ANALYTICAL METHODS COMPARISON FOR DISSOLVED ARSENIC SPECIATION.

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Introduction

Arsenic has received increased attention in recent years because of its carcinogenic and toxic properties. Widespread instances of arsenic contamination in areas such as Bangladesh, as well as in the US, have prompted USEPA to lower the current US drinking water MCL (Maximum Contaminant Level) for arsenic to 10ppb from a proposed level of 5ppb[1] (Federal Register: 65 FR 38888). While this guideline is established for total arsenic concentrations, arsenic can be present in several forms in natural waters. Speciation of inorganic and organic forms of arsenic is often as important as total quantification because of the varying degrees of toxicity and removal mechanisms of the different species [2,3,4].

Originally, our work in this area focused on a need to determine the most reliable and convenient method of arsenic speciation in groundwaters and acid mine drainage (AMD). Inorganic species, namely arsenite [As(III)] and arsenate [As(V)], usually predominate in such environments. However, organoarsenicals can often also be significant in surface waters, especially when they have been impacted by human activities. Several forms of organic arsenicals are used as animal feed supplements and as cotton herbicides. Little is known of the chemistry and ultimate fate of these compounds once distributed in the environment. Currently we are investigating the chemistry, particularly photooxidation, of these compounds in natural systems. The perspective of our work is the implementation of passive treatment of waters contaminated by different forms As, therefore, speciation of As in these waters must be understood.

Several methods are available for arsenic speciation, some of which are designed specifically for inorganic species, while others can determine both organic and inorganic forms. The first step in this research was to compare existing techniques to determine their strengths and weaknesses[5]. Results showed that modifications of some existing methods provided improvements. Published methods were often incompatible with our matrices of interest (for example AMD samples and HPLC phosphate eluents), which also necessitated modifications of existing methods. Because our interests also include organoarsenicals, we developed new methods for the parent compounds as well as their degradation products. Additionally, sample preservation and storage are important considerations[5,6], and are also being examined, especially the effects of light, dissolved iron(III), natural organic matter (NOM), and oxyhydroxide colloids.

Analytical Methods

For our round robin study, arsenite and arsenate stock solutions were made from reagent grade chemicals, stored below 4°C, in the dark, and for most samples, analyzed within 24 hours. To investigate storage effects, some samples were reanalyzed over a period of up to 4 weeks. Our comparison of existing methods focused only on techniques for arsenite and arsenate. The four methods investigated were: anion exchange chromatography with off-line GF-AAS detection[7], selective hydride generation atomic absorption (HG-AAS)[8], and two forms of HPLC-ICP-MS (labeled HPLC and CETAC in Table 1)[9,10], one of which utilized hydride generation as the ICP sample introduction mechanism[9]. Method development focused on modifications to the anion exchange method [5,11] because of its simplicity and portability, and modification of the HPLC-ICP-MS method, because of its speed and reliability. Our main goal for the anion exchange method was to improve percent recovery, whereas the modifications to the HPLC methods focused on eluent-sample matrix compatibility.

Modifications to the anion exchange method primarily involved a change of eluent composition and volume used. A 5mL sample was added to a column, prepared as in the literature, then the arsenite fraction was collected by eluting with 15mL of deionized water. The arsenate fraction was collected by elution with 20mL of 0.48M HCl. The new HPLC method also involves an eluent change, from the recommended ~35mM sodium phosphate at pH=5.7, to ~6mM ammonium malonate/17mM ammonium acetate buffered at pH~4.7. This eluent is more chemically compatible with AMD samples than is the published phosphate method[9]. It is also a stronger buffer than the 5mM ammonium malonate eluent at pH=8 used in the second HPLC method investigated in our comparison study[10]. We further modified the HPLC eluent (~200mM ammonium acetate at pH~4.4) for a study of the degradation of a phenyl arsenic acid compound (Roxarsone). Figure 1 shows a representative chromatogram of a solution of 10ppb arsenite, 10ppb arsenate, and 10ppb Roxarsone using our modified HPLC method.

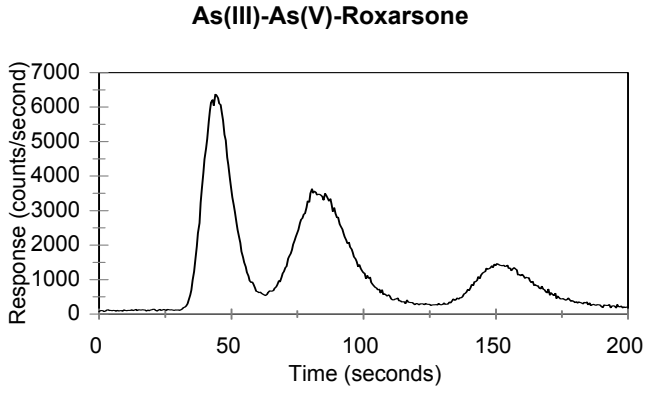

Figure 1. 10ppb As(III) + 10ppb As(V) + 10ppb Roxarsone standard. Speciation by HPLC on a 50mm LC-SAX column with 200mM ammonium acetate, pH~4.4 and gradient elution with flow rate from 1.0 to 2.9mL/min. Arsenic detection was by ICP-MS.

Results and Disscussion

Selected results of the methods comparison are shown in Table 1. Solutions of arsenite and arsenate were prepared at concentrations ranging from 1 to 1000ppb. Various background electrolytes were included, such as sulfate, chloride, iron(III), aluminum, and calcium, to examine potential problems with percent recovery and interferences. Measured values of arsenite and arsenate using the four methods are compared to the calculated values for arsenic solutions prepared in the indicated matrix. For the most part, when iron(III) and aluminum concentrations were low, the two HPLC methods and HG-AAS gave comparable results. The initial HPLC eluents were not compatible with the iron(III) and aluminum matrices, but were later modified to allow analysis of samples with these constituents. The anion exchange method suffered from low recovery of arsenite and generally underestimated the As(III):As(V) ratio. Modifications to the anion exchange method improved results somewhat. By slight changes in the published anion exchange technique, we are more confident in comparing speciation results from the field with samples brought back to the lab for speciation. Work is continuing to further test and improve the field portable method, however, other results in our studies suggest that samples can be stabilized for transportation back to the laboratory for more accurate analysis. This may reduce the need for further modifications to the anion exchange method.

Table 1. Arsenite and arsenate concentrations as determined by five methods for samples with different matrices and arsenic concentrations.
[Fe(III)]=[Al]=1ppm, $[SO_4^{2-}]$=10ppm, [Cl]=1000ppm, [As] given in ppb.

Matrix	Calculated		CETAC			HPLC			HG-AAS			GFAAS	Anion	Exchange
	As(III)	As(V)	As(T)	As(III)	As(V)	As(T)	As(III)	As(V)	As(T)	As(III)	As(V)**	As(T)	As(III)	As(V)
T-159*	0	27.5	30	0	26	27.5	0	27.5	27	0	27	30.1	.6	17
DI Water	1000	500	1250	940	560	1370	912	539	1560	960	600		540	432
												Modified	Anion	Exchange
													700	340
DI Water	50	25	72	46	26	67.4	41.3	26.1	80	48	32	76	31.6	23.2
DI Water	45	5	25	44	6.2	45.6	41.7	5.4	53	42	11		30.8	7.2
DI Water	5	45	55	6.5	42	56.3	5.4	51.3	57	5.5	51.5	61.4	9.8	26.4
DI Water	1	5	7.2	1.1	5.3	6.3	1.0	5.2	6.7	0.6	6	6.2	0	1.4
DI Water	4	1	5.4	5.4	1.9	6.6	3.7	2.3	5.7	3.8	1.9	7.9	1	2.8
DI Water***	4	1	8.1	5.3	4.1	8.8	3.9	4.7	5.6	3.7	1.9		1.4	3.8
Al, Fe	45	5							48	40	8		26.2	24.4
Al,Fe,SO_4	45	5							49	38	11		25.8	22.6
Chloride	45	5	38	48	3.6	47.6	40.8	6	48	42	6		26.6	5
Al,Fe,SO_4	50	5							55	46	9		23.6	11.4
												Modified	Anion	Exchange
													30.4	6.4

* T-159 USGS Trace Element Reference Water Sample, certified [As]= 27.5ppb
** As(V) by difference
*** Blind duplicate

References

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