ANL/CMT-ACL/CP--87198
CONF-951164--1

DETECTING AND QUANTIFYING LEWISITE DEGRADATION PRODUCTS IN ENVIRONMENTAL SAMPLES USING ARSENIC SPECIATION*

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FEB 16 1996
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to be published in the
Proceedings of the 1995 U.S. Army Edgewood Research, Development
and Engineering Center
Scientific Conference on Chemical and Biological Defense Research
Aberdeen Proving Ground, MD
November 14-17, 1995

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* Work supported by the U.S. Army and the U.S. Department of Energy under Contract W-31-109-ENG-38.

DETECTING AND QUANTIFYING LEWISITE DEGRADATION PRODUCTS IN ENVIRONMENTAL SAMPLES USING ARSENIC SPECIATION

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ABSTRACT

A high performance liquid chromatography - inductively coupled plasma - mass spectrometry (HPLC-ICP-MS) method has been developed at Argonne National Laboratory to identify and quantify lewisite degradation products in soil and water samples. This method distinguishes among As(III), As(V), 2-chlorovinyl arsenous acid (CVAA), and other lewisite degradation products. Soil samples were analyzed to support the thermal desorption treatability studies for agents and pesticides being conducted for Rocky Mountain Arsenal. These data demonstrate that this technique is useful for the sensitive determination of lewisite degradation products. It is applicable to the analyzing a variety of materials.

INTRODUCTION

The measurement of lewisite degradation products in environmental samples is important to identify contamination areas, to determine the degradation products present, and to aid in the treatment of contaminated materials[1,2]. Typically, lewisite degradation analysis has been performed using a derivitization process followed by measurement using gas chromatography (GC) with one of the following: flame ionization detector (FID), photo ionization detector (PID), flame photometric detector (FPD), or a mass spectrometer (MS)[3]. These methods may have interferences in the derivitization process or from other organic compounds with similar retention times to the lewisite degradation products. Our method offers better detection limits than any of the GC methods, does not require the derivitization step and distinguishes the lewisite degradation products better.

The method uses inductively coupled plasma - mass spectrometry (ICP-MS) to detect the arsenic present in the sample. The arsenic species are separated using high performance liquid chromatography (HPLC). Interfacing the two creates an integrated HPLC-ICP-MS system that can identify not only lewisite degradation products, but other arsenic compounds as well. The method was developed previously to distinguish between organic and inorganic arsenic in soil[4]. The system can also be used to identify other metal species simultaneously.

INSTRUMENTATION

The arsenic species were separated using reversed phase, ion-pairing chromatography. The column (SGE, Inc.) was interfaced to the ICP-MS (Fisons Instruments) using a direct injection nebulizer (DIN) (CETAC, Inc), which operates with low flow rates, such as those used in the microbore HPLC column. The following specifications were used:

HPLC Column specifications

Column Length	10 cm
Column I.D.	1 mm
Packing	Inertsil ODS-2™ (C18)
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 parameters

Masses monitored	75 and 77
Collection rate	2 points per second per mass
Collection mode	Time resolved; peak hopping

RESULTS AND DISCUSSION

Identification of arsenic species. Dimethyl arsinic acid (DMAA), As(III), and As(V) standards are well separated as shown in Figure 1. The separation indicates that these species could be easily identified in an aqueous sample. Figures 2 and 3 show a CVAA and 2-clorovinylarsonic acid (CVAOA) standard in water. The CVAOA is an oxidized form of the CVAA and was prepared by adding hydrogen peroxide to the CVAA standard.

Degradation of lewisite from the soil and extraction procedure. Lewisite and its degradation products can be changed by the soil and by the extraction of the soil for analysis. A peak corresponding to CVAA is observed (Figure 4) when a soil containing CVAO is extracted. This is due to the hydrolysis of 2-chlorovinyl arsenous oxide (CVAO) during the extraction to form CVAA. When CVAA was spiked on the soil it is oxidized to form CVAOA and a peak corresponding to CVAOA was observed (Figure 5). This is consistent with the fact that the soil is oxidizing in character and previous results which showed the oxidation of As(III) to As(V)[1]. The examples in Figures 4 and 5 show how two separate lewisite degradation products could be easily identified in soil.

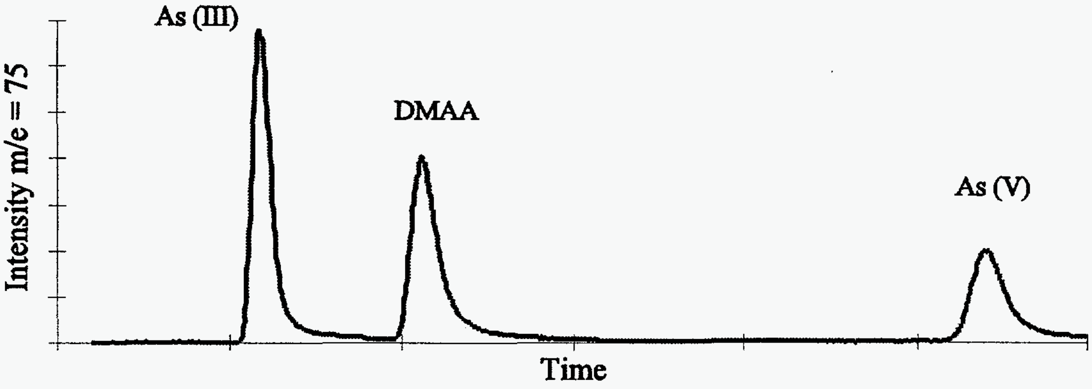

FIGURE 1. Aqueous standard containing 100 ppb As(III), DMAA, and As(V).

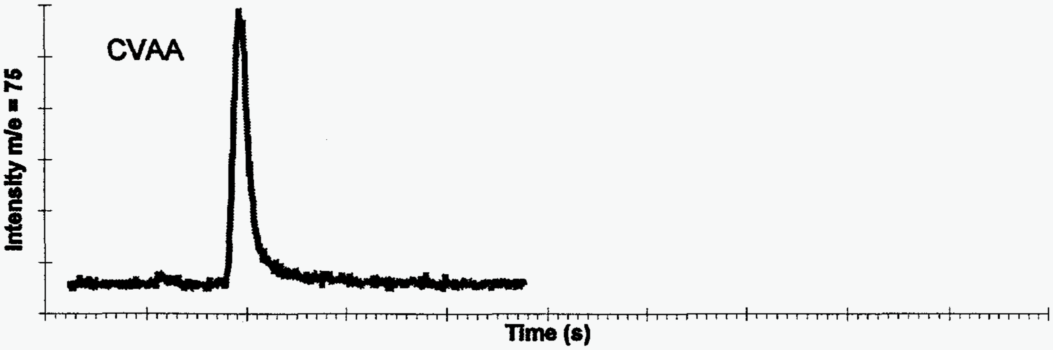

FIGURE 2. CVAA aqueous standard.

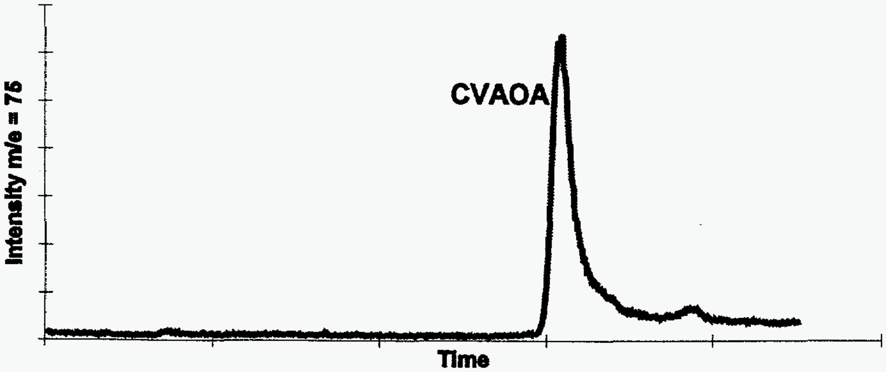

FIGURE 3. CVAOA aqueous standard.

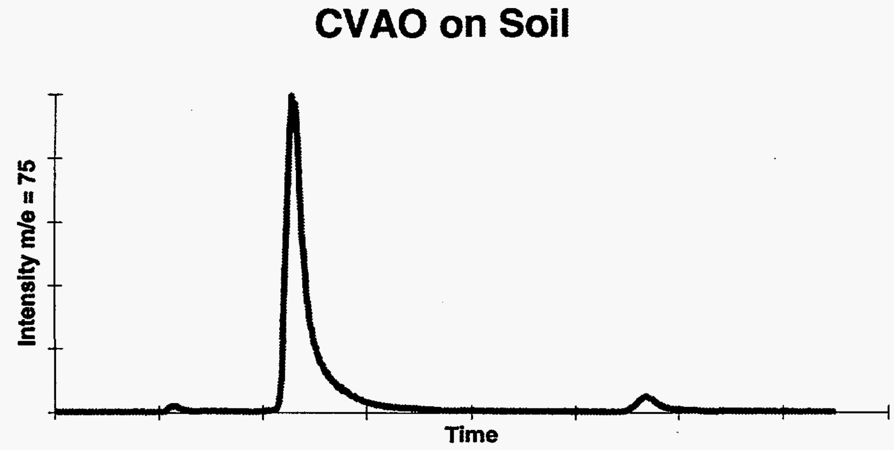

Figure 4. Extract from soil spiked with CVAO.

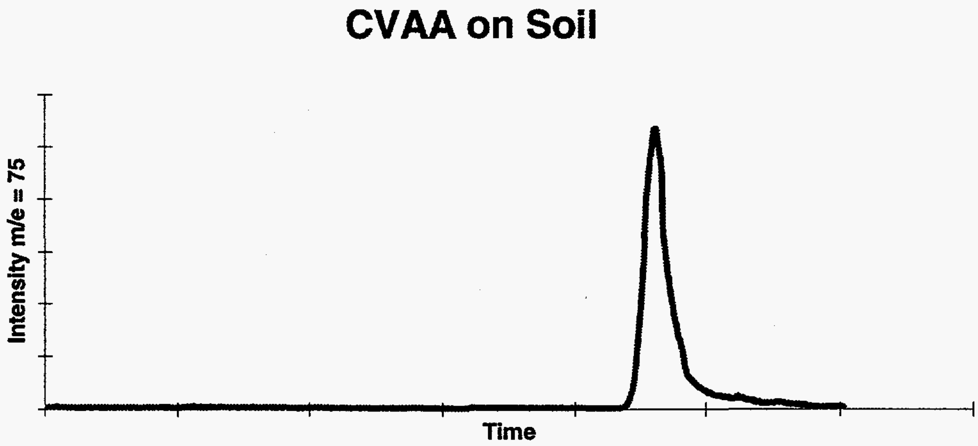

Figure 5. Extract from soil spiked with CVAA.

Thermal decomposition of CVAA. This method can also be used to monitor soil thermal treatment processes. Figure 5 shows a soil spiked with CVAA without thermal treatment. Figures 6, 7, and 8 show chromatograms of soil spiked with CVAA and heated to 200°C (400°F), 320°C (600°F), and 430°C (800°F), respectively. As shown in each of these figures, we can tell the final form of the arsenic at each stage in the treated soil, the temperature at which any of the organic arsenic species are destroyed, and the intermediate species that might be formed. This can be useful in determining how to best treat contaminated soils and whether any organic arsenic degradation products remain.

Quantitation. Potential quantitation procedures for this method involve running calibration standards, check standards, internal standards, duplicates, surrogates, and matrix spikes. Results without the internal standard varied as much as 40%. DMAA was used as an internal standard. With an internal standard, reproducibility is improved to less than 10% relative standard deviation (RSD). DMAA can potentially interfere with other organic arsenic compounds, such as CVAA, and better internal standards should be developed. A matrix spike and surrogate have not yet been implemented in this method.

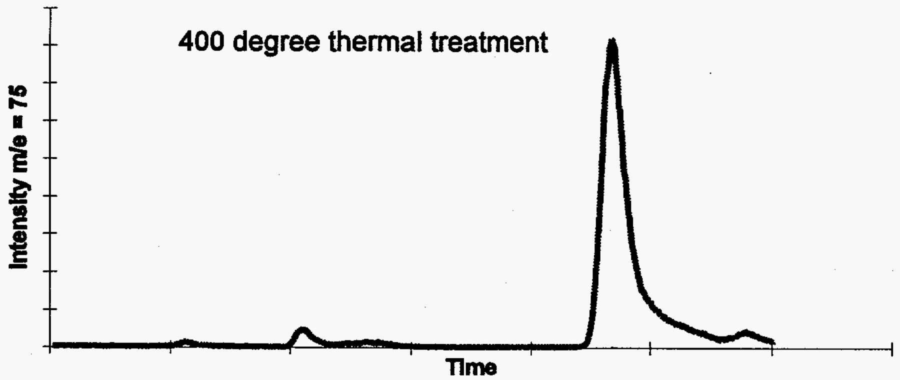

Figure 6. Extract from soil spiked with CVAA and heated to 200°C.

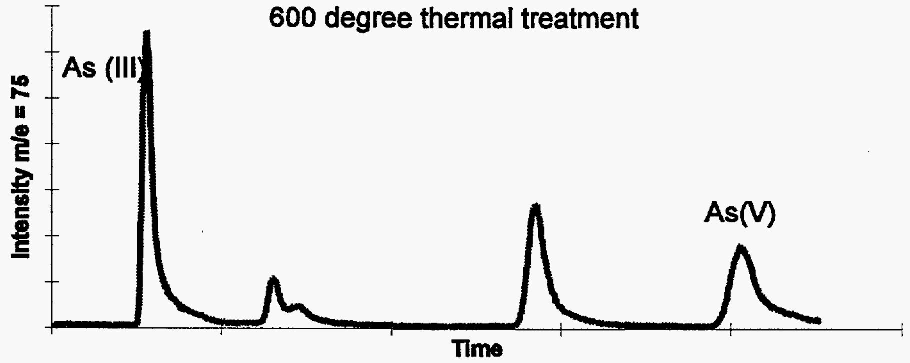

Figure 7. Extract from soil spiked with CVAA and heated to 320°C.

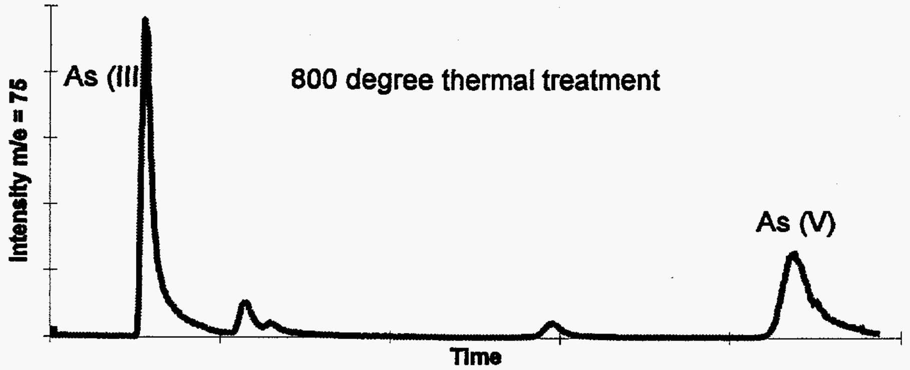

Figure 8. Extract from soil spiked with CVAA and heated to 430°C.

Figures of merit. The detection limit for this technique is 0.1 pg or 0.1 ppb of arsenic, which is equivalent to approximately 0.2 ppb CVAA. Figure 9 shows the resulting chromatogram from an arsenic standard containing 1 pg each of arsenic (III), arsenic (V), and DMAA. The estimated reproducibility, using a 50 ppb standard is 5% RSD using an internal standard. Similar reproducibility is possible without an internal standard, although periodic instrument drift can greatly increase the uncertainty of the measurement. The instrument is linear up to 500 ppb of arsenic with a correlation coefficient of 0.999.

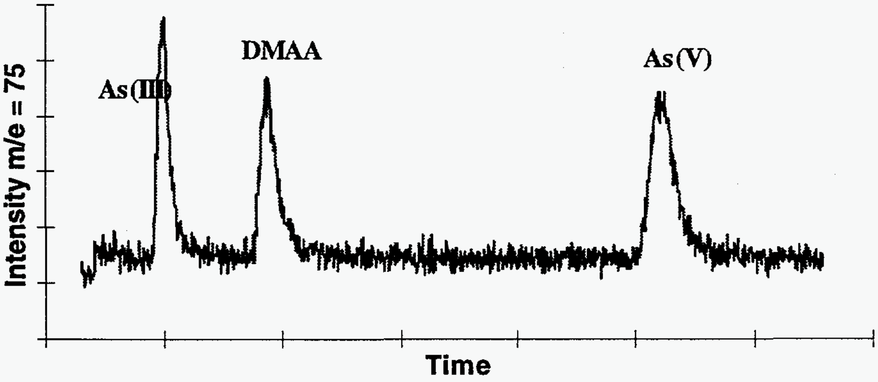

Figure 9. Arsenic species at concentrations near the detection limit (1 ppb each).

CONCLUSIONS

An HPLC-ICP-MS method has been developed for measuring lewisite degradation products in a variety of environmental samples. It allows us to detect trace levels (< 1 ppb) of As(III) and As(V), as well as lewisite degradation products and to distinguish among them. The method is relatively free of interferences, particularly because it does not require the derivatization step, as the GC method does. This method can also be used to speciate other metals simultaneously. Additional work is needed to develop matrix spikes, surrogates, and a better internal standard.

ACKNOWLEDGMENTS

This work was supported by the U. S. Army and the U. S. Department of Energy under Contract W-31-109-ENG-38.

REFERENCES

1. Shem, L.M., O'Neill, H.J., Bass, D.A., O'Reilly, D., Besmer, M., "Thermal Desorption Screening of Agent-Simulant-Spiked Soil from the Rocky Mountain Arsenal," The 1995 U.S. Army Edgewood Research, Development, and Engineering Center Scientific Conference on Chemical and Biological Defense Research, November 1995, Edgewood, MD.

2. Shem, L.M., O'Neill, H.J., Bass, D.A., O'Reilly, D., Besmer, M., "Rocky Mountain Arsenal Agent Treatability Study."

3. Albro, T.G., Lippert, J., "Use of the Atomic Emission Detector for Screening and Detection of Chemical Warfare Agents and their Breakdown Products," presented at the Scientific Conference on Chemical and Biological Defense Research, November 1994, Edgewood, MD.

4. Bass, D.A., Yaeger, J.S., Parish, K.J., Crain, J.S., Kiely, J.T., Gowdy, M.T., Mohrman, G.B., "Arsenic Speciation in Soil Using High Performance Liquid Chromatography - Inductively Coupled Plasma - Mass Spectrometry (HPLC-ICP-MS)," Argonne report to be published.

Detecting and Quantifying Lewisite Degradation Products in Environmental Samples Using Arsenic Speciation

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Rocky Mount

Measurement of Lewisite Degradation Products

- How do we perform the analyses
- What are the advantages of the method
- Results

GC Methods

- AED, MS, PID, FPD, HID
- DL from 1 to 200 pg
- TMS Derivatization
- Potential interferences
- High temperature separation

High Performance Liquid Chromatography - Inductively Coupled Plasma - Mass Spectrometery (HPLC-ICP-MS)

- HPLC - Separation of Arsenic Species
- ICP-MS - Detection of Arsenic

Method Features

- Solids or liquids
- Not a GC Method
- Low detection limits (<1pg)
- Distinguish CVAA, CVAOA
- Follow changes in As species
- Few interferences
- Low sample volume required
- General metal speciation capability

Method Features

- Solids or liquids
- Valid GC Method
- Low detection limits (<1pg)
- Distinguish between degradation products (e.g., CVAA, CVAOA)
- Follow changes in As species
- Few interferences
- Low sample volumes required

Instrument slides

Instrumentation

- 10cm microbore Inertsil-ODS column
  1 µL injection
  - 50 µL/min
- 0.005M TBAH / 5% methanol
- Direct injection nebulizer (DIN)
- ICP-MS
- Excel spreadsheet for data reduction

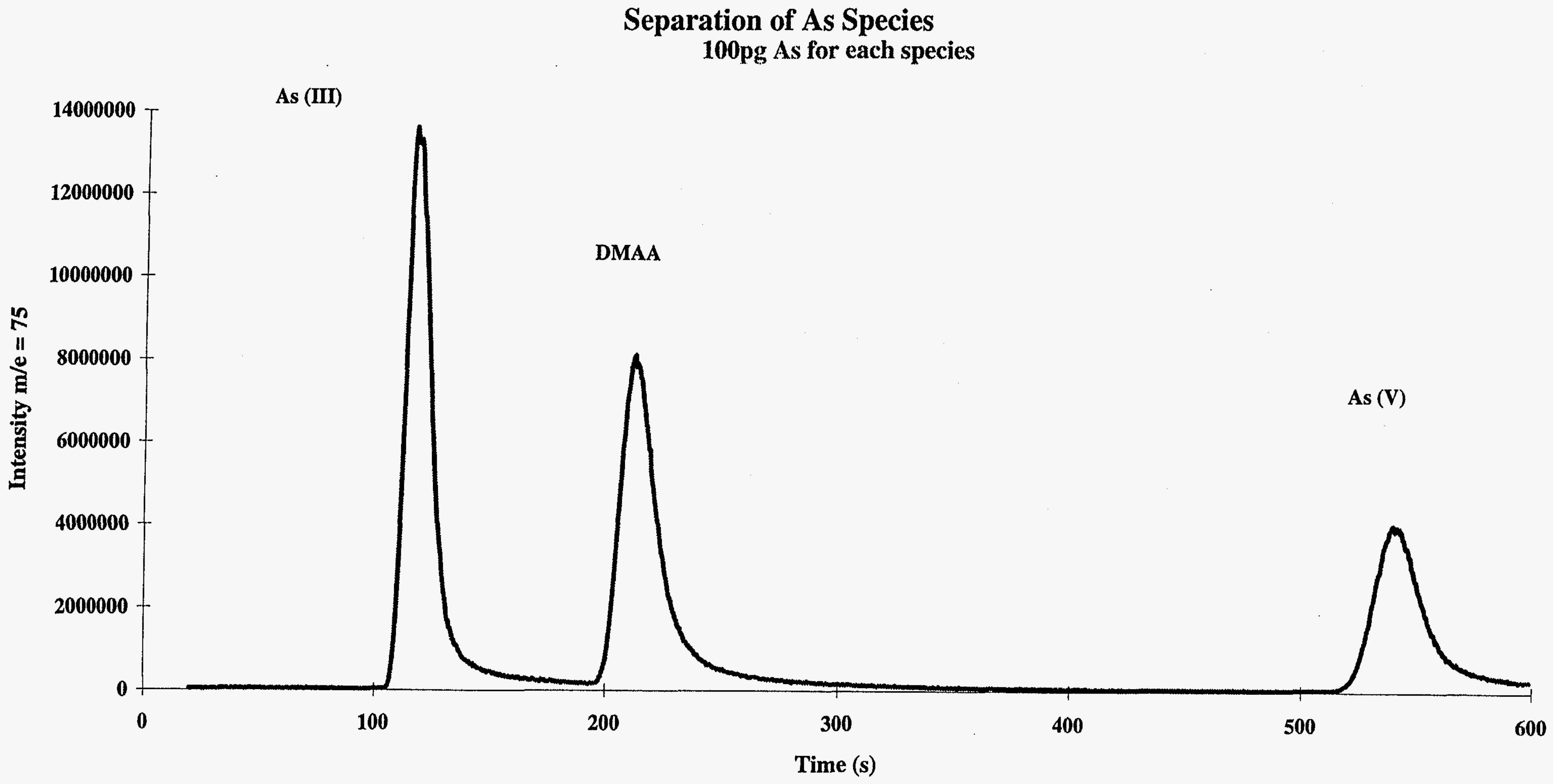
Analysis of solids and solutions

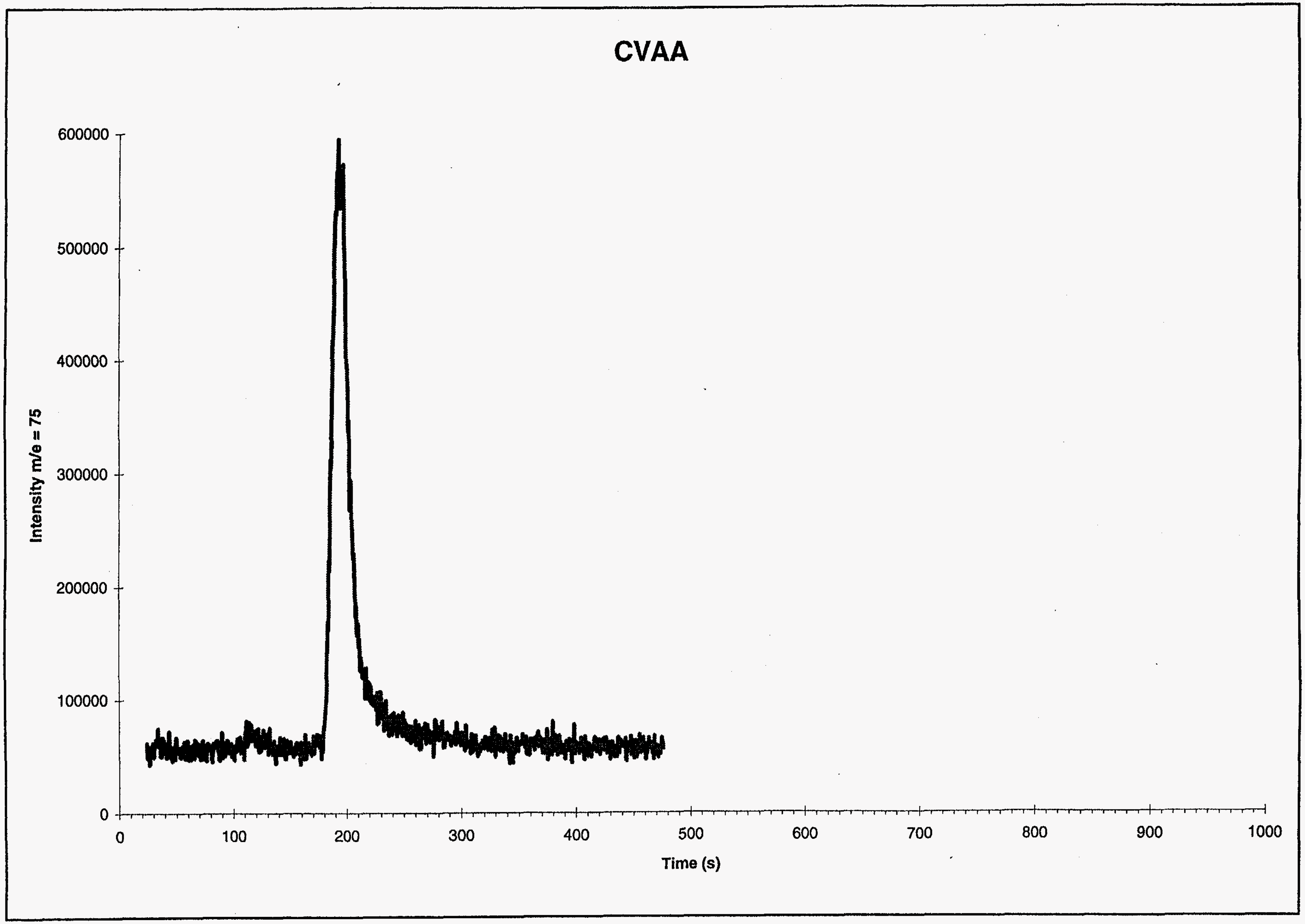
Solutions measured directly

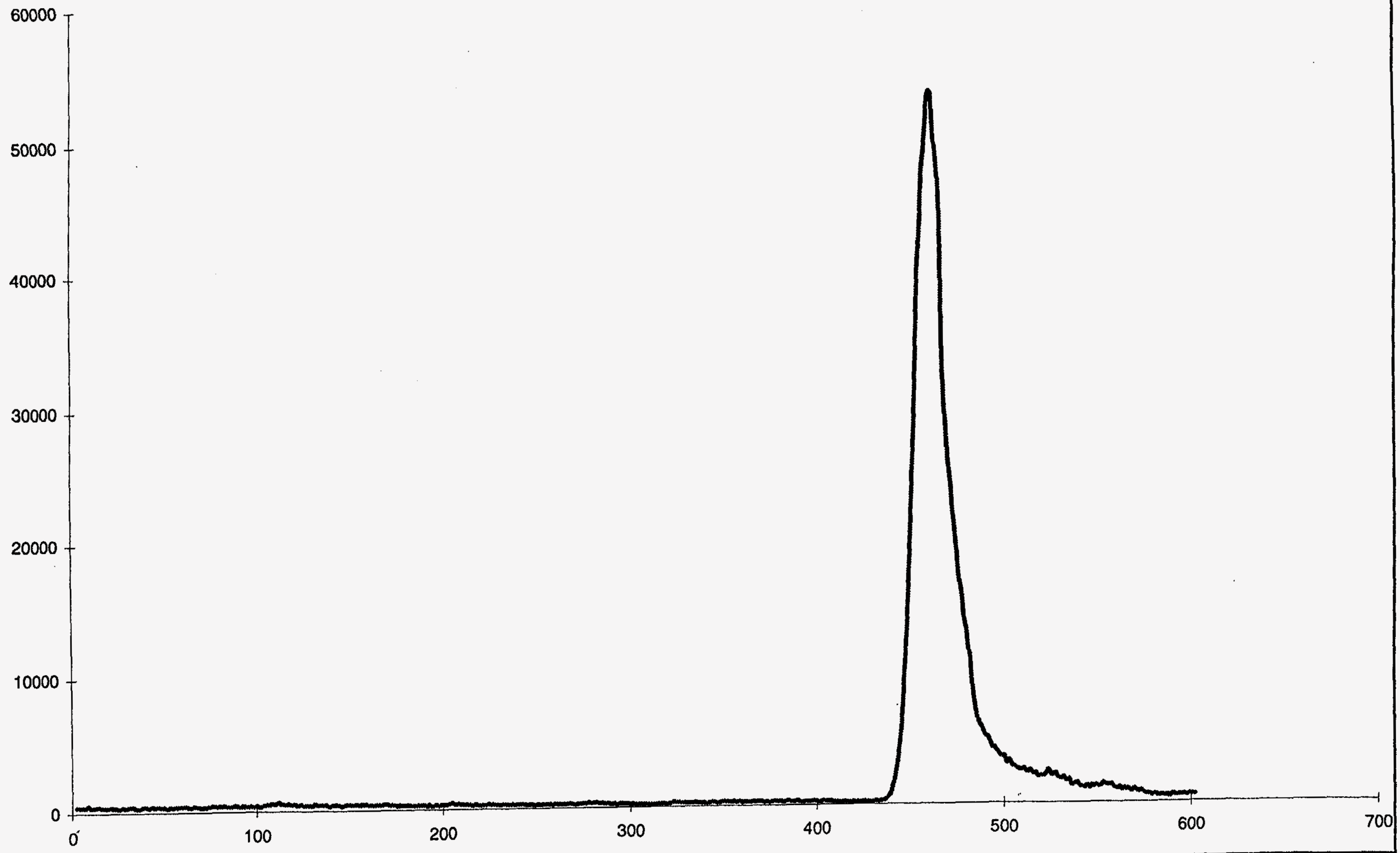
v Solids require extraction (using ultrasonic probe)

Results

- Separation of As(III), As(V), and DMAA
- CVAA (aqueous)
- CVAA (in soil)
- CVAOA(aqueous)
- CVAO (in soil)
- Thermal degredation of CVAA in soil

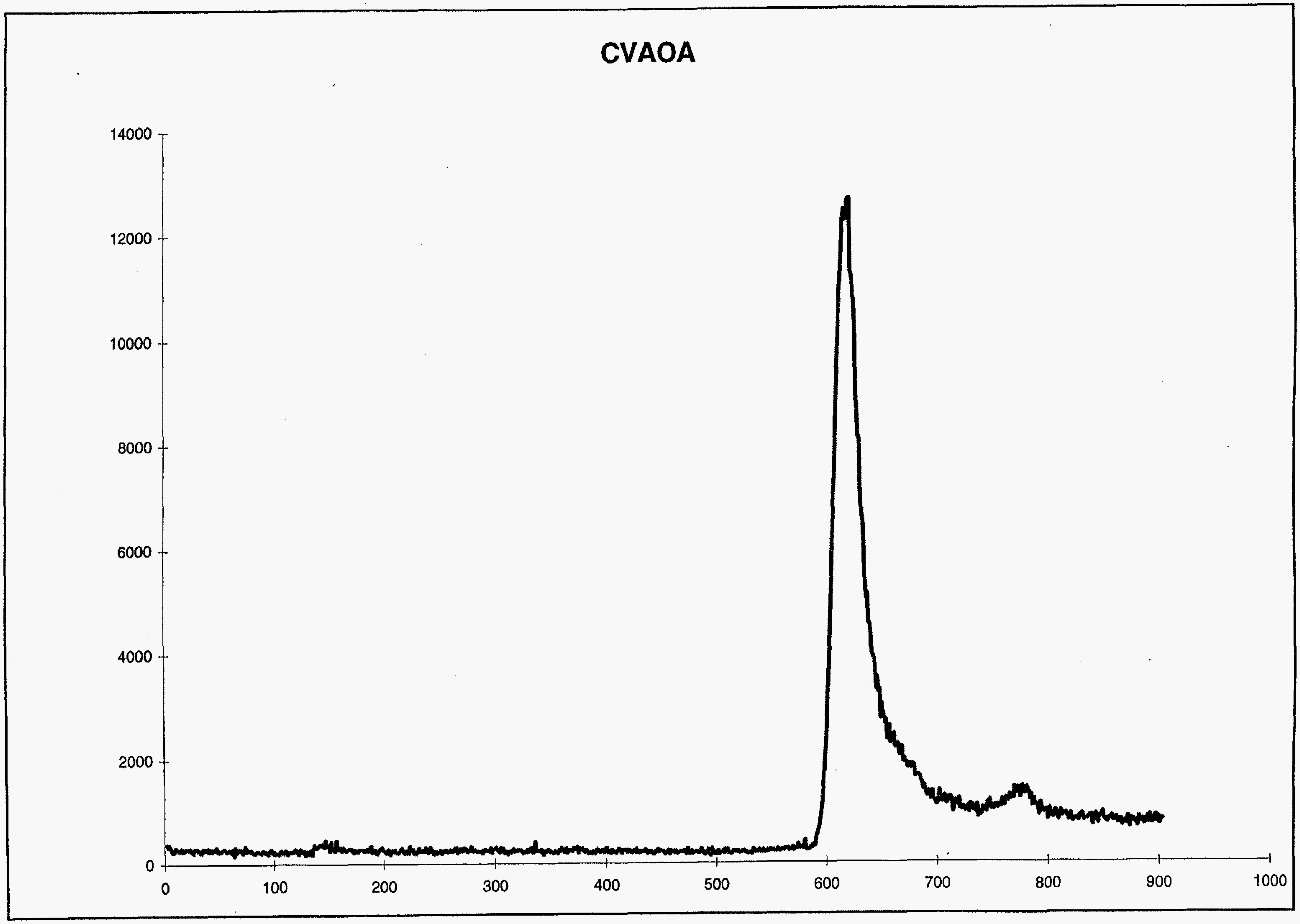

Separation of As Species
100pg As for each species
As (III)
DMAA
As (V)
Intensity m/e = 75
14000000
12000000
10000000
8000000
6000000
4000000
2000000
0
0
100
200
300
400
500
600
Time (s)


CVAA
Intensity m/e = 75
600000
500000
400000
300000
200000
100000
0
0
100
200
300
400
500
600
700
800
900
1000
Time (s)



CVAA on Soil

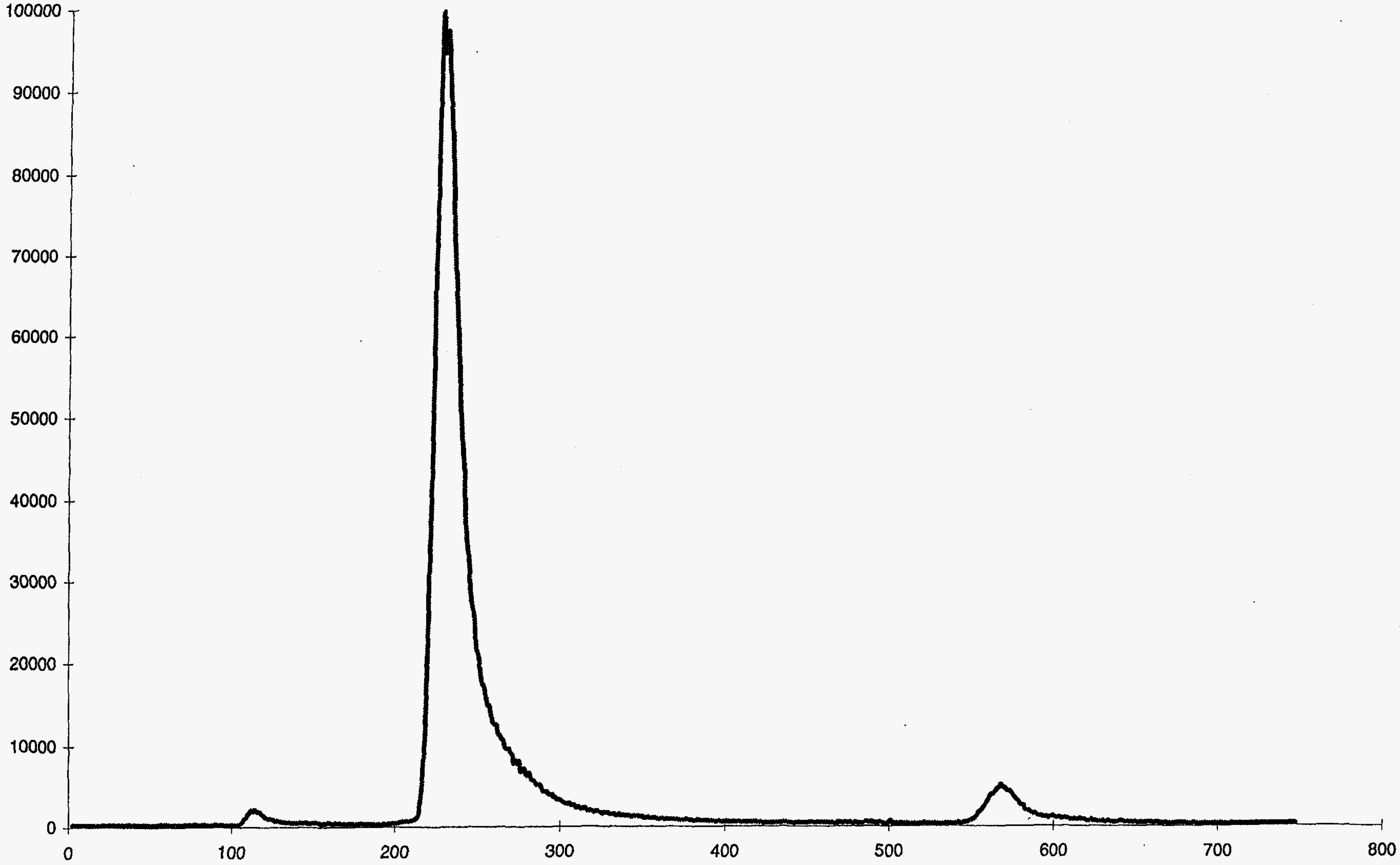
60000
50000
40000
30000
20000
10000
0
0
100
200
300
400
500
600
700

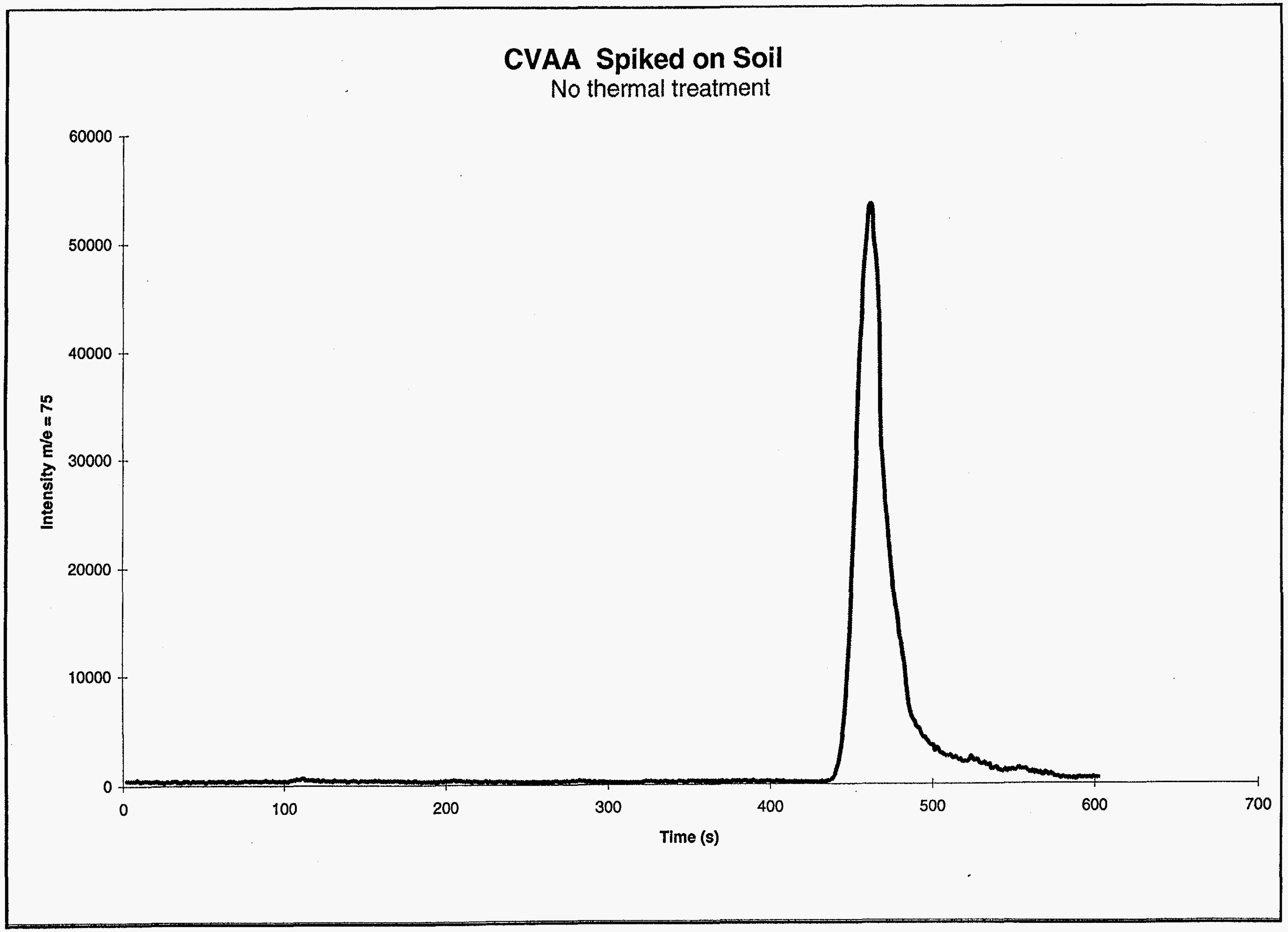


CVAOA

14000
12000
10000
8000
6000
4000
2000
0
0
100
200
300
400
500
600
700
800
900
1000

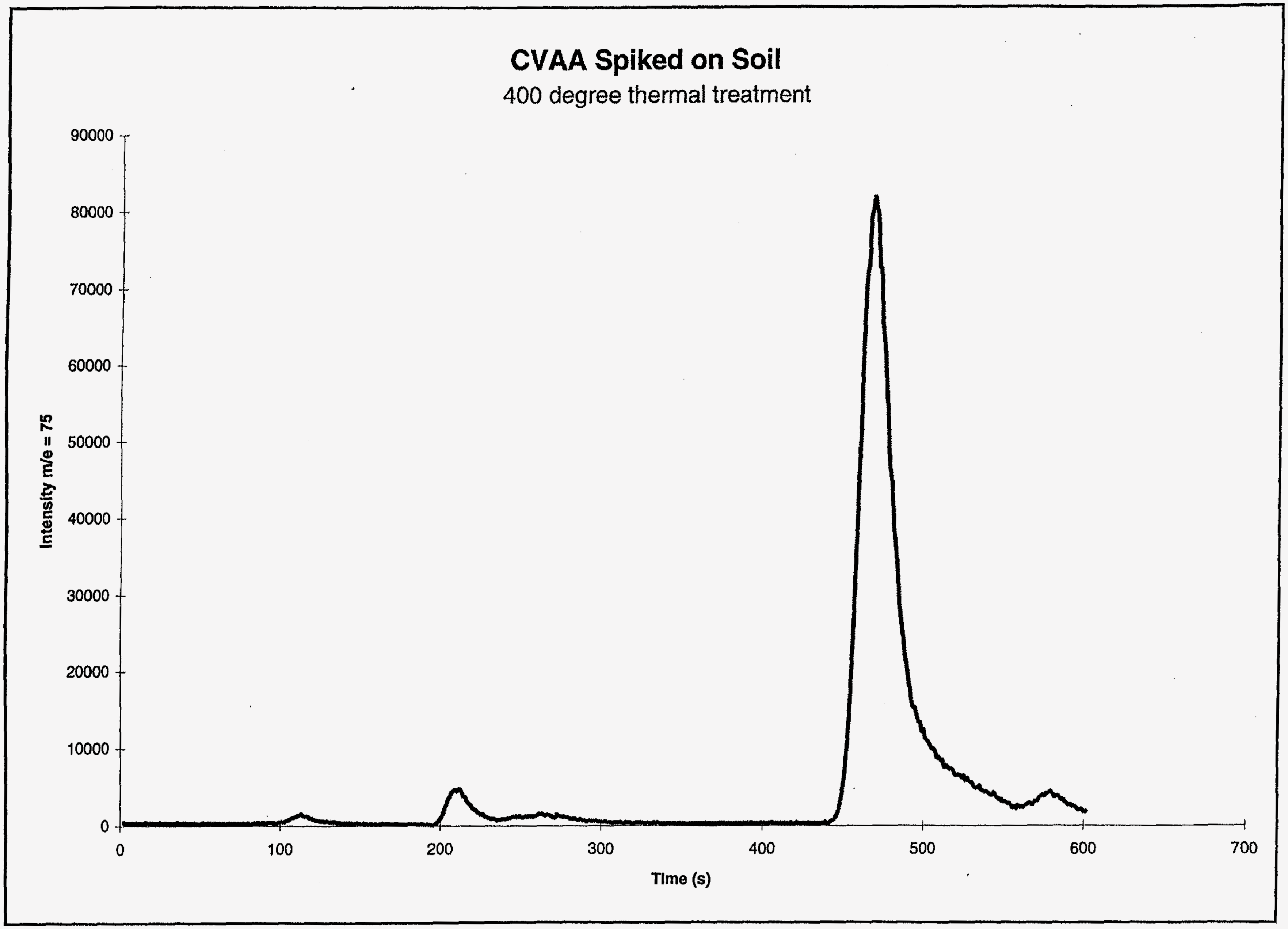
CVAO on Soil

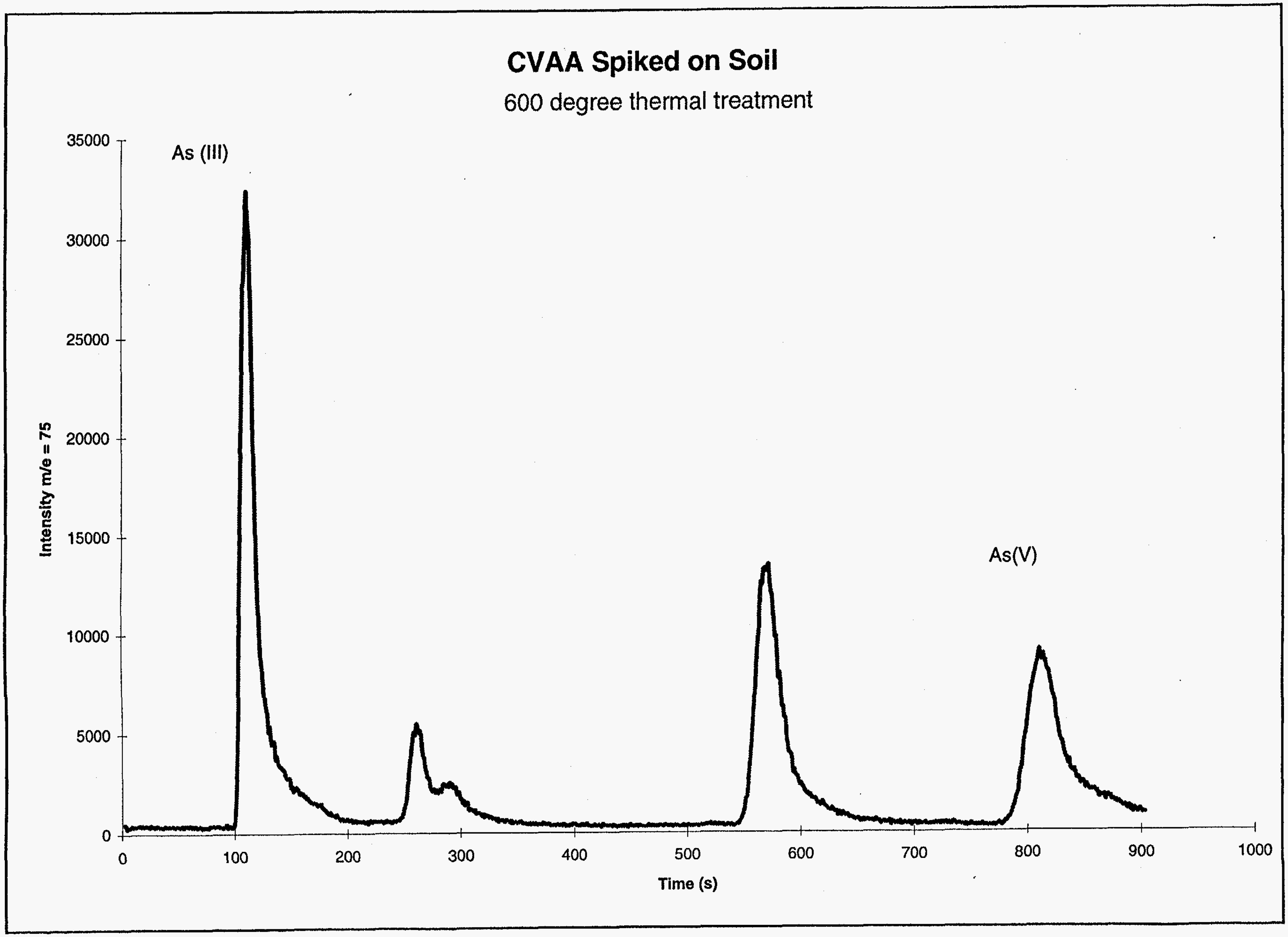

100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
0
100
200
300
400
500
600
700
800

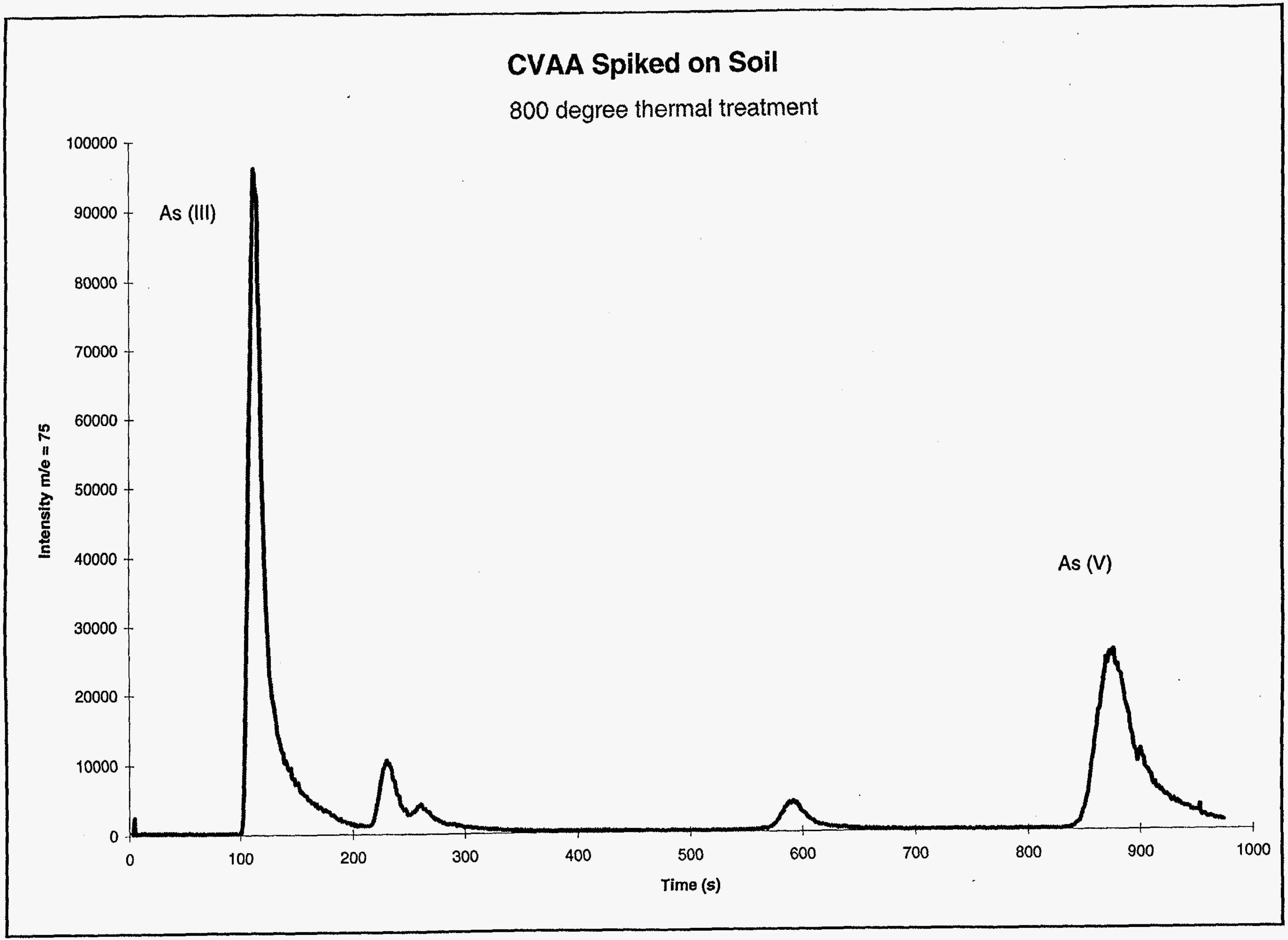


CVAA Spiked on Soil

No thermal treatment


CVAA Spiked on Soil
400 degree thermal treatment
Intensity m/e = 75
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
0
100
200
300
400
500
600
700
Time (s)


CVAA Spiked on Soil
600 degree thermal treatment
As (III)
As(V)
Intensity m/e = 75
35000
30000
25000
20000
15000
10000
5000
0
0
100
200
300
400
500
600
700
800
900
1000
Time (s)


CVAA Spiked on Soil

800 degree thermal treatment

Analytical Figures of Merit

- Detection limit - 0.1 pg (ppb)
- Reproducibility - <10% with internal standard
- Calibration linear range up to 500 ppb

Conclusions

- Unique method
- As(III), As(V), and Lewisite degradation products identified and quantified
- Analysis linear to 500 ppb and reproducibility at 5% RSD
- Detection limit of 0.1 pg (ppb)
- General metal speciation capabilities
- Areas for additional [illegible]

Acknowledgements

Jack O'Neill; Energy Systems Division
Argonne National Laboratory

Peter [illegible]; Analytical Chemistry Laboratory
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