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ARSENIC SPECIATION IN SOIL USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/INDUCTIVELY COUPLED PLASMA/MASS SPECTROMETRY

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ABSTRACT

A method has been developed to identify and quantify As(III), As(V), and organoarsenic compounds in soil samples from the Rocky Mountain Arsenal (RMA) by high performance liquid chromatography/inductively coupled plasma/mass spectrometry (HPLC/ICP/MS). The soils were extracted using tetrabutylammonium hydroxide (TBAH) and sonication. The percentages of As(III), As(V), and organoarsenic species extracted from soil samples were 30, 50, and 100 respectively. The arsenic species were not altered during the extraction process. They were separated by reversed-phase, ion-pairing, HPLC using a microbore Inertsil-ODS™ column. The HPLC column effluent was introduced into an ICP/MS system using a direct injection nebulizer (DIN). Detection limits of less than 1 pg were readily obtained for each arsenic species. Internal standards are recommended to increase accuracy and precision. Soil samples spiked with arsenic oxide, sodium arsenate, dimethylarsinic acid (DMAA), and chlorovinyl arsenious acid (CVAA) were extracted, identified and quantified with the HPLC/ICP/MS system. The soil samples were analyzed in support of the analytical needs of a thermal desorption treatability study being conducted at the RMA.

I. INTRODUCTION

Most routine inorganic analysis methods, such as standard EPA methods, are designed to determine and report "total" metals. While the "total" metals content of environmental samples can provide important information for assessing the impact of various potentially toxic metals, it must be recognized that different forms of these metals, i.e., metal species, can have significantly different toxicity[1] or environmental mobility.[2] Some forms are nontoxic, while others are highly toxic. In addition, the leachability of metals as determined by the Toxicity Characteristic Leaching Procedure (TCLP), as well as other physiochemical properties, is a function of the metal species present.[3] Thus, analysis methods must be developed to determine selected metal species in environmental sample materials.

Projects designed to assess the impact of treatment technologies on the fate and transport of potentially toxic metals in the environment require quantitative analysis data on total metals and qualitative and quantitative analysis data on inorganic and organic metal species. Soil thermal treatability studies conducted for the U.S. Army's Rocky Mountain Arsenal (RMA) environmental restoration project on arsenic laden soils required analysis data to determine the presence of arsenic, the types and amounts of both inorganic and organic arsenic compounds present, and the changes in these compound due to treatment.[4] While standard EPA methods could be employed to determine total arsenic content, methods for the qualitative and quantitative determinations of arsenic species had to be evaluated and implemented. Recently published research has focused on the measurement of metal species, including arsenic species using high performance liquid chromatography/inductively coupled plasma/mass spectrometry (HPLC/ICP/MS).[5-8] This technique applies reverse phase, ion-pairing chromatography to separating arsenic species, which are detected by ICP/MS. For this work the HPLC was interfaced to the ICP/MS using a direct injection nebulizer (DIN).

The HPLC/ICP/MS allowed the analysis of small sample solution volumes to low detection limits (0.1 pg). Soil samples (or other solids) must first be extracted to obtain the required aqueous samples. It is important that the extraction be efficient and reproducible, to optimize the accuracy of the determination. Furthermore, the extraction process must not change the form of the arsenic. Sonication was successfully used to extract As(III), As(V), and organic arsenic species from soil. Several extraction fluids were investigated and tetrabutylammonium hydroxide (TBAH) was selected.

II. EXPERIMENTAL

The experimental section contains details regarding the preparation of a standard soil, the spiking standards used to prepare the soils, and a description of how the soils were spiked. The extraction of the arsenic containing soils and the instrumental setup are also described.

A. Preparation of Standard Soil

Standard soils containing As(III), As(V), and DMAA were prepared from RMA soil to investigate the effectiveness of the extraction process and the HPLC/ICP/MS measurement. The soil was a medium-to-coarse, sandy silt and low in moisture content (about 6%). The soil sample had previously been blended following ASTM Method D346.[9] The material was twice coned and quartered and most of the gravel was removed. Numbers 20 and 30 mesh stainless steel screens were used to separate out any remaining clods and rocks. Soil that passed through both screens was used for preparing the standard soils. The standard soils were prepared by spiking with known quantities of As(III), As(V), and DMAA aqueous solutions.

B. Spiking Standards

Three different arsenic standards (1000 ppm As each) were prepared for spiking the soil. The compounds used to prepare the standards were arsenic oxide [As(III)], sodium arsenate [(As(V)], and dimethylarsinic acid [As(DMAA)]. Arsenic oxide was dissolved in approximately

0.2% sodium hydroxide; the other two standards were dissolved in distilled water. An additional organic arsenic solution, 2-chlorovinyl arsenious acid (1000 ppm CVAA), was obtained from U.S. Army Edgewood Research Center. The CVAA was chosen because it is a derivative of a warfare agent and of interest to the Army. Detailed studies on CVAA are described elsewhere.[10] These same stock spiking solutions were used to prepare the more dilute HPLC/ICP/MS aqueous standards. These standard concentrations ranged from 1 to 1000 ppb and were prepared fresh from the original stock spiking solution at least weekly.

C. Spiking the Soil Samples

Initially, three soils were spiked each with 100 ppm of one of the following As species: As(III), As(V), or As(DMAA). A fourth sample of soil and one of sea sand were spiked with 300 ppm total of all three species (100 ppm each of all three species). Several other soil samples were spiked with CVAA, either alone or combined with As(III) and As(V). The procedure for preparing the spiked soil standards was a variation of one described previously in the literature.[11]

Enough soil was screened (see Preparation of Standard Soil) to obtain 200-gram portions for each soil to be spiked. Two hundred grams of soil were placed into each of four tared polyethylene jars and weighed.

Approximately 100 grams (±5%) of soil were taken from each jar and placed into 4-inch-diameter petri dishes that had been acid-cleaned. To prepare the As(III) spiked soil sample, 20 mL portions of the As(III) spiking standard were carefully transferred onto the soil. Distilled water was meticulously added from a fine-tipped wash bottle while stirring with a disposable spoon to form a slurry. The slurry was stirred for an additional five to ten minutes to evenly distribute the spiking solution. The other standard soils were prepared similarly. The fourth soil sample was spiked with 20 mL of each of the three spiking standards and that provided enough water to create a slurry.

The petri dishes were placed overnight in a 45°C oven. The soil that contained all three arsenic species was allowed to dry 24 hours to completely remove the additional water, and was stirred periodically to avoid uneven distribution of the spikes due to layering of solids and liquids. The petri dishes were kept covered with ribbed watch glasses while drying and cooling to prevent contamination.

The hardened, dried soil was carefully broken up and transferred into a clean ceramic mortar with a stainless steel spatula. The chunks of soil were ground with a pestle until the soil resembled the original sandy silt. The remaining unspiked soil (100 grams) was added from the polyethylene jars to the mortar and mixed manually with a spoon until homogenous (approximately ten minutes). Since the spiked soil had a tendency to settle into layers (due to particles of different sizes), it was stirred again before weighing out a sample aliquot.

D. Arsenic Species Extraction

Four extraction solutions were examined to determine the optimum extractant:

- 2% nitric acid "Instra-Analyzed" with an arsenic content of less than 0.004 ppm
- 0.005 M heptyltriethylammonium phosphate (HTAP) Regis' Q7 Ion Pair cocktail with 5% methanol and the pH adjusted to 6.0 with 2-5% nitric acid
- 0.005 M TBAH with 55% solution from Southwestern Analytical, 5% methanol and the pH adjusted to 6.0 with 2-5% nitric acid
- distilled water.

The methanol used was ChromAR HPLC grade. The HTAP was prepared using Regis' Q7 Ion Pair cocktail diluted to 0.005 M. The TBAH was prepared from a 55% solution from Southwestern Analytical. The pHs were adjusted to 6.0. Filtered HTAP and TBAH were used as mobile phases for the HPLC/ICP/MS system, to extract soils, and to make dilutions of extracts.

Twenty-five mL of extraction fluid were pipetted into 50-mL beakers that contained 1-5 grams of spiked soil. Extractions were performed using a W-385 (475 watt) Ultrasonic Processor (Heat Systems-Ultrasonics, Inc.). The 1/8-inch standard tapered Microtip™ titanium ultrasonic probe was placed well within the extraction solution, but above the soil layer. Samples were extracted for 15 minutes, with the sonicator set on a 50 percent duty cycle and 1-second cycle time. Output control of the sonicator was set on five, as recommended for the Microtip probe. After the extraction was completed, soil and extraction fluid were carefully transferred to a 50-mL disposable centrifuge tube, using the supernatant to quantitatively transfer the sample. The sample was centrifuged for five to ten minutes.

Dilutions for injection into the HPLC/ICP/MS system were made according to expected concentrations of arsenic. A known volume of the clear supernatant was diluted into a known volume of HPLC mobile phase, calculated to contain approximately 100 ppb arsenic. Samples were filtered before they were injected into the HPLC using a 0.45-micron nylon membrane filter. The HPLC mobile phase was also filtered using a 0.45-micron nylon filter.

E. Instrumental Setup

The separations were performed using reversed phase, ion-pairing chromatography followed by detection using ICP/MS. The following specifications were used:

HPLC Column Specifications

Manufacturer:	SGE, Inc.
Column length:	10 cm
Column I.D.:	1 mm
Packing:	ODS2
Particle size:	5 micron
Pore size:	300 Angstrom

Chromatographic Conditions

Mobile phase:	tetrabutylammonium hydroxide (TBAH)/5% methanol
Flow rate:	40 - 50 µL/min
Injection volume:	1 µL

ICP/MS Instrumentation and Parameters

ICP/MS:	Fisons Instruments, Inc., VG Plasma Quad
DIN:	CETAC, Inc.
Masses monitored:	75, 77, and 80
Collection rate:	6 points per second (2 points per mass)
Collection mode:	time resolved; peak hopping

III. RESULTS AND DISCUSSION

A. Separation of Arsenic Species

The DMAA, As(III), and As(V) in the standard are well separated, as shown in Fig. 1. This figure shows the monitoring of mass to charge ratio (m/e) for mass 75, which corresponds to arsenic, as a function of time. The separation shows that at the 100 ppb As concentration level these species could be easily identified on the basis of retention time in an aqueous sample. Figure 2 shows the same analytes plus CVAA. As seen in Fig. 2, CVAA and DMAA were not separated. Figure 3 shows the structure of each compound. Additional chromatographic development could allow separation of these species but was not pursued in this study.

B. Extraction of Soils

There are two important aspects to consider in the extraction of soils for the purposes of arsenic speciation. The extraction process must be optimized so that the percent of arsenic species extracted is as high and as reproducible as possible. The extraction process must also

not change the arsenic species. To initially examine these parameters and find an optimum extraction fluid, stock soils were extracted using water, nitric acid, and the HTAP used for the HPLC mobile phase. The concentration of arsenic extracted was measured using atomic absorption spectrophotometry. Each extraction fluid was evaluated on soils spiked with 100 ppm As(III), then with As(V), DMAA, and a combination of all three (see the experimental section). Figure 4 shows the percent arsenic extracted from each spiked soil with each extraction fluid. The HTAP was determined to be the best extractant of DMAA. While nitric acid was acceptable, it has the potential to break down or change organoarsenic compounds and to oxidize As(III) to As(V).

Water formed a cloudy, emulsion layer and thus was more difficult to handle. The supernatant of the distilled water extractions required filtering through a Whatman #42 paper filter. Two layers of deposit were seen with the nitric acid and water extractions: one layer appeared sandy, while the other was a much finer sediment. Extractions performed with the methanol-containing extraction fluids had little of the finer sediment layer. The HTAP was selected as the extraction fluid. The results shown in Fig. 4 are based on total extracted arsenic and do not account for the conversion of arsenic species spiked on the soil.

During analysis using HPLC/ICP/MS, the HTAP appeared to be forming phosphate crystals on the nebulizer tip and thereby contributing to a change in sensitivity as a function of time, so the mobile phase was changed to improve the ICP/MS performance. The new mobile phase TBAH was also tried as the extractant and performed comparably to the HTAP.

C. Stability of Arsenic

The stability of arsenic species in standards and samples under normal conditions and the effect of the soil extraction process on the arsenic species were determined. During normal operations, no degradation of the aqueous arsenic standards was observed. The addition of

standards to soil samples, however, did result in the conversion of arsenic species. When the standard soil spiked with 100 ppm As(III) was extracted, both As(III) and As(V) were observed as shown in Fig. 5. This indicates a conversion of As(III) to As(V), either from the soil or from the extraction process.

It is of primary importance to distinguish whether this conversion is caused by the soil or by the extraction process. To determine if the conversion was caused by the soil or the extraction process, sea sand (which is less reactive than soil) was spiked with 100 ppm As(III), DMAA, and As(V) and extracted. The conversion of As(III) to As(V) was less for the spiked sea sand than for the spiked soil. During the extraction, sample temperatures rose approximately 17°C, based on one sample that measured 20°C before sonication and 37°C after. To determine if the sonication and/or temperature increase was responsible for the conversion of As(III) to As(V) on the spiked soil, the 1 ppm As(III) standard was sonicated for 15 minutes. The standard solution did not change temperature as rapidly as the samples containing soil and extraction fluid, nor did the As(III) convert to As(V). A 1 ppm As(III) standard solution was also heated for 15 minutes at approximately 50°C and injected into the HPLC/ICP/MS system. No conversion occurred: thus, the conversion demonstrated in Fig. 5 is the result of processes unrelated to the extraction procedure.

Another arsenic species that was affected by the soil was CVAA. Figure 2 shows the appearance of a CVAA standard coincident with the DMAA. Therefore, these two compounds appear as one peak in Fig. 2. When CVAA is spiked on a soil sample, it is completely converted to an unknown arsenic species, which is shown in Fig. 6. This unknown species was identified in later research as 2-clorovinylarsonic acid (CVAOA), which is an oxidized form of CVAA.[10] The same conversion occurred when CVAA was deposited on sea sand. When a CVAA standard was added to soil and immediately extracted (without drying), the CVAA was partially converted to CVAOA. A CVAA standard was sonicated and heated without being converted to CVAOA.

The amount of arsenic extracted is important for quantifying the arsenic species in soil. The amount of arsenic extracted using the TBAH buffer solution is summarized in Table 1. As previously mentioned, CVAA is converted to CVAOA in both soil and sea sand. The CVAOA is extracted at about 100%, and as shown in Table 1, As(III) and As(V) are extracted at less than 100%. Because of the conversion of As(III) to As(V) in soil and to a lesser degree in sea sand, the percent extractions listed in Table 1 are estimated. For soil, these estimations are made by measuring the As(III) and As(V) extracted from the 100-ppm As(III)-spiked soil sample. For the data shown in Table 1, the 100-ppm As(III)-spiked soil standard yielded 21 ppm of As(V) and 13.6 ppm of As(III). Assuming 45% extraction of the As(V), the soil contained 47 ppm of As(V) that was converted from As(III), leaving 53 ppm of As(III) in the soil for a percent extraction of 13.6 ÷ 53 or 25.6%. Both As(III) and As(V) were spiked on a single sea sand sample. The percent extraction was also estimated for these species based on the combined recovery of 93% and knowing that some of the As(III) was converted to As(V). Lower concentrations of arsenic species spiked on soil were also examined with similar results.

Table 1. Extraction of As Species from Soil as Determined by HPLC/ICP/MS

		Soil			Sea Sand		
As Compound	Conc. (ppm)	% Extraction	% RSD[a]	n	% Extraction	% RSD[a]	n
CVAA	44	104	9	2	109	15	2
DMAA	100	119	0.8	2	99.6	3	2
As(III)	100	25.6(13.6)[b]	7	3	86-100(67.9)[b]	10	2
As(V)	100	45.5	13	3	86-100(118)[b]	7	2

[a]RSD as percent of mean.

[b]The number in ( ) indicates the concentration of arsenic measured. Because some conversion of As(III) to As(V) occurred, the extraction is estimated.

D. Reproducibility

Table 2 shows the results from a series of replicate runs of a standard solution containing 100 ppb of each arsenic species listed. The units of the replicate measurements are counts at m/e = 75. Based on this table, a relative standard deviation (RSD) of less than 10% is expected for this measurement. However, in later measurements, unexplained deterioration of the reproducibility was observed with RSDs ranging from 10 to 30%. To correct for this deterioration, DMAA was used as an internal standard. When DMAA was used as an internal standard, the RSD was below 10% for a 50 ppb standard.

Table 2. Reproducibility

	As(III)	DMAA	As(V)
Replicate 1	2.27e+08	2.13e+08	1.79e+08
Replicate 2	2.13e+08	2.07e+08	1.82e+08
Replicate 3	2.24e+08	2.18e+08	2.01e+08
Replicate 4	2.20e+08	2.29e+08	2.08e+08
Replicate 5	2.44e+08	2.16e+08	2.01e+08
Replicate 6	2.10e+08	2.18e+08	2.05e+08
Replicate 7	2.30e+08	2.27e+08	1.84e+08
Average	2.24e+08	2.18e+08	1.94e+08
Standard Deviation	1.14e+07	7.65e+06	1.21e+07
RSD	5.11%	3.60%	6.20%

E. Estimated Detection Limits

An estimated detection limit was determined for each arsenic species used. Detection limits were estimated from the analysis of 1 μL of a standard containing 1 ppb of each arsenic species. Figure 7 shows the resulting chromatogram from this standard. The detection limit is

estimated from the peak height using three times the standard deviation of the noise (baseline). The estimated detection limit for each of the arsenic species using a 1 μL sample is 0.1 ppb.

F. Correction for Chloride Interferences

The ICP/MS uses argon as the plasma support gas. In the presence of high chloride levels, an interference for arsenic from ArCl may be present. Both arsenic and ArCl are present at mass 75. Because chlorine also has a significant isotope at mass 37, the interference can be corrected by measuring the amount of ArCl at mass 77. The ratio of chloride ions (mass 35 and 37) is 3:1, therefore, subtracting three times the mass 77 peak from the mass 75 peak successfully corrected for the chloride interference. Figures 8 and 9 show the effectiveness of this correction.

G. Linear Range

The linear range of the method was determined using peak area calculations and performing a linear regression on the results of 0, 10, 50, 100, 500, and 1000 ppb standards. Table 3 summarizes these results. The CVAA was used as an internal standard for As(III) and As(V); and As(III) was used as an internal standard for CVAA.

Table 3. Linear Range

	Without Internal Standards						With Internal Standards		
Species	As(III)		As(V)		CVAA		As(III)	As(V)	CVAA
r^2	0.9991	0.9776	0.9998	0.9763	0.9995	0.9816	0.9999	0.9998	1.000
Range (ppb)	0-500	0-1000	0-500	0-1000	0-500	0-1000	0-500	0-500	0-500

H. Quality Assurance/Quality Control

The necessary QC parameters and checks for this analytical method must still be developed and tested. The types of parameters and checks include the following: calibration, check standards, laboratory duplicates, matrix spikes, internal standards, surrogates, and laboratory control samples.

Calibration. Calibration for each arsenic species is performed by measuring the peak area from three replicates of a 100-ppb standard of the arsenic species of interest.

Check Standard. A 100-ppb check standard containing each of the As species of interest should be analyzed prior to the first sample, after every five samples, and after the last sample. If the results are outside ±20%, then the problem must be corrected and the check sample should be reanalyzed. All necessary samples should also be reanalyzed.

Internal Standard. An internal standard which is not present in the sample and will not interfere with the other analytes of interest should be selected. This internal standard should be added to every sample and standard. If the internal standard result is outside ±20%, then the problem should be corrected and the impacted samples rerun.

Selection of a better internal standard was also investigated. Indium and yttrium solutions were tried, but they were not clearly separated by the HPLC under current operating conditions. Different operating conditions, elements, or species of elements should be investigated to determine the best internal standard. DMAA was used as the internal standard, but it requires running unknown samples without the internal standard to allow for correction of any organoarsenic compounds that co-elute with the DMAA.

Laboratory Duplicate. Periodically a sample should be run in duplicate to assure the reproducibility of the measurement. Quality control limits and corrective actions have not yet been established for this parameter.

Surrogate or Matrix Spike. A surrogate or matrix spike should be used when extractions are required. They can be used to estimate matrix effects during the extraction. Matrix spikes and surrogates were not developed for incorporation into this method.

I. Sample Results

This method is being developed to determine the quantity and form of arsenic in contaminated soil before and after treatment in a rotary kiln desorber. Figure 10 shows the results of a contaminated soil (Soil 1), before treatment. The arsenic is all in the form of As(V). After treatment, as shown in Fig. 11, the arsenic is in the form of both As(III) and As(V). Results for a contaminated soil (Soil 2) from another location is shown in Fig. 12. This plot has been corrected for chloride interference and shows As(III), As(V), and organoarsenic species. Results for this same soil sample (Soil 2) after treatment are shown in Fig. 9. No organic arsenic was observed and the amount of As(V) decreased, while the amount of As(III) increased. This treatment always resulted in a portion of the As(V) being reduced to As(III).

IV. CONCLUSIONS

The work presented here describes an instrumental method for the identification and quantification of As(III), As(V), and organoarsenic compounds. Two different mobile phases on an Inertsil-ODS column were shown to give comparable separation. As(III), DMAA, and As(V) were all well separated. A fourth compound, CVAOA, generated from the conversion of CVAA, was also measured and resolved from As(III), DMAA, and As(V). The CVAA and DMAA were not resolved.

Results were demonstrated to be reproducible within 10%. However, the use of an internal standard is essential in order to maintain good precision. The estimated detection limit is 0.1 pg, or 0.1 ppb for a 1-μL injection. The presence of chloride in a sample can produce an interference on arsenic, but monitoring mass 77 allows correction of the chloride interference. The method is linear up to 500 ppb. Samples that exceed this concentration should be diluted and reanalyzed. Quality control samples are effective in measuring the performance of the

method. Internal standards and check standards are particularly useful in measuring and correcting for instrument drift. One problem encountered was the difficulty in finding an internal standard that does not interfere with arsenic species present in the sample, and yields a good peak under current chromatographic conditions.

Results were obtained using this method for contaminated and treated soil samples. Results from these measurements showed that as a result of treatment, a portion of the As(V) was reduced to As(III) and the organic arsenic species was decomposed. Also, the chloride content of some soils was high both before and after treatment (i.e., the chloride was not removed during treatment).

The HPLC/ICP/MS method was specifically designed for arsenic speciation in soil, but is also applicable to water samples. The method can be readily adapted to identify and quantify other metals, such as mercury, selenium, chromium, tin, and lead.

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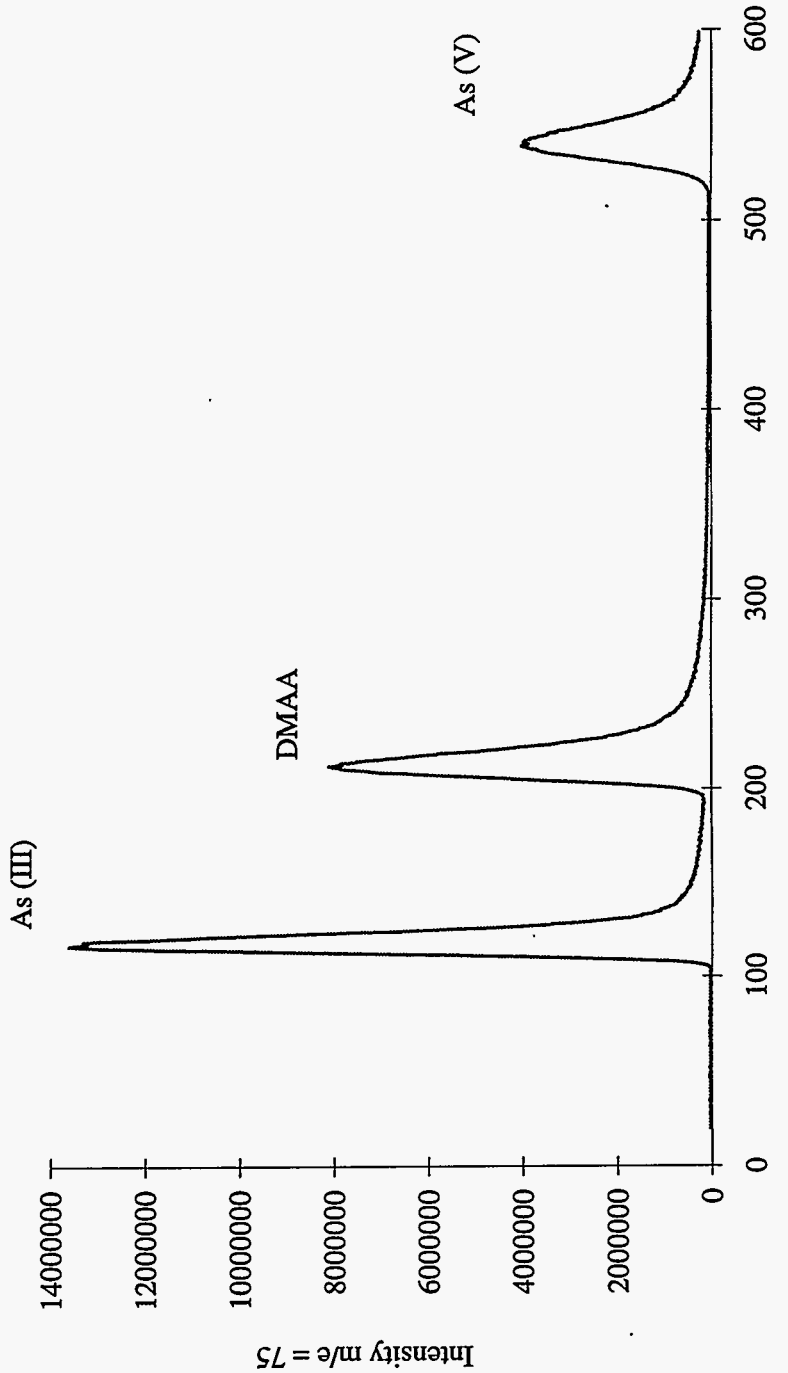


Fig. 1. Chromatogram of a DMAA, As(III), and As(V) Standard

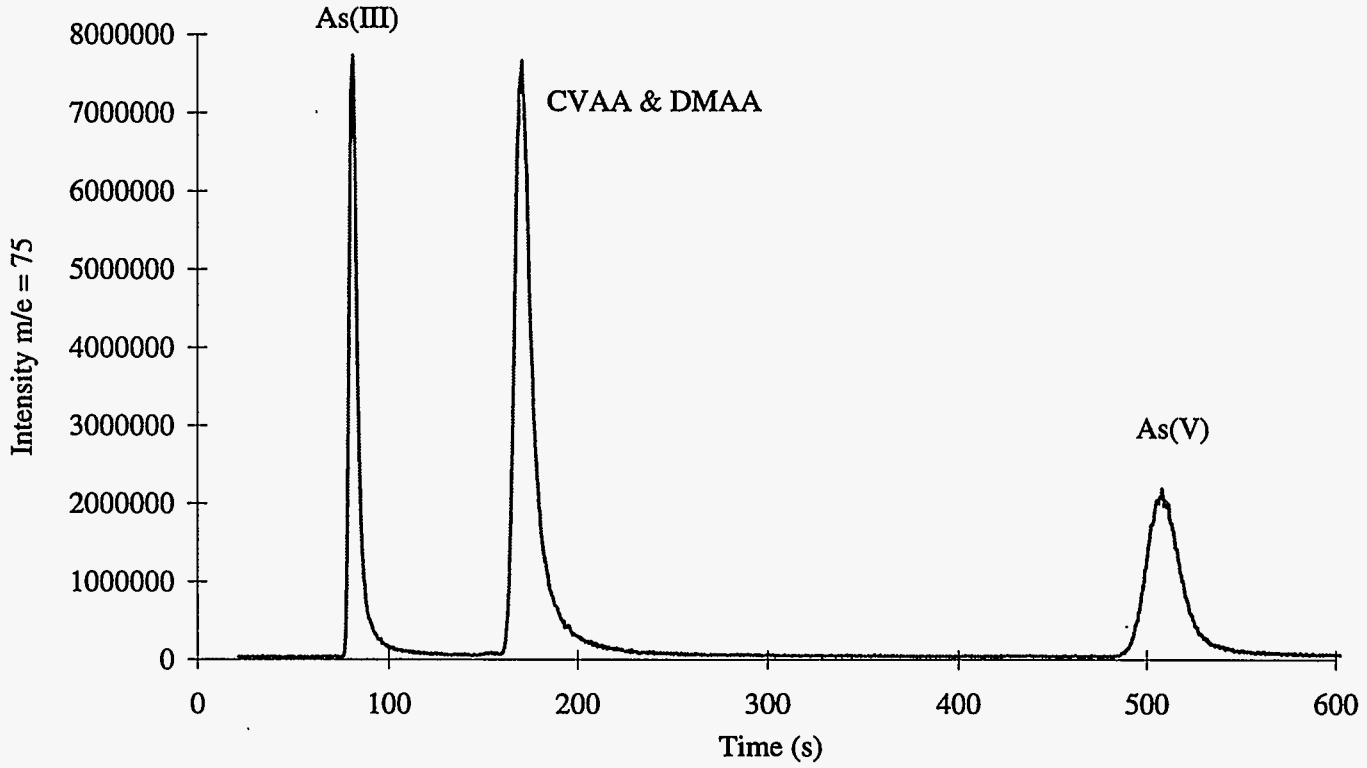
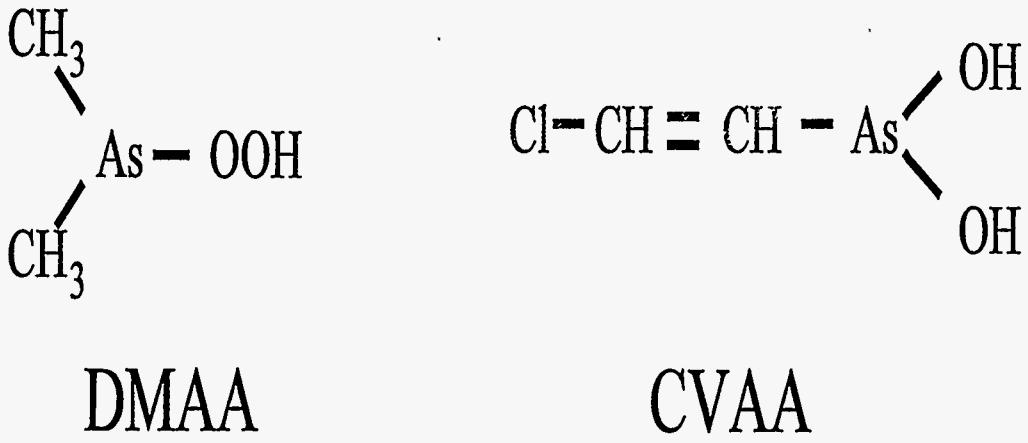


Fig. 2. Chromatogram of a DMAA, As(III), As(V), and CVAA Standard (CVAA and DMAA Not Separated)



DMAA CVAA

Fig. 3. Structures of DMAA and CVAA

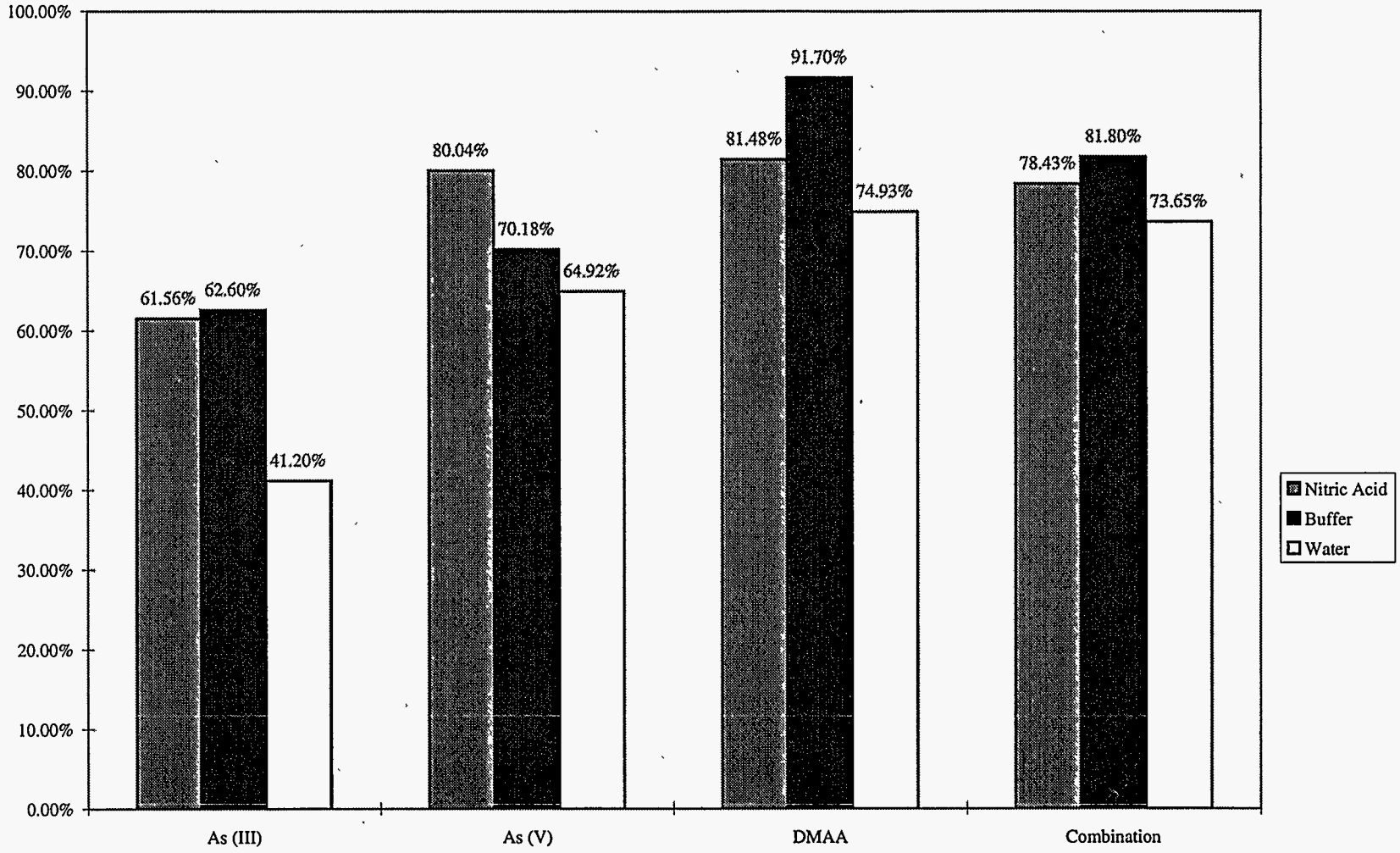


Fig. 4. Extraction Efficiency of Arsenic Species from Soil

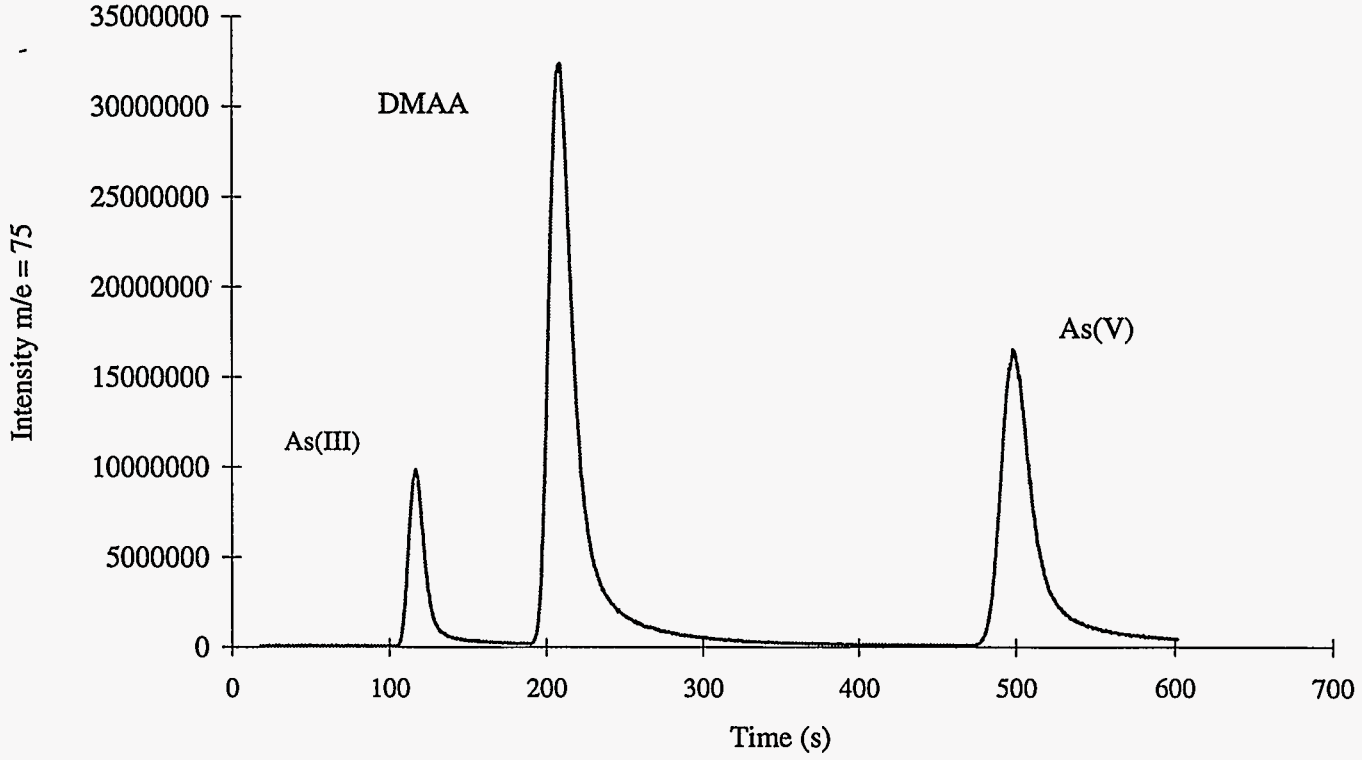


Fig. 5. Chromatogram Demonstrating the Conversion of As(III) to As(V) in Soil

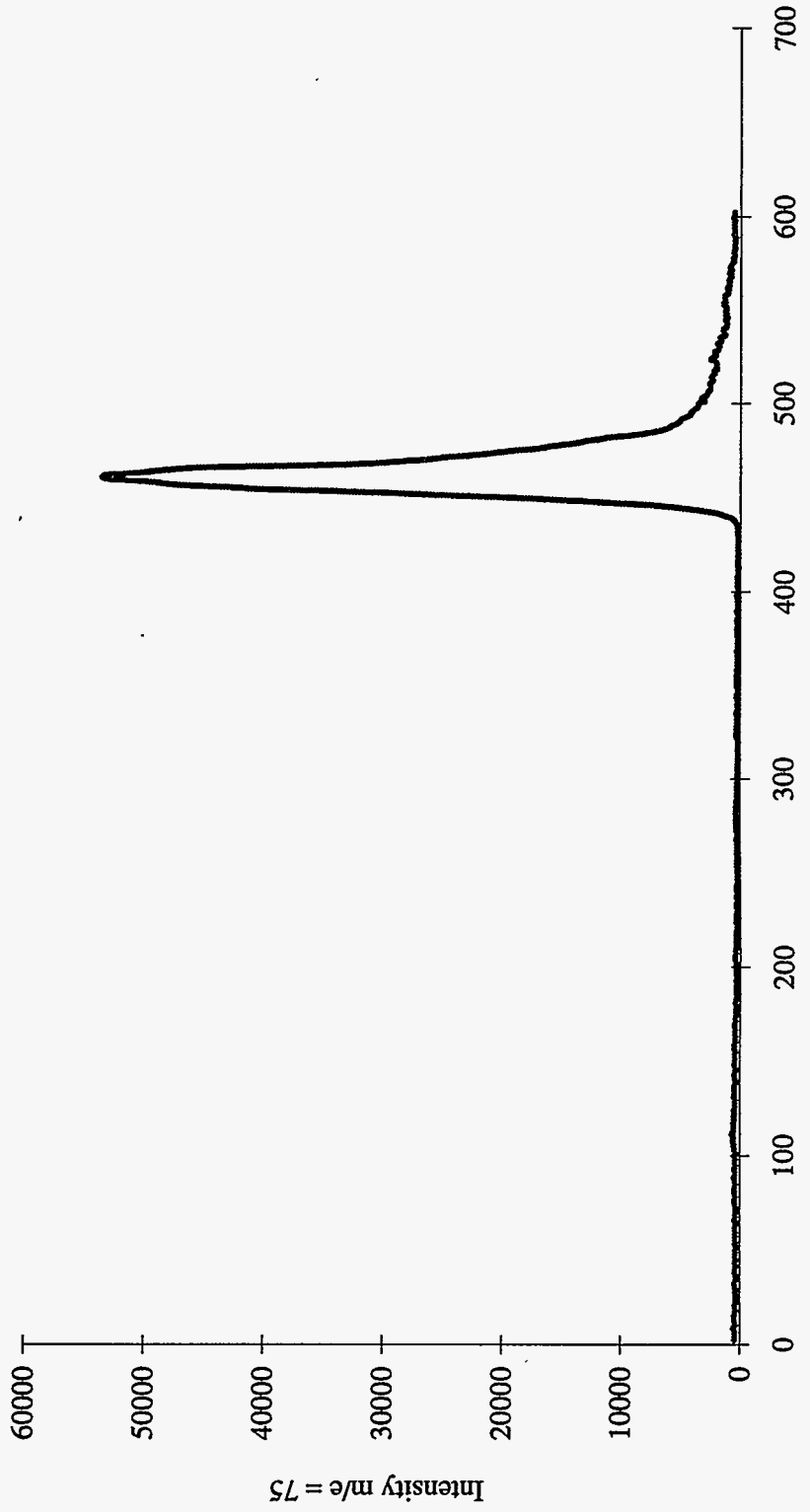


Fig. 6. Chromatogram of a CVAA-Spiked Soil Extract

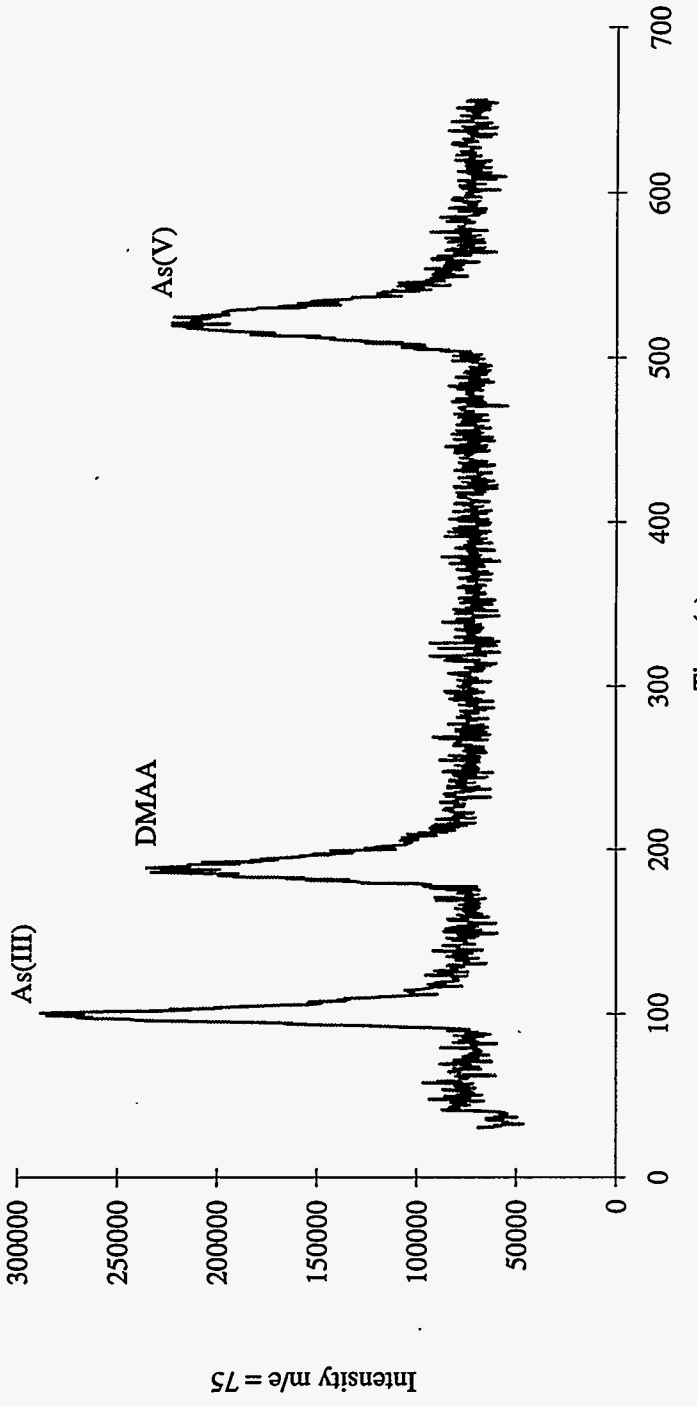


Fig. 7. Chromatogram of 1 µL of a Standard Containing 1 ppb of Each As Species

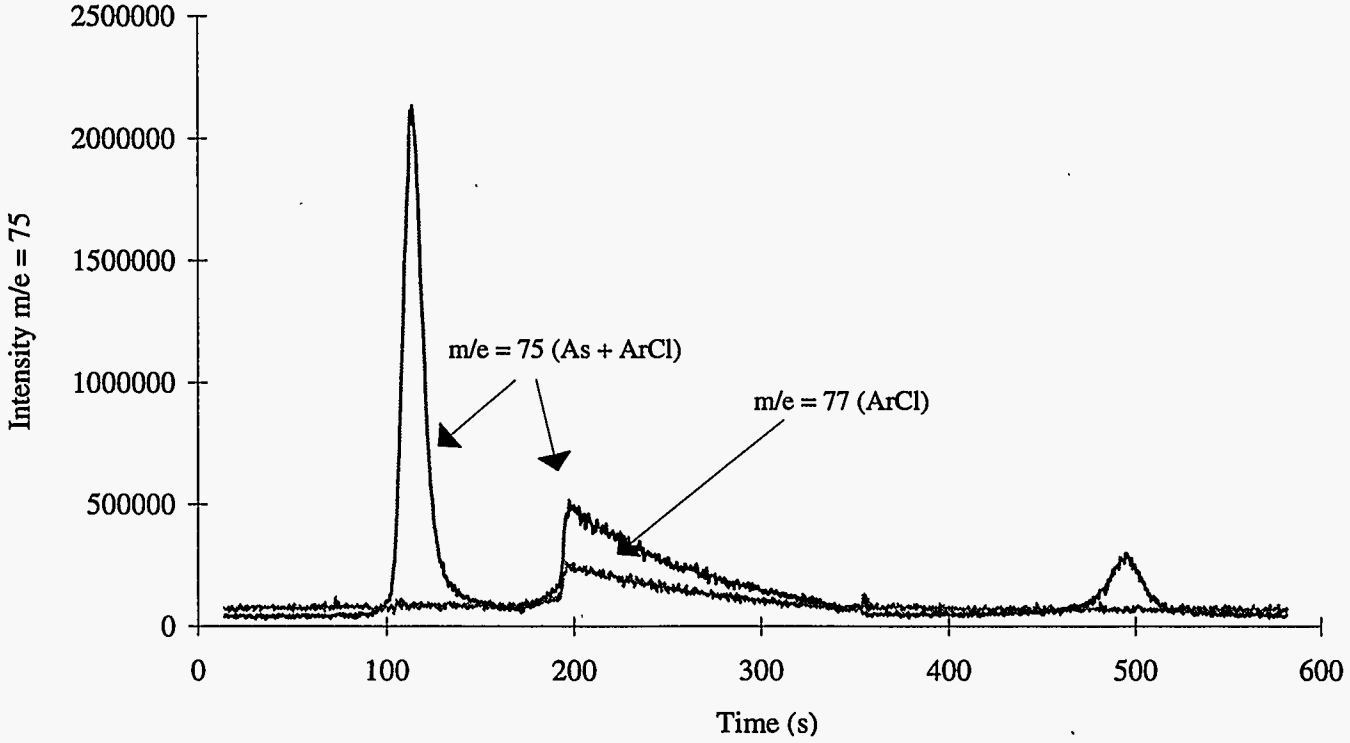


Fig. 8. Chromatogram of Contaminated Soil Showing Chloride Interference

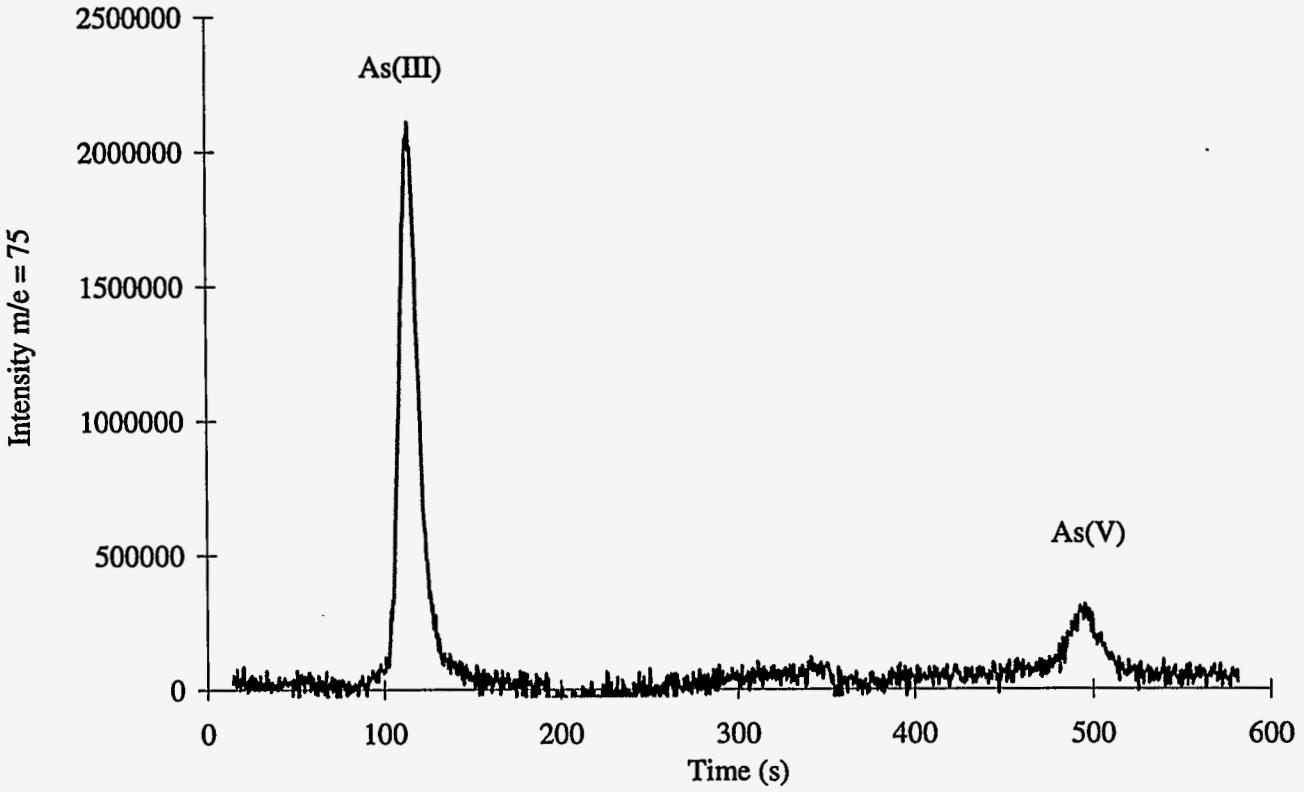


Fig. 9. Chromatogram of Contaminated Soil (Soil 2) Corrected for Chloride Interference

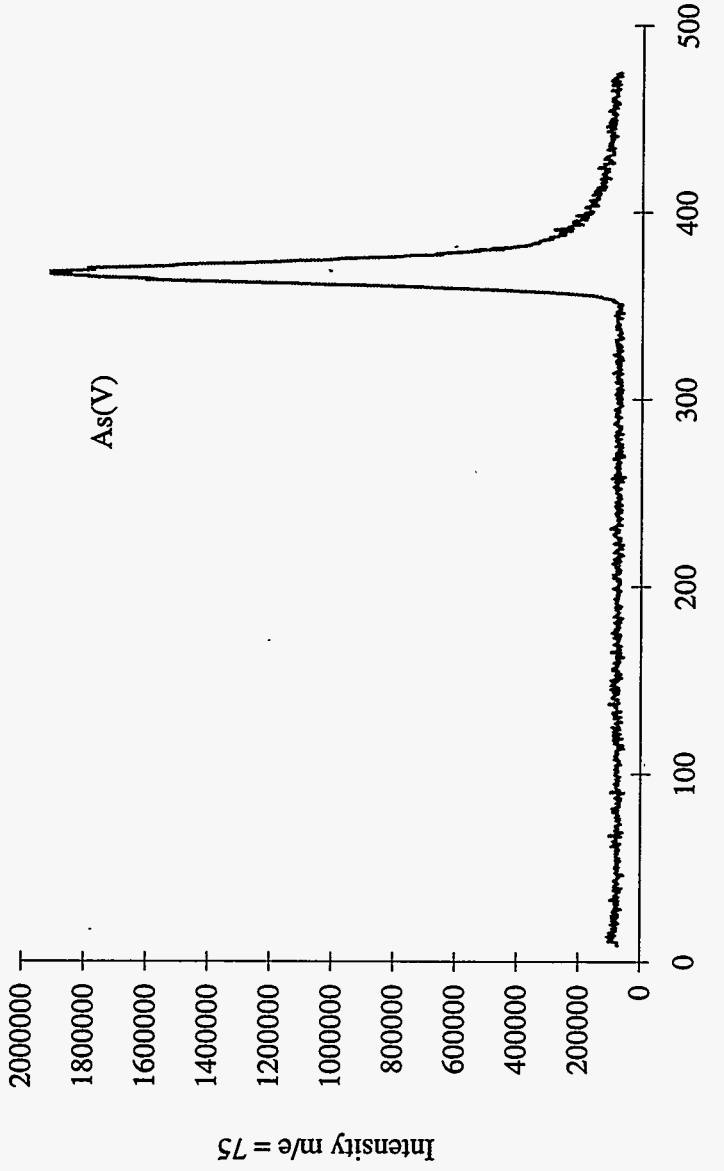


Fig. 10. Chromatogram of Contaminated Soil (Soil 1) before Treatment

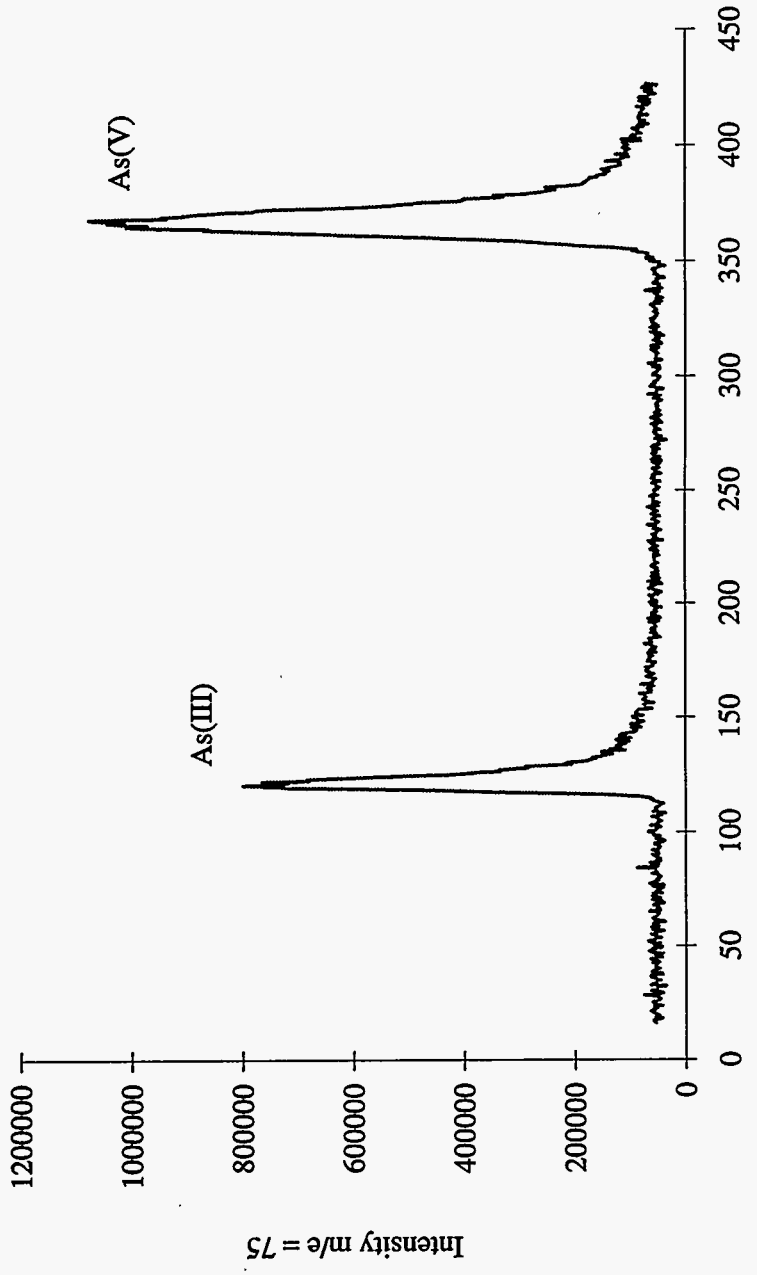


Fig. 11. Chromatogram of Contaminated Soil (Soil 1) after Treatment

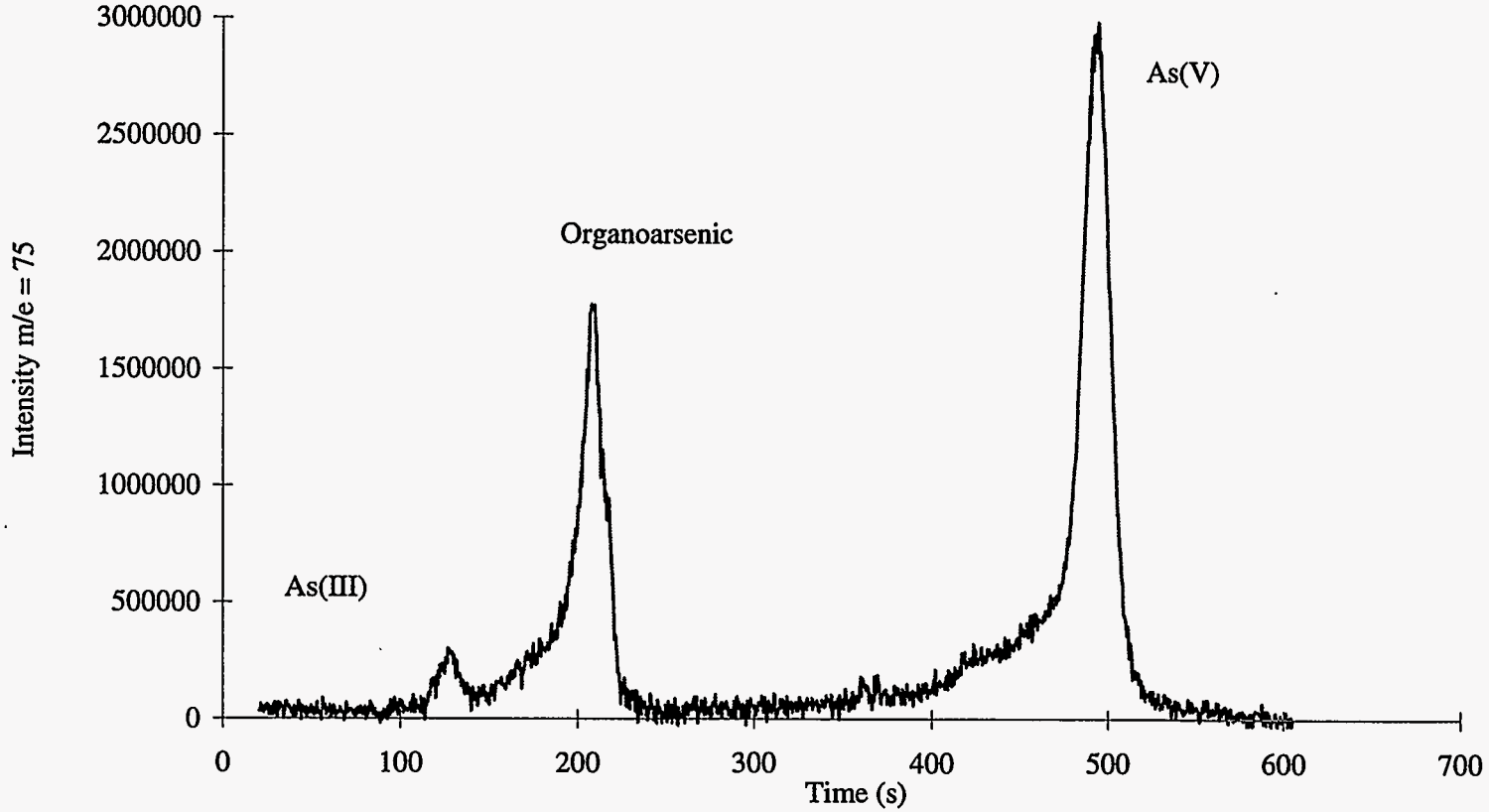


Fig. 12. Chromatogram of Contaminated Soil (Soil 2) Corrected for Chloride Interference

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