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

by

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**to be presented at the
Workshop on Metal Speciation and Contamination of Surface Water
Jekyll Island, GA
June 25-28, 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.

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ARSENIC SPECIATION USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY - MASS SPECTROMETRY (HPLC-MS)

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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 arsenous 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.

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

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

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 separation. Heptyltriethyl ammonium phosphate (HTAP) in 5% methanol was also used with almost identical results 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).

Stability of As Species

The stability of arsenic species in standards and samples under normal conditions is of concern. Under normal conditions of operation, no degradation of standards was observed. The addition of standards to analytical samples resulted in the conversion of arsenic species. Figure 3 shows the partial conversion of As(III) to As(V). This was not observed when As(III) was added to sea sand. Figure 4 shows the complete conversion of CV to As(V). The same conversion occurred when CVAA was deposited on sea sand. The results 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 (1 µL of 1ppb) species. Figure 5 shows the results from this standard. The detection limit is estimated from the peak height 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 present at mass 75. This interference can be corrected by measuring the amount of ArCl at mass 77 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.

MANAGE LIQUID CHROMATOGRAPHY - INDIRECTLY COUPLED

SPECTROMETRY (HPLC-ICP-MS)

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RESULTS AND DISCUSSION

methanol with the pH adjusted to 6, was used as a mobile phase for this separation. TBAH was used phosphate (HTAP) in 5% methanol was also used with almost identical results. TBAH was

(Figure 2).
are not separated,
the arsenic species,
dissolved in water,
as arsenic oxide

species in standards and samples under normal conditions is of concern. Under the normal course of arsenic species. Figure 2 shows the partial conversion of As(III) to As(V). The conversion was added to sea sand. Figure 4 shows the complete conversion of CVAA on soil to an (III) was added to sea sand. Figure 4 shows the complete conversion of CVAA on soil to an

used a spike of As(V) to show relative retention time to the unknown species. The extract analyzed

As(III)	DMAA	As(V)
Replicate #1	2.77e+08	1.79e+08
Replicate #2	2.13e+08	1.82e+08
Replicate #3	2.24e+08	2.01e+08
Replicate #4	2.20e+08	2.08e+08
Replicate #5	2.44e+08	2.01e+08
Replicate #6	2.10e+08	2.05e+08
Replicate #7	2.30e+08	1.84e+08
Average	2.24e+08	1.94e+08
Standard Deviation	1.14e+07	1.20e+07
RSD	5.11%	6.20%

shows results
Based on this
than 10% is
measurement.
RSDs ranged
of an internal
SD less than
standard. The
measurements

limits were estimated using a standard which contained 1 pg (1pg of 1pgb) of each arsenic
The results from this standard. The detection limit is estimated from the peak height using three
times the noise (baseline).

Detection Limit = 0.1 pg

Interferences
presence of high levels of chloride, an interference for arsenic from AsCl can be present (both are
This interference can be corrected by measuring the amount of AsCl at mass 77. The ratio of
is 3:1, as such, subtracting three times the mass 77 peak from the mass 75 peak will correct for
Figures 6 and 7 show the effectiveness of this correction.

CONCLUSIONS

This method is being developed to determine the quantity and form of arsenic in soil, before and after
treating. Figure 3 shows the results of a contaminated soil, prior to treatment. The arsenic is all in the form of As(V).
After treatment, Figure 3, 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 As(V). As(V) is increased.
species. After treatment (Figure 7) the organic arsenic is not present, As(V) has been reduced, and As(III) is increased.

Soil Sample Results

The work presented here shows an instrumental method for the identification of As(III), As(V), and
organospecific compounds. The method was specifically designed for arsenic species 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 organospecific 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 0.1pgb for
a 1pg injection. The presence of chloride in a sample can produce an interference mass 77 allows
correction of the chloride interference. The method is linear up to 500pgb. Samples which exceed the 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.

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, surrogate, laboratory control samples.

Species	As(III)	As(V)	CVAA	As(III)	As(V)	CVAA
Range (pgb)	0.500-1.000	0.500-1.000	0.500-1.000	0.500-1.000	0.500-1.000	0.500-1.000
r ²	0.9991	0.9776	0.9998	0.9763	0.9995	0.9816
CVAA	0.9999	0.9998	0.9998	0.9998	0.9998	0.9999

Without internal standards
With internal standards

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 pgb standards.

Acknowledgements

The authors would like to thank Jack O'Neill and Linda Sherr for their contribution 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

CVAA + As(V) on Soil

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

Figure 6 - Contaminated Soil B
TREATED (with chloride interference)

Figure 7 - Contaminated Soil B

TREATED (corrected for chloride interference)

Figure 8 - Contaminated Soil A

UNTREATED

Figure 9 - Contaminated Soil A

TREATED

Figure 10 - Contaminated Soil B

UNTREATED (Corrected for chloride interference)