	< DL	< DL
	Fluoropore Filter 2	< DL	< DL
	Support Pad 2	< DL	< DL
DMA	Fluoropore Filter 1	55.65 ± 0.48	55.43 ± 4.63
	Support Pad 1	< DL	< DL
	Fluoropore Filter 2	< DL	< DL
	Support Pad 2	< DL	< DL
p-APA	Fluoropore Filter 1	48.26 ± 0.72	49.53 ± 4.31
	Support Pad 1	< DL	< DL
	Fluoropore Filter 2	< DL	< DL
	Support Pad 2	< DL	< DL

DL = ~ 0.5 ug/m³

EVALUATION OF DEVELOPED SAMPLING AND ANALYSIS PROCEDURE FOR DETERMINATION OF ORGANOARSENICALS IN AIR

A highly sensitive, automated analytical method has been developed for the determination of organoarsenicals in air. The optimized procedures for both sampling and analysis are described in detail below. A Youden-Steiner ruggedness test (15) of the proposed analytical procedure was performed and the entire method evaluated for precision and accuracy. The results of the method evaluation show that the proposed analytical procedure can yield precise and accurate data.

PROPOSED PROCEDURE FOR DETERMINATION OF AIRBORNE ORGANOARSENICALS

The developed sampling and analysis technique for the determination of airborne concentrations of organoarsenicals is described below.

Sampling Procedure

Atmospheric particulate matter is collected quantitatively on 37 mm Fluoropore® (PTFE/polyolefin) membrane filters (Millipore, Type FA, 1 μ m pore size). This is done by sampling air at the rate of about 1.5 liters per minute through a three-piece polystyrene filter holder containing the filter and a cellulose support pad. This device is compatible with personal sampling pumps and can be attached to a worker's collar or lapel for the collection of a breathing zone sample. The equipment necessary for the collection of the sample includes a personal sampling pump and tubing which can be connected to the filter unit in the line and calibrated to an accuracy of $\pm 5\%$ at the recommended flow rate. At the end of the sampling period, the air flow rate and collection time are recorded to calculate the total volume of air sampled.

Analytical Procedure

The optimized analytical procedure for determination of MMA, DMA, p-APA, as well as inorganic arsenic (III) and arsenic (V) is described below.

The organoarsenical particulates are extracted ultrasonically from the filters using an aqueous carbonate/bicarbonate/borate buffer (Eluent 1, Table 12). Each filter sample is placed into a clean, 50 mL beaker with its exposed side in direct contact with the surface of 25 mL of the extraction buffer. Each beaker is covered with parafilm and partially submerged in the ultrasonic water bath, which is held at constant temperature for the duration of the extraction (30 minutes). After sonication the resulting extracts are ready for analysis and no further sample preparation is necessary.

The determination of organoarsenicals in the resulting extracts is achieved using the automated analytical system depicted in Figure 9. This system uses the basic components of an ion chromatograph such as a liquid pump, anion-

Table 12. Instrumental conditions for the analysis of organoarsenicals in air particulate samples

Ion Chromatograph Parameters

Column	Dionex 3x500 mm Anion-Exchange
Mobile Phase Flow Rate	2.6 mL/min
Eluent 1	0.0024 M NaHCO ₃ /0.0019 M Na ₂ CO ₃ / 0.001 M Na ₂ B ₄ O ₇
Eluent 2	0.005 M Na ₂ B ₄ O ₇
Injection Loop	Variable

Arsine Generation Parameters

15% HCl w/saturated potassium persulfate	0.8 mL/min
1% NaBH ₄ /0.2% KOH	2.0 mL/min
Argon Carrier Gas	300 cc/min

AAS Parameters

Arsenic EDL	8 watts
Wavelength	193.7 nm
Slit Width	0.7 nm
Quartz Furnace	800°C
D ₂ Background Correction	None
Signal	Absorbance
Scale Expansion	3x
Recorder	10 mv full scale
Chart Speed	1 cm/min

exchange separator column and injection valve, coupled with an arsine generation system and a quartz furnace/AAS detector.

A sample is injected onto the 3 x 500 mm anion-exchange separator column and the organoarsenicals are eluted with the appropriate buffer at a flow rate of 2.6 mL/min. The organoarsenical species which are separated by ion chromatography are reduced to their respective arsine derivatives as they exit the column in the eluent stream. This is achieved by mixing the eluent stream with a solution of 15% HCl acid saturated with potassium persulfate, and then reducing the arsenic species with 1% sodium borohydride (NaBH₄). The arsine derivatives are carried to a heated quartz furnace (~800°C) aligned in the light path of the AAS where thermal decomposition of the arsines into free arsenic atoms occurs. The AAS instrumental parameters are adjusted to optimum following the manufacturer's recommendations. A detailed list of instrumental parameters for the total analytical system is given in Table 12.

Two separate analyses of a sample, utilizing two eluent buffer systems of different ionic strength, are required for the complete characterization of a sample because As(III), if present in the sample, will interfere with the resolution and determination of DMA. Composition of the two eluent buffers

Eluent 1 allows the separation and determination of MMA, p-APA, and As(V). If As(III) is not present in the sample, DMA is also effectively determined. The order of elution using Eluent 1 is: unresolved DMA-As(III), MMA, p-APA, and As(V). The entire chromatogram requires ~10 minutes and the analysis can be performed at the rate of 5 samples per hour.

Automated System --

Choice of Analytical Systems --

RUGGEDNESS TESTING OF PROPOSED PROCEDURE

Variables which may have an effect on any analytical procedure can be placed in three categories:

- Variables associated with sample preparation.
- Variables associated with the physical-chemical characteristics of the samples.
- Variables associated with instrumental characteristics.

The variables which were chosen for this experiment are shown in Table 13, along with the Youden-Steiner experimental design. These variables are primarily associated with the sample preparation and were selected by examining carefully the developed procedure and then selecting those steps of the procedure most likely to show variation from one laboratory to another or even within a laboratory. The number of variables studied is limited because: 1) the sample preparation/extraction procedure is very simple and few procedural steps are required; 2) the number of physical-chemical variables which could be studied at this time were few since, a) there is no dissolved filter material contributing to the final sample matrix which could have an effect on the accuracy, and b) the precision of the analysis as a function of concentration had previously been studied; and 3) those variables or parameters which will have the greatest effect on the precision and accuracy of this method are those associated mainly with the operation of the analytical system. Previous experience in performing ruggedization experiments and the experience acquired during the development of this method has shown that instrumental conditions are very critical, especially when working close to the analytical detection limit, and must be carefully optimized in order to obtain precise data. Therefore, the variables associated with the instrumental characteristics were not studied in this experiment.

The Youden-Steiner experimental design presented in Table 13 allows the testing of seven variables with eight experiments. The effect of each variable in the ruggedness test is determined by the difference between the average high and low levels and is estimated by using equation 1:

$$E_A = \frac{\sum ER(+)_i - \sum ER(-)_i}{N/2} \quad (1)$$

The low (-) and high (+) levels of each variable were selected in a range corresponding to changes which may take place in an analysis either within or between laboratories. Four of the variables were dummy variables. A dummy variable is a vacant space in the experimental matrix which does not represent any procedural change, but is a measure of the standard error. The Youden-Steiner experiment is performed in duplicate and standard error is calculated by equation 2:

$$s = \sqrt{\frac{2 \left[(E_{A1} - E_{A2})^2 + (E_{B1} - E_{B2})^2 + \dots + (E_{G1} - E_{G2})^2 \right]}{7}} \quad (2)$$

where

$E_{A1}, E_{B1}, \dots, E_{G1}$ are the calculated effects of variables A, B, ..., G

Table 13. Youden-Steiner ruggedization experimental design.

Experiment Number	A	B	C	D	E	F	G
1	+	+	+	+	+	+	+
2	+	+	-	+	-	-	-
3	+	-	+	-	+	-	-
4	+	-	-	-	-	+	+
5	-	+	+	-	-	+	-
6	-	+	-	-	+	-	+
7	-	-	+	+	-	-	+
8	-	-	-	+	+	+	-

The following procedural parameters were studied with this design using spiked Fluoropore filters:

A	Extraction time	10 min (-) vs 30 min (+)
B	Storage temperature	4°C (-) vs 25°C (+)
C	Time after spiking before extraction	3 days (-) vs same day (+)
D	Dummy	
E	Dummy	
F	Dummy	
G	Dummy	

in the first experiment, and $E_{A2}, E_{B2}, \dots, E_{G2}$ are the calculated effects of variables A, B, ..., G in the second experiment. For an effect to be significant at the 95% confidence level, it must exceed 1.18 s:

$$E_A = \frac{E_{A1} + E_{A2}}{2} > 1.18s \quad (3).$$

This is based on the Student's t-test for seven degrees of freedom at the 5% significance level.

For the ruggedization experiment a set of eight filters was spiked and allowed to dry at room temperature three days before a second set of eight filters was spiked. The 16 spiked filters were then extracted ultrasonically the same day according to the experimental design (10 min vs 30 min) and the extracts stored accordingly (4°C vs 25°C) for another three days. All 16 samples were analyzed the same day. The results of the ruggedization experiment showed no variables to be significant.

PRECISION AND ACCURACY OF PROPOSED METHOD

The precision and accuracy of the combined sampling and analytical method was tested using filter samples loaded in the aerosol generation and sampling system. Replicate samples were analyzed using the developed IC-AAS analytical procedure, and also by Neutron Activation (NAA) and X-Ray Fluorescence (XRF) analyses performed by an independent laboratory. For this, mixed aerosols containing MMA, DMA, and p-APA were generated in concentrations of 5, 10, and 20 µg arsenic per cubic meter of air for each of the compounds and sampled for 4 hours at 10 equivalent positions in the aerosol generation and sampling system. Three of these positions were used to collect samples for NAA and XRF analyses. The flow rate of air sampled across each position was controlled by a critical orifice and calibrated before the experiment began. The procedure for the IC-AAS analysis of the replicate samples at each of the three concentration levels was to analyze five calibration standards before and after each set of seven replicates. The volume of the IC injection loop for each range of calibration standards was selected such that the AAS instrumental responses were within the optimum linear working range.

Data for the seven replicates of each level, analyzed by the developed IC-AAS procedure, are presented in Table 14. The data are expressed in µg/m³ (as arsenic) and an average and standard deviation were calculated for each species. Depending on the concentration and the species, the relative standard deviation was found to range from ±14.4% at the lowest level to ±4.7% at the highest level.

The accuracy of the analytical method was established by independent analysis of three filters from each of the 5, 10, and 20 µg/m³ generation runs using both NAA and XRF analyses. Because NAA and XRF analysis techniques provide only a total arsenic measurement, the IC-AAS speciation results obtained for

RECEIVED
JAN 10 1971
FBI - NEW YORK
AIRTEL
TO DIRECTOR
FROM NEW YORK
RE NEW YORK
AIRTEL
JAN 10 1971

Table 14. Precision of combined sampling and analytical method using Fluoropore filters loaded in the aerosol generation/sampling system. All concentrations are expressed in micrograms of arsenic per cubic meter of air (N = 7).

Approximate Aerosol Concentration Level for Each Species ($\mu\text{g}/\text{m}^3$)	MMA Found ($\mu\text{g}/\text{m}^3 \pm \text{Std. Dev.}$)	DMA Found ($\mu\text{g}/\text{m}^3 \pm \text{Std. Dev.}$)	p-APA Found ($\mu\text{g}/\text{m}^3 \pm \text{Std. Dev.}$)	Total Arsenic ($\mu\text{g}/\text{m}^3 \pm \text{Std. Dev.}$)
5	4.93 $\pm$ 0.68	5.08 $\pm$ 0.65	4.16 $\pm$ 0.6	14.17 $\pm$ 0.64
10	10.27 $\pm$ 0.62	10.58 $\pm$ 0.32	8.07 $\pm$ 0.91	28.92 $\pm$ 1.25
20	22.03 $\pm$ 1.48	21.62 $\pm$ 1.01	19.49 $\pm$ 1.32	63.14 $\pm$ 1.66

MMA, DMA, and p-APA were used to estimate the total amount of arsenic. Table 15 presents the total arsenic concentration determined by each of the three techniques. The accuracy of the IC-AAS technique ranged from 90-120% of the values obtained by NAA and XRF.

Table 15. Comparison of total arsenic concentrations on generated filters determined by IC-AAS, NAA, and XRF analysis techniques.

Approximate Total Arsenic Aerosol Concentration Level ($\mu\text{g}/\text{m}^3$)	Average Found Concentration ($\mu\text{g}/\text{m}^3$) ± Std. Dev. of Total Arsenic		
	IC-AAS (N = 7)	NAA (N = 3)	XRF (N = 3)
15	14.17 ± 0.64	12.04 ± 0.54	11.87 ± 0.76
30	28.92 ± 1.25	28.28 ± 3.67	30.52 ± 0.93
60	63.14 ± 1.66	56.25 ± 5.90	62.02 ± 3.53

CENTER OF
IMAGE AREA

SUMMARY AND CONCLUSIONS

A method for the collection and analysis of the organoarsenical compounds MMA, DMA, p-APA, as well as inorganic arsenic (III) and arsenic (V), has been developed, ruggedized, and tested for precision and accuracy. Particulate arsenicals are collected on a 37 mm Fluoropore membrane filter (1.0 μ m diameter pore size) at an air flow rate of 1.5 liters per minute. The arsenicals are extracted ultrasonically from the filters in aqueous carbonate/bicarbonate/borate buffer and analyzed. The developed technique makes use of automated ion chromatography which is coupled with a continuous arsine generation system to a quartz furnace atomizer and atomic absorption detector. The arsenical species are thus separated and quantitatively determined by continuous monitoring of the arsine derivatives.

The detection limits for DMA, arsenic (III), MMA, p-APA, and arsenic (V) in solution are 7, 8, 9, 8, and 6 ng/mL, respectively. For a 300 liter air sample extracted with 25.0 mL of solution and analyzed using ~0.8 mL injection volume, these correspond to concentrations in air of approximately 0.62, 0.71, 0.72, 0.64, and 0.46 μ g arsenic per cubic meter of air, respectively.

The selection of the Fluoropore membrane filter for sampling the organoarsenicals is based on experiments demonstrating the quantitative collection of the particulate forms of these compounds as well as their chemical stability on this media. Cellulose ester and Mitex filters were also tested.

The first was found to cause artifact changes in the organoarsenicals and the second had very poor collection efficiency. It was also demonstrated that vapor concentrations of the organoarsenical acids were negligible. The sampling technique was tested to determine the effects of temperature, humidity, and SO₂, and it was shown that none of these had a measurable effect on the performance of the sampling device.

The precision of the combined sampling and analytical method was tested using filters loaded with particulates of the three organoarsenical compounds in a dynamic aerosol generation and sampling system. The concentration levels tested for each species were 5, 10, and 20 micrograms of arsenic per cubic meter of air. Depending on the concentration and species, the relative standard deviation was found to range from $\pm 4.4\%$ at the lowest concentration level to $\pm 4.7\%$ at the highest concentration level.

The accuracy of the combined sampling and analytical method was tested by using both Neutron Activation (NAA) and X-Ray Fluorescence (XRF) analyses. Since NAA and XRF techniques provide only the elemental arsenic, the total arsenic obtained from the IC-AAS analysis was used for comparison. The accuracy ranged from 90-120% of the values obtained by NAA and XRF.

REFERENCES

1. "Pesticide Use Report," California Department of Agriculture. 1972.
2. Soderquist, C.J., Crosby, D.G., and Bowers, J.B. 1974. Anal. Chem. 46, No. 1, 155.
3. Braman, R.S., Johnson, D.L., Foreback, C.C., Ammons, J.M., Bricker, T.L. 1977. Anal. Chem. 49, 621.
4. Talmi, Y. and Bostic, D.T. 1975. Anal. Chem. 47, 2145.
5. Crecelius, E.A. 1978. Anal. Chem. 50, 826.
6. Portman, J.E., and Piley, J.P. 1964. Anal. Chim. Acta 31, 509.
7. Casvalho, M.B., and Hercules, D.M. 1978. Anal. Chem. 50, 2030.
8. Yamamoto, M. 1975. Soil Sci. Soc. Am. Proc. 39, 859.
9. Elton, R.K., and Geiger, W.E. Jr. 1978. Anal. Chem. 50, 712.
10. Henry, F.T., and Thorpe, T.M. 1980. Anal. Chem. 52, 80.
11. Iverson, D.G., Anderson, M.A., Holm, T.R., and Starforth, R.R. 1979. Environ. Sci. and Technol. 13, 1492.
12. Federal Register, Vol. 39, No. 125. Thursday, June 27, 1974. Table G-1.
13. Colovos, G., Eaton, W.S., Ricci, G.R., Shepard, L.S., Wang, H. 1979. "Collaborative Testing of NIOSH Atomic Absorption Method" DHEW (NIOSH) Publication No. 79-144.
14. Vijan, P.N., and Wood, G.R. 1974. Atomic Absorption Newsletter 13, 33.
15. Youden, W.J. and Steiner, E.H. Statistical Manual for the AOAC. P.O. Box 540, Ben Franklin Station, Washington, D.C. 20044.
16. Walsh, P.R., Duce, R.A., and Fasching, J.L. 1977. Environmental Science and Technology 11(2), 163-166.

