ARSENIC SPECIATION USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY-INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY*

by

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ABSTRACT

A method has been developed by Argonne National Laboratory to identify and quantify As(III), As(V), and organoarsenic compounds in environmental samples. The arsenic species were separated by reversed-phase, ion-pairing, HPLC using a microbore Inertsil-ODS™ column. Only 1 µL of sample was injected on the column, and the mobile phase flow rates were typically on the order of 40 µL min^{-1}. The HPLC mobile phase was a mixture of methanol and tetrabutylammonium hydroxide (TBAH), and the column effluent was introduced into an ICP-mass spectrometer using direct injection nebulization. Detection limits of less than 1 pg As (as injected on the column) were easily obtained for each arsenic species. The effect of changes in mobile phase composition and ICP-MS conditions will be described, as well as quality control measures, e.g., the use of surrogates, internal standards, and matrix spikes. Precision and accuracy information will be presented from the analysis of aqueous standards and soil extracts that were spiked with arsenic oxide [As(III)], sodium arsenate [As(V)], dimethylarsinic acid (DMAA), or chlorovinyl arsenious acid (CVAA). We believe that these data demonstrate the utility of this technique for the sensitive determination of arsenic species present in water or soil.

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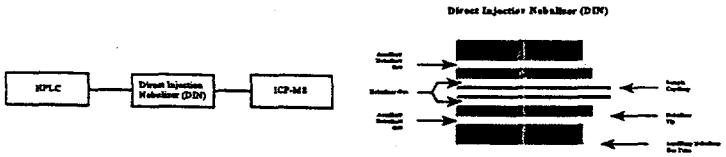
INSTRUMENTATION

Separation (HPLC)

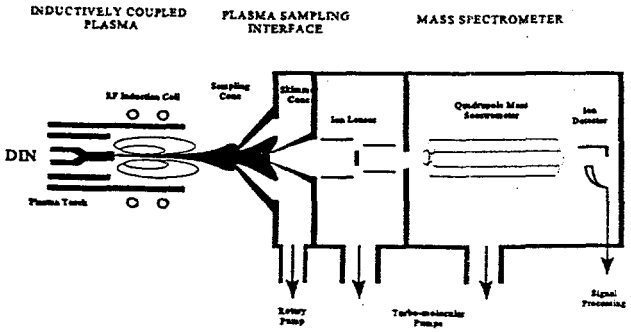
Column:	10 cm microbore Inertsil-ODS™
Pump/valves:	CETAC
Mobile phase:	tetrabutyl ammonium hydroxide (TBAH)
Operating Conditions:	
Flow rate:	40-50 µL/min
Injection volume:	1 µL
Masses monitored:	75,77
Points per second:	2 per mass

Detector: VG Plasma Quad Inductively Coupled Plasma - Mass Spectrometer (ICP-MS)

Direct Injection Nebulizer (DIN): CETAC



ICP-MS SCHEMATIC



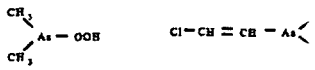
RESULTS AND DISCUSSION

Choice of Mobile Phase

0.005M TBAH in 5% methanol with the pH adjusted to 6, was used as a mobile phase for this sep Heptyltriethyl ammonium phosphate (HTAP) in 5% methanol was also used with almost identical re used because HTAP formed phosphate deposits on the DIN tip, increasing long term signal drift.

Separation of As Species

As(III) and As(V), present as arsenic oxide and sodium arsenate dissolved in water, were well separated in the chromatograms (Figure 1). The organic arsenic species, DMAA and CVAA were not separated under these conditions (Figure 2).



DMAA CVAA

Stability of As Species

The stability of arsenic species in standards and samples under normal conditions is of concern. Under t of operation, no degradation of standards was observed. The addition of standards to analytical samp result in the conversion of arsenic species. Figure 3 shows the partial conversion of As(III) to As(V). Th not observed when As(III) was added to sea sand. Figure 4 shows the complete conversion of CV unknown arsenic species. The same conversion occurred when CVAA was deposited on sea sand. The in Figure 4 also contained a spike of As(V) to show relative retention time to the unknown species.

Reproducibility

The following data shows results from a series of replicate runs of a 100ppb standard. Based on this table an RSD of less than 10% is expected for this measurement. However, periodic deterioration of the reproducibility was observed. During this time, RSDs ranged from 10 to 30%. Use of an internal standard kept the RSD less than 10% for a 50ppb standard. The units of the replicate measurements are counts at m/e = 75.

	As(III)	DMAA	
Replicate #1	2.27e+08	2.13e+08	1.
Replicate #2	2.13e+08	2.07e+08	1
Replicate #3	2.24e+08	2.18e+08	2
Replicate #4	2.20e+08	2.29e+08	2
Replicate #5	2.44e+08	2.16e+08	2
Replicate #6	2.10e+08	2.18e+08	2
Replicate #7	2.30e+08	2.27e+08	1.
Average	2.24e+08	2.18e+08	1
Standard Deviation	1.14e+07	7.85e+06	1
RSD	5.11%	3.60%	6

Estimated Detection Limits

Detection limits were estimated using a standard which contained 1 pg (1µL of 1ppb) species. Figure 5 shows the results from this standard. The detection limit is estimated from the peak he times the standard deviation of the noise (baseline).

Detection Limit = 0.1 pg

Correction for Chloride Interferences

In the presence of high levels of chloride, an interference for arsenic from ArCl can be p present at mass 75). This interference can be corrected by measuring the amount of ArCl at mass 7 chloride ions (35 and 37) is 3:1, as such, subtracting three times the mass 77 peak from the mass 75 peak the chloride interference. Figures 6 and 7 show the effectiveness of this correction.

RMANCE LIQUID CHROMATOGRAPHY - INDUCTIVELY COUPLED
S SPECTROMETRY (HPLC-ICP-MS)*

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RESULTS AND DISCUSSION

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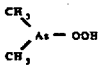
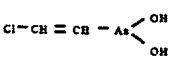


DMAA



CVAA

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(III) was added to sea sand. Figure 4 shows the complete conversion of CVAA on soil to an
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ed a spike of As(V) to show relative retention time to the unknown species.

	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	7.85e+06	1.20e+07
RSD	5.11%	3.60%	6.20%

shows results
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Based on this
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was observed.
RSDs ranged
of an internal
SD less than
andard. The
measurements
5.

imits
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iation of the noise (baseline).

Detection Limit = 0.1 pg

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ce. Figures 6 and 7 show the effectiveness of this correction.

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.

	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	0.9999
Range (ppb)	0-500	0-1000	0-500	0-1000	0-500	0-1000	0-500	0-500	0-500

Quality Assurance / Quality Control

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

Calibration. Calibration is performed by taking three replicates of a 100ppb standard. The 100ppb standard should contain 100ppb of each arsenic species of interest.

Check Standard. A 100ppb check standard containing each of the species of interest shall be analyzed every 5 samples and after the last sample. If the results are outside ±20%, then the problem shall 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 sample rerun.

Laboratory Duplicate. A sample should be periodically run in duplicate to assure the reproducibility of the measurement.

Surrogate, matrix spike. A surrogate or matrix spike should be used when extractions are required. They can also be used to estimate matrix effects.

Soil Sample Results

This method is being developed to determine the quantity and form of arsenic in soil, before and after treating. Figure 8 shows the results of a contaminated soil, prior to treatment. The arsenic is all in the form of As(V). After treatment, Figure 9, the sample is in the form of both As(III) and As(V). A contaminated soil from another location is shown in Figure 10. This plot has been corrected for chloride interference and shows As(III), As(V), and organoarsenic species. After treatment (Figure 7) the organic arsenic is not present, As(V) has been reduced, and As(III) is increased.

CONCLUSIONS

The work presented here shows an instrumental method for the identification of As(III), As(V), and organoarsenic compounds. The method was specifically designed for arsenic speciation in soil, but the method is directly applicable to water samples. The method could also be readily adapted to other metals, such as, mercury, selenium, chromium, tin, and lead.

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 unknown compound, generated from the conversion of CVAA was also measured and resolved from As(III), DMAA, and As(V). The separation of other organoarsenic compounds may require additional chromatographic development.

Results were demonstrated to be reproducible within 10%. However, use of an internal standard is essential because of the possible deterioration of instrument reproducibility. The estimated detection limit is 0.1pg or 0.1ppb for a 1µL injection. The presence of chloride in a sample can produce an interference on arsenic. Monitoring mass 77 allows correction of the chloride interference. The method is linear up to 500ppb. Samples which exceed this concentration should be diluted and rerun. Quality control samples are effective in measuring the performance of the instrument. Internal standards and check standards are particularly useful in measuring and correcting for instrument drift. One problem with internal standards is to find one that does not interfere with arsenic species present in the sample, yet gives a good peak under current chromatographic conditions.

Results were obtained using this method for contaminated and treated soil samples. Using preliminary results from these measurements, we have learned the effect of the treatment on the form of the arsenic, that certain arsenic compounds are not stable in some soil samples, and that some soils were high in chlorides both before and after treatment.

Acknowledgements

The authors would like to thank Jack O'Neill and Linda Shem for their contributions to this work.

Figure 1 - Separation of As Species

100pg As for each species

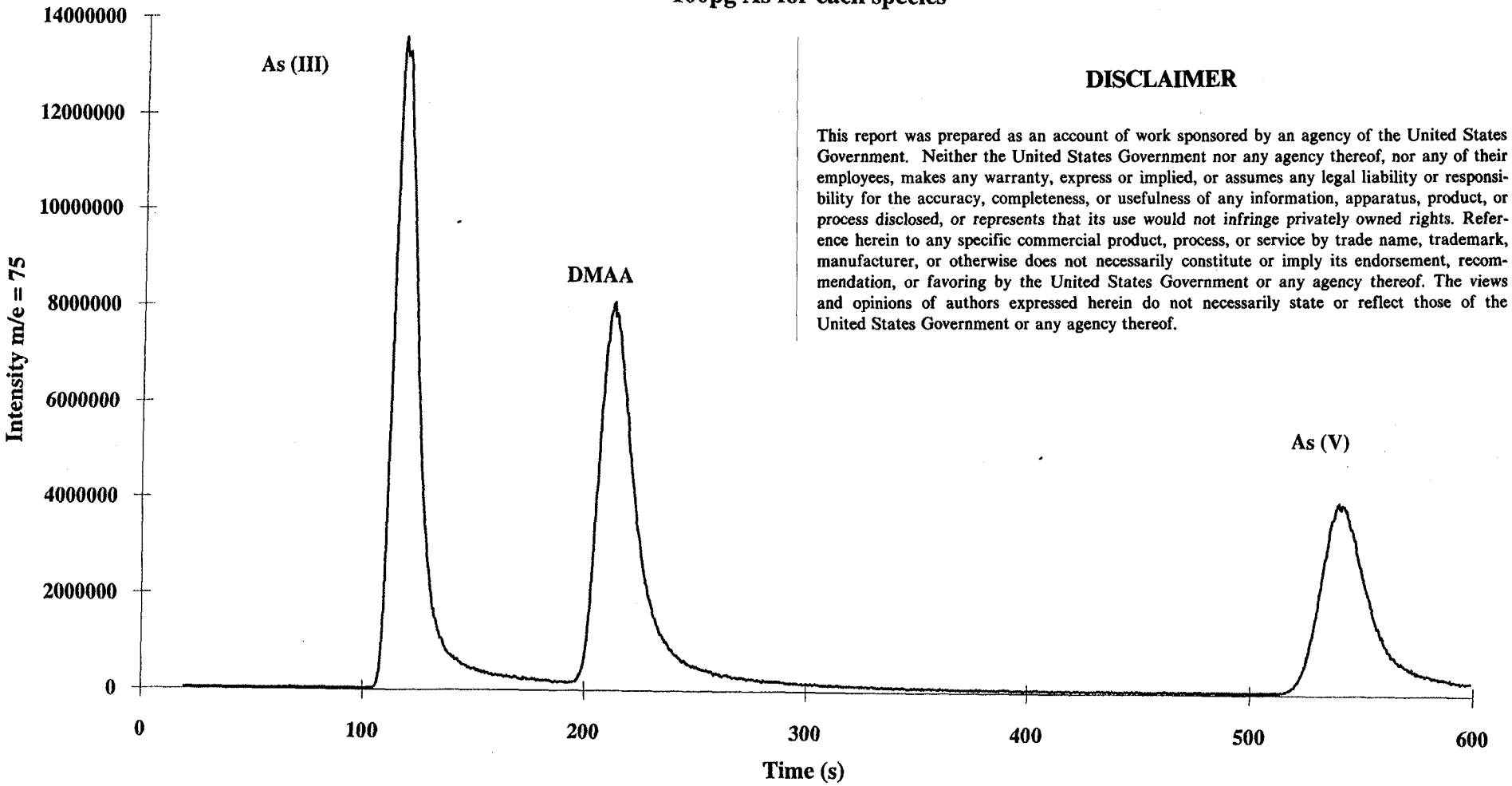

Figure 2 - Separation of CVAA and DMAA

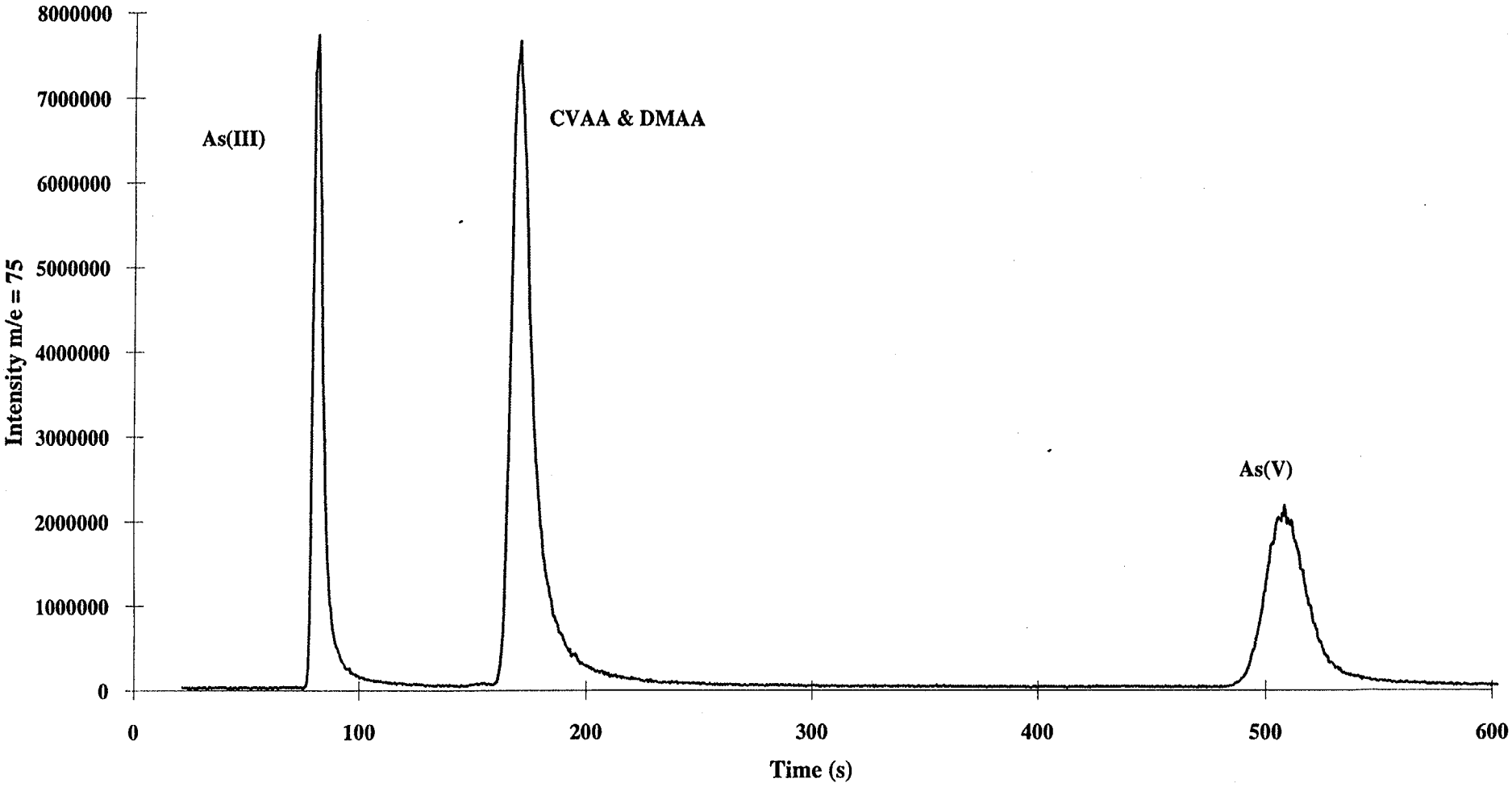

Figure 3 - Conversion of As(III) to As(V) in Soil

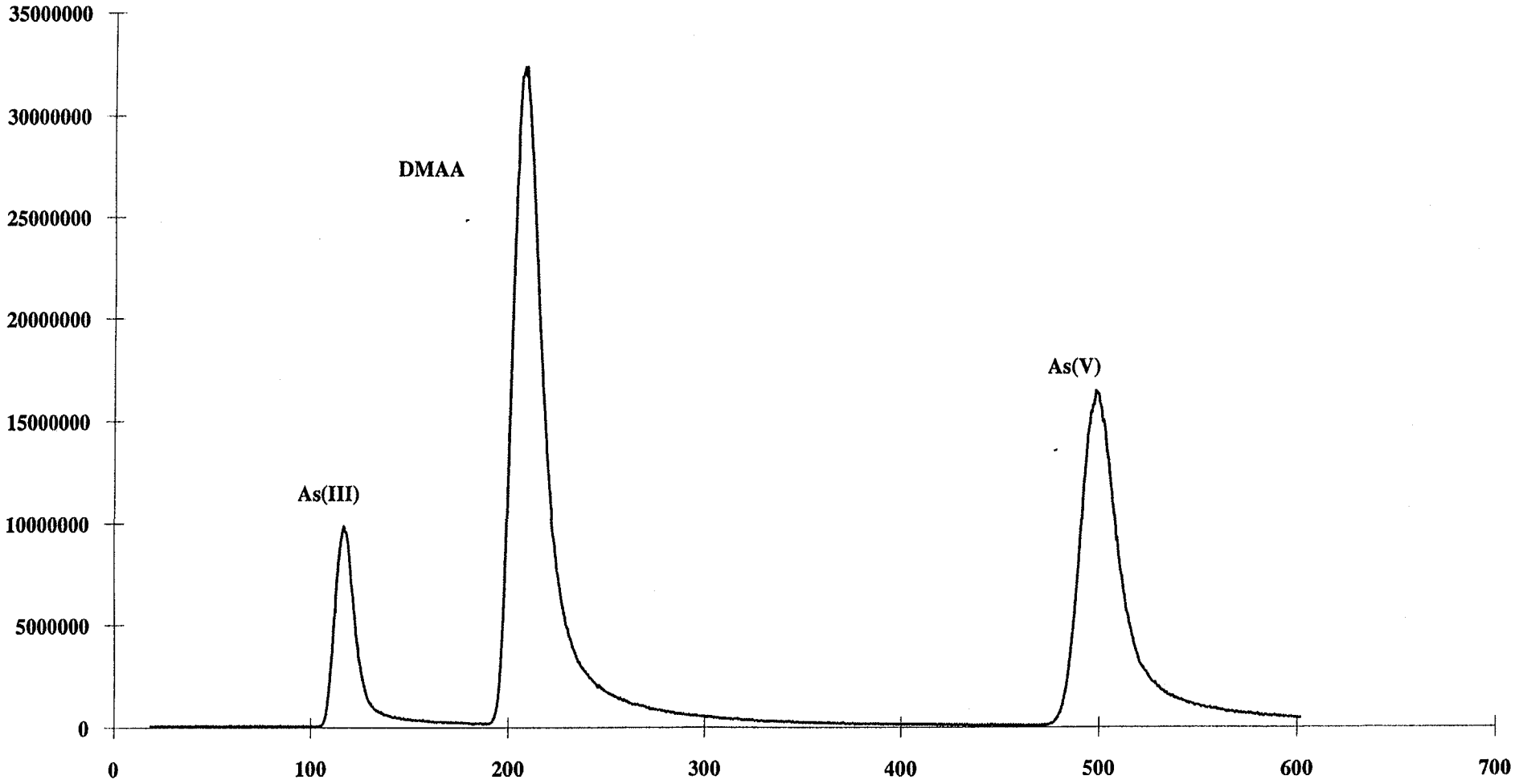

Figure 4 - CVAA Conversion When Dried

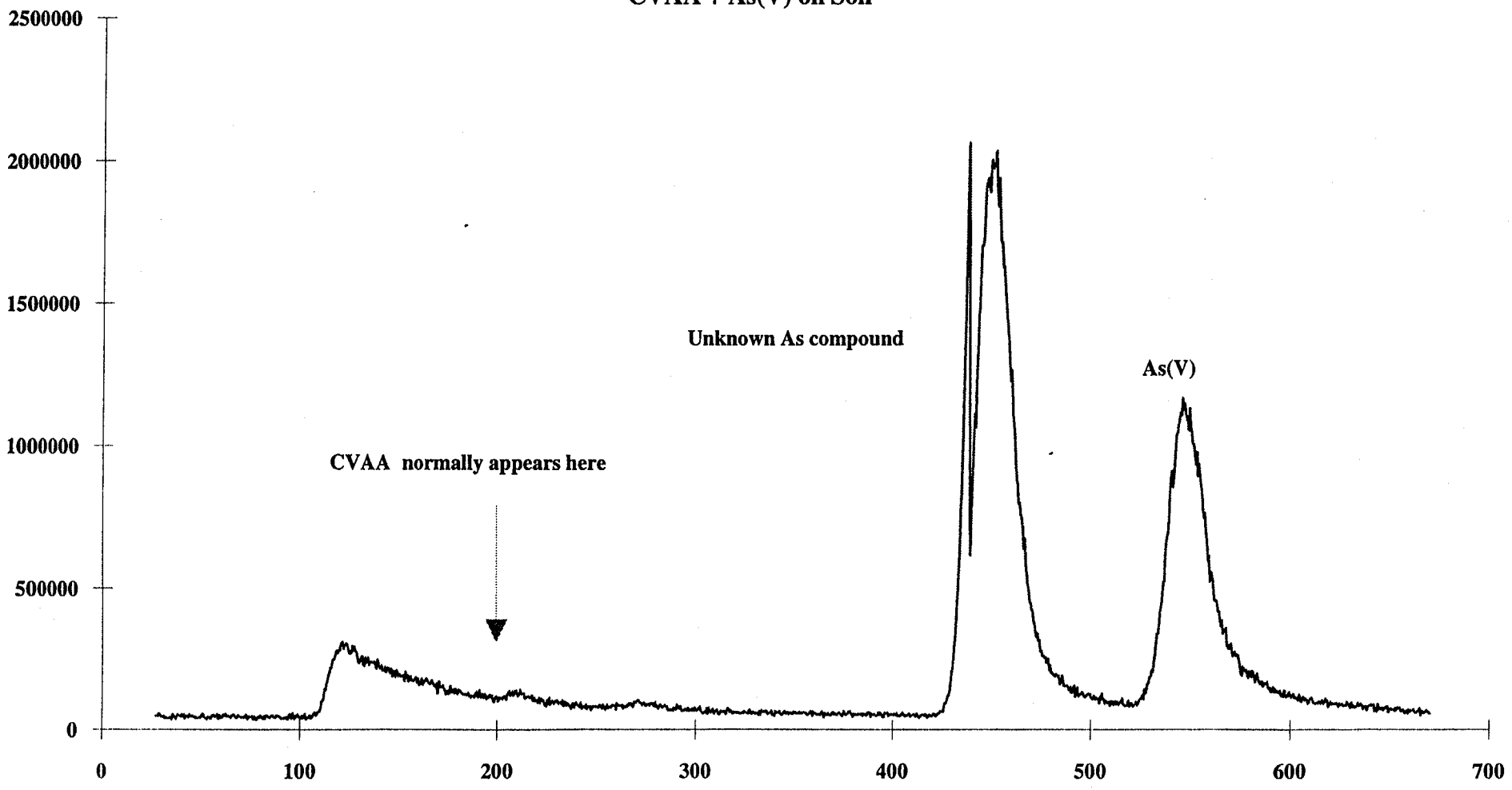

Figure 5 - 1 pg (ppb) of each As species

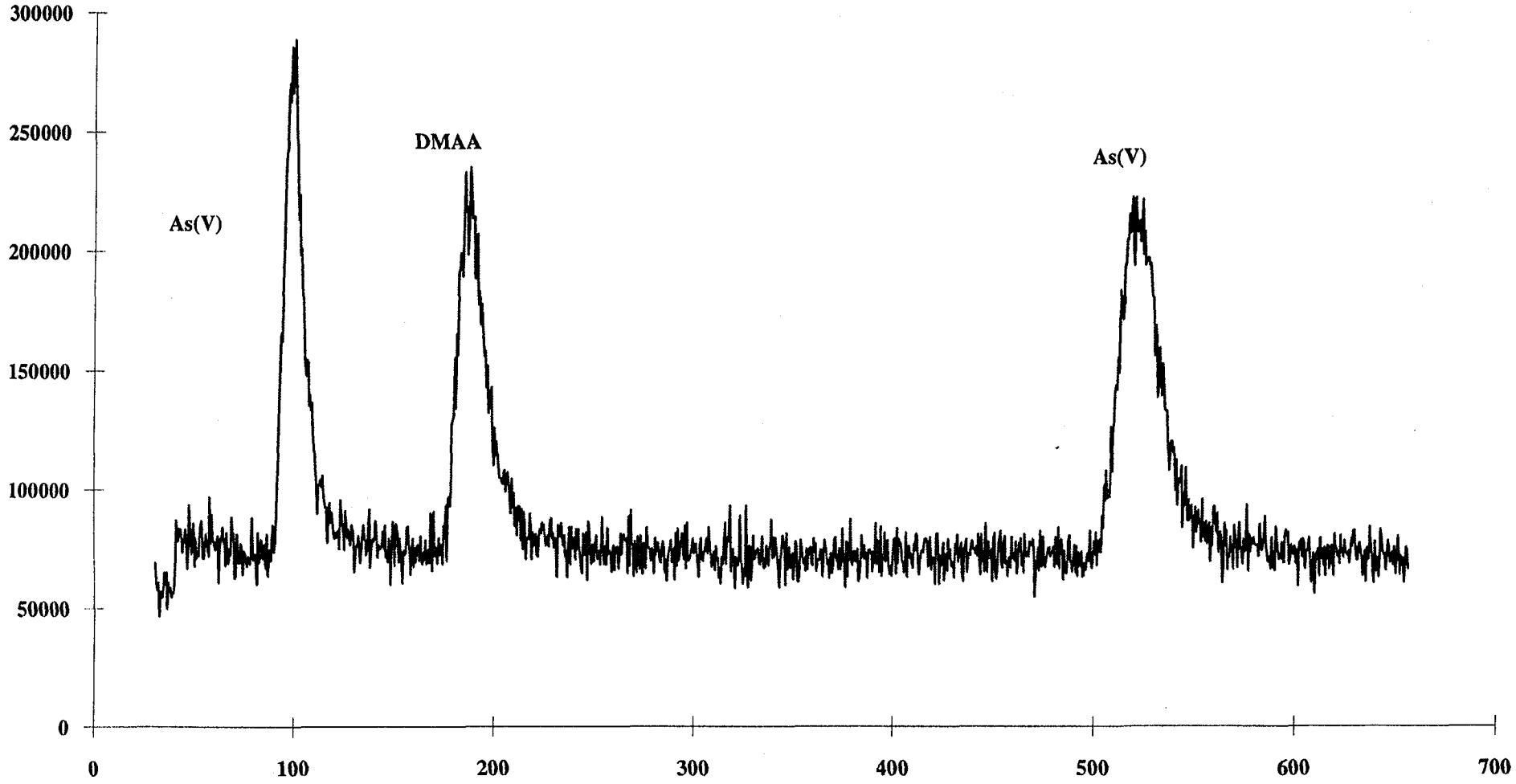

Figure 6 - Contaminated Soil B

TREATED (with chloride interference)

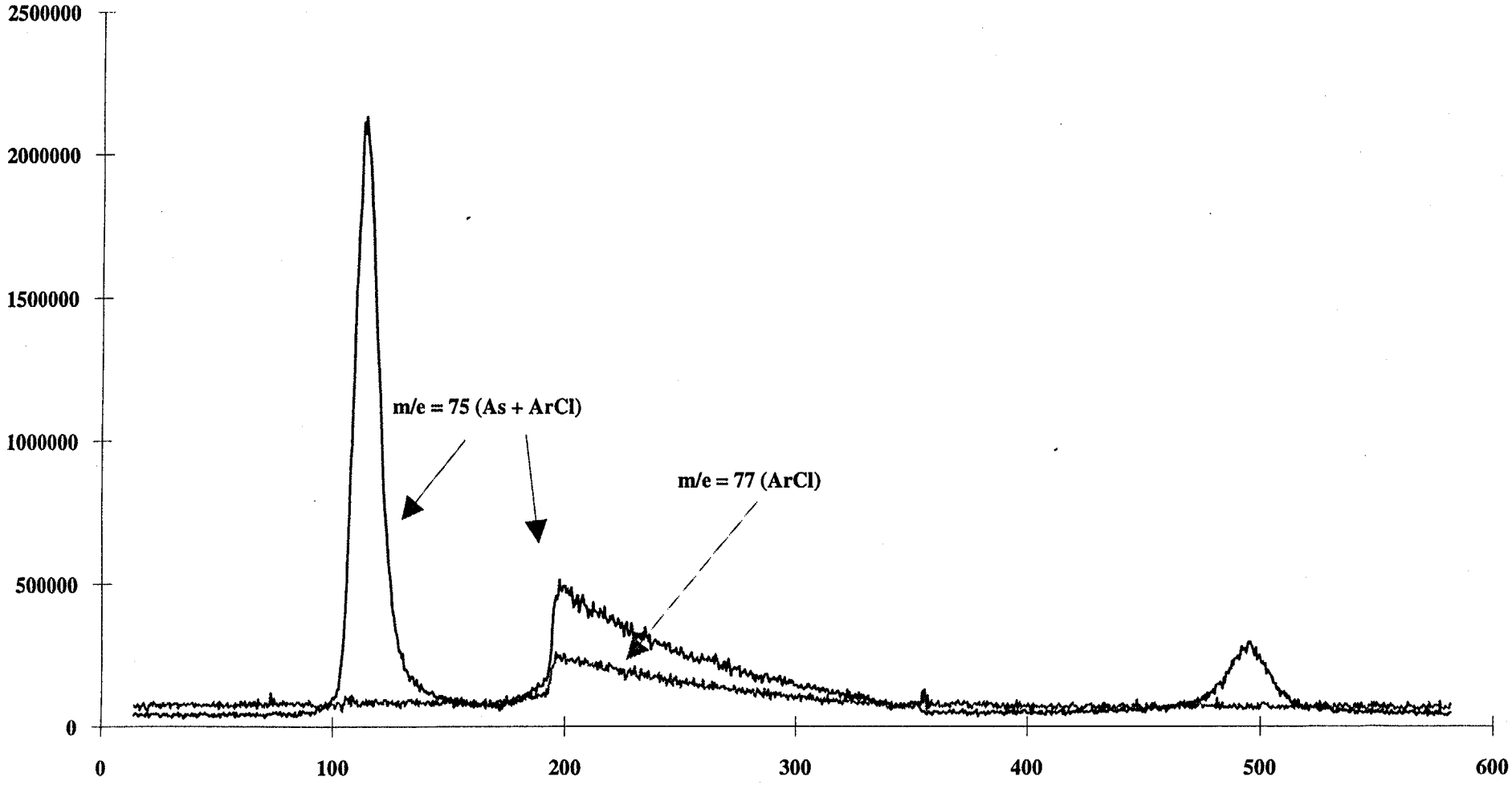

Figure 7 - Contaminated Soil B

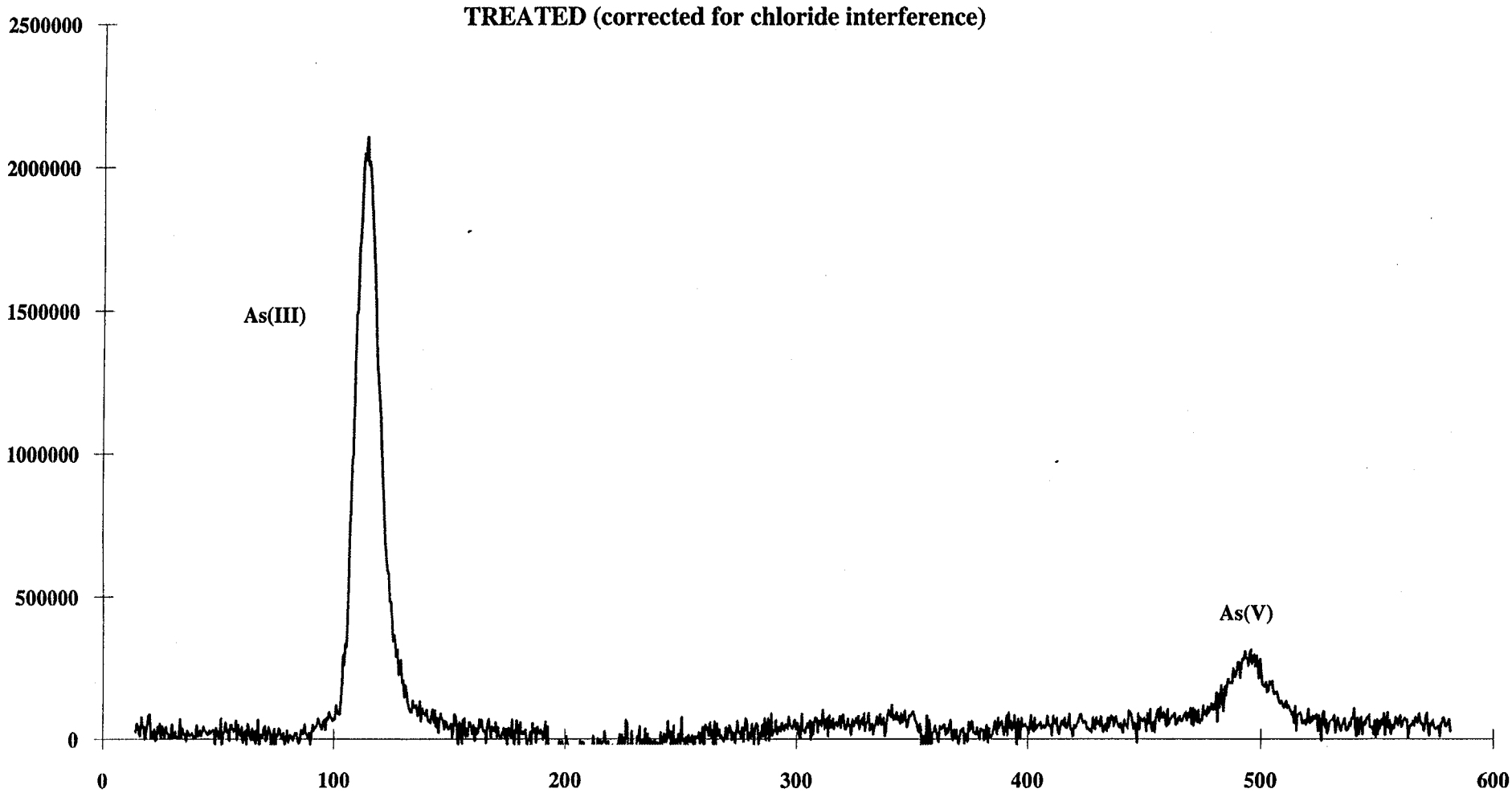

Figure 8 - Contaminated Soil A

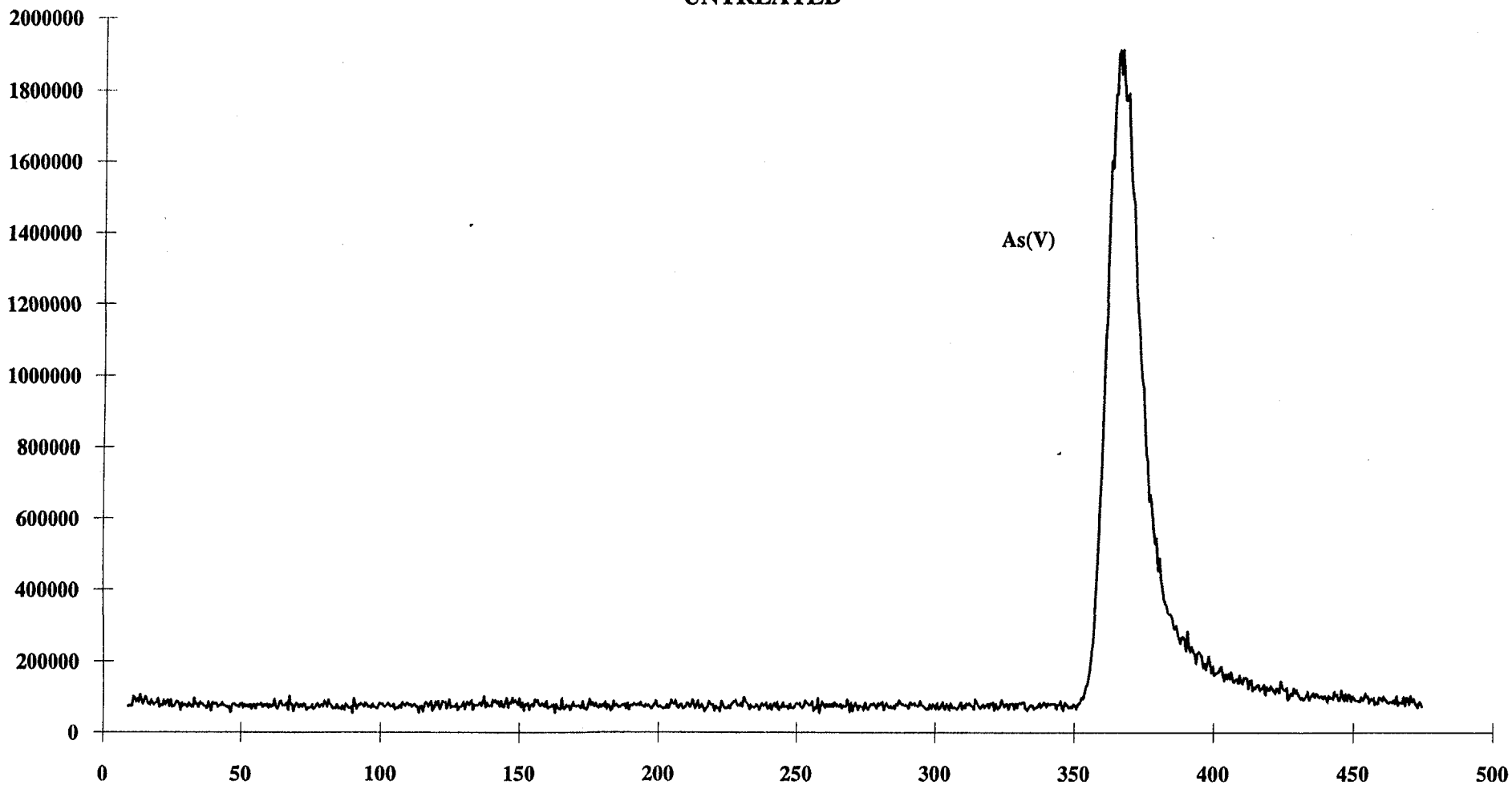

Figure 9 - Contaminated Soil A

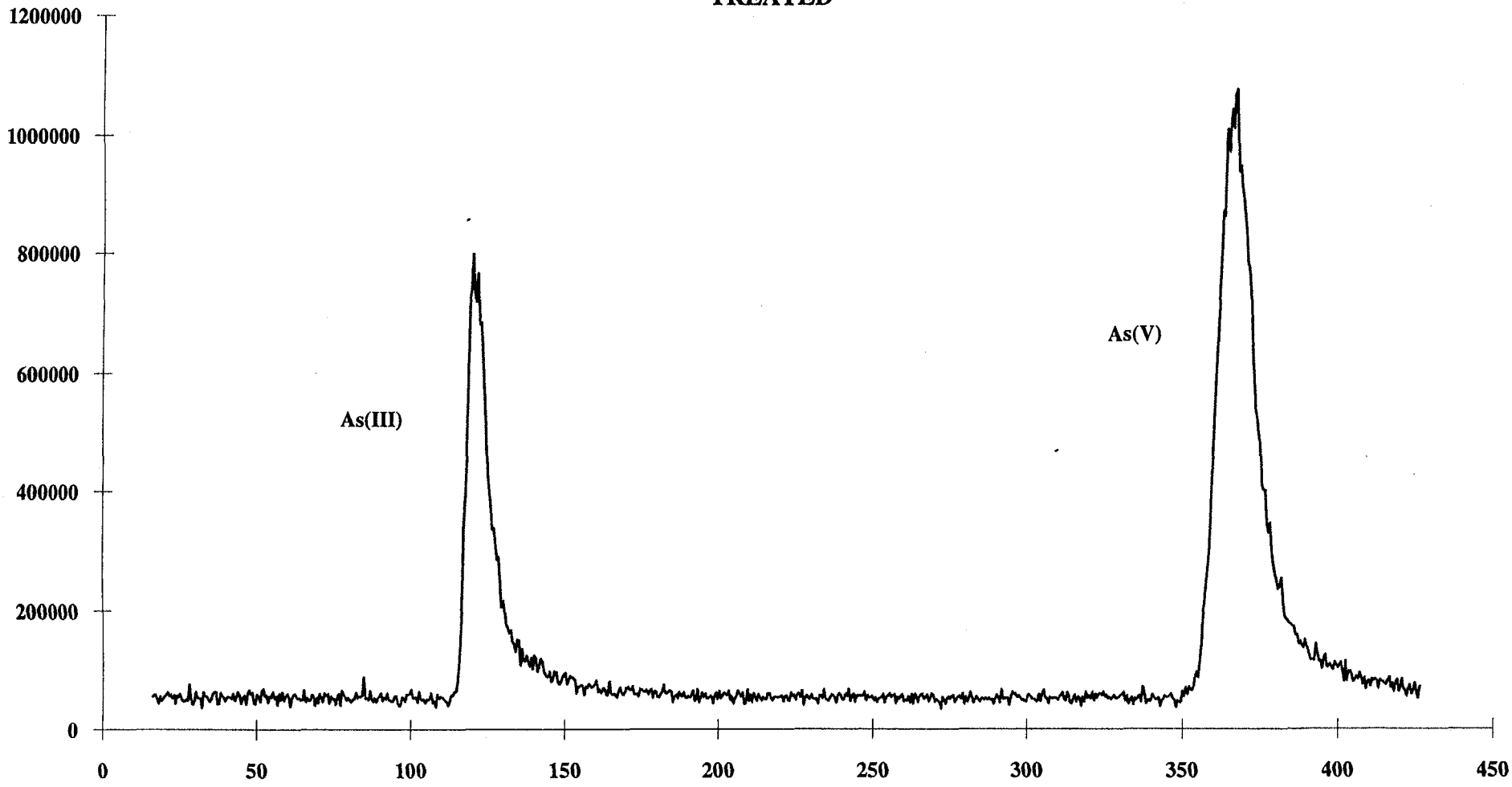

Figure 10 - Contaminated Soil B