

## Separation of Inorganic Arsenic Species in Groundwater Using Ion Exchange Method

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It is much more important to determine the species of arsenic than to detect only total arsenic concentration in environmental samples because the forms of arsenic control not only its toxicity but its transport mechanisms and environmental persistence. A great deal of effort has been expended in the search for better practical methods for determination of arsenic species. Those include capillary zone electrophoresis (Li and Li 1995), high performance liquid chromatography (HPLC) (Manning and Martens, 1997), ion exchange method (Ficklin 1983; Grabinski 1981), solvent extraction (Mok et al. 1986), and chemical precipitation (van Elteren et al. 1991). The methods for the determination of the arsenic species in natural waters entail considerable problems. In most cases, the equipment for the separation is not portable, so it is difficult to perform the experiment in the field and to obtain the exact values of arsenic species. The best way to obtain exact values of arsenic species may be to separate the species right after collecting the groundwater sample. Otherwise, the forms of species may change even though preservation is done. Therefore, a simple and portable ion exchange method was chosen for the separation of inorganic arsenic species in this study. Strong anion-exchange resin was selected.

Ion exchange method as an effective separation method is based on acid dissociation constants of the arsenic species. The values for the  $pK_a$  of the inorganic arsenic species are shown in Table 1. When the ion exchange method is used, arsenic species can be separated by controlling pH. Flow rate should also be considered because one species should be held by the resin at an appropriate flow rate. Therefore, optimum pH and flow rate were investigated in natural groundwater, and the efficiency of the ion exchange method was evaluated under different conditions. The stability of arsenic species in groundwater samples by time was also tested.

### MATERIALS AND METHODS

Each apparatus and bottle utilized in the experiment was washed using nitric acid. All reagents were of analytical grade and were used without further purification. All solutions were prepared with deionized water. The pH of each solution was measured with an Orion Model 250A pH meter. A graphite furnace atomic absorption spectrophotometer (GFAAS) was used for arsenic determination.

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**Table 1.** pK<sub>a</sub> values of arsenic species

	pK <sub>1</sub>	pK <sub>2</sub>	pK <sub>3</sub>
As(III)	9.2	12.1	13.4
As(V)	2.2	6.9	11.5

Source: Korte and Fernando (1991)

An electrodeless discharge lamp was used. A matrix modifier of 5 µg of Pd and 3 µg of Mg(NO<sub>3</sub>)<sub>2</sub>, was used for each 20µL of sample, and was added into the blank, standards, and samples. All samples (20µL aliquots) were analyzed twice and the detection limit of arsenic was 3 µg/L.

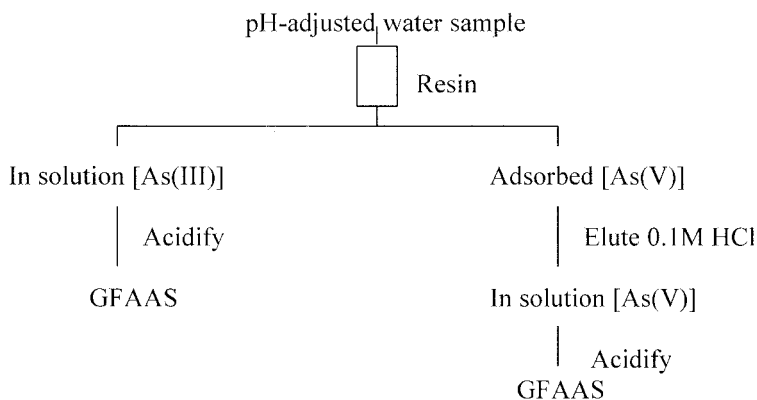
The solutions used in this study to find the optimum flow rate and pH for the ion exchange method were prepared by spiking arsenic into groundwater. Background arsenic concentration in groundwater used was negligible (<3 µg/L). Standard solutions of arsenic compounds (1000 mg/L as As) were prepared by dissolving 0.1782g of NaAsO<sub>2</sub> and 0.4363g of Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O in groundwater, respectively. Stock solutions were prepared by diluting the standards by the factor of 100 twice and the final concentration of each stock solution was 100 µg/L. Arsenic solutions for this experiment were prepared daily.

For the speciation of inorganic arsenite [As(III)] and arsenate [As(V)], ion exchange methods of Ficklin (1983) and Grabinski (1981) were adapted and modified. Strong anion-exchange resin (AG1-X8, 100 to 200 mesh chloride form) was slurry packed into polyethylene columns (20cm×8mm) and kept moist with deionized water. Contaminants were removed from the resins by washing them with 50 mL of 1M HCl. Then, the column was washed with 10 mL of deionized water of pH≈5.

In order to find the optimum condition for the separation of arsenic species, artificial water samples were used: the samples were prepared by spiking arsenic into groundwater. The samples were acidified using 1M HCl. 50 mL of acidified sample were allowed to pass through the resin in the column, followed by 30 mL of 0.1M HCl as eluent. The As(III) species from the sample was in the pass-through solution, and the As(V) species was in the eluted solution. The procedure used for the separation and determination of the arsenic species is schematically represented in Figure 1.

In order to find the optimum flow rate and pH for the experiment, a controlled test was performed in groundwater. As(III) and As(V) were spiked into groundwater to make two arsenic solutions of approximately 100 µg/L. The percent recovery for each test was calculated to determine the best condition (Percent recovery = concentration of recovered arsenic species/ concentration of spiked arsenic species × 100).

**Figure 1.** Procedure of arsenic speciation in water sample



First, the optimum flow rate for the separation of As(III) and As(V) was investigated. In order to determine the effect of only the flow rate, the pH was fixed between 4 and 6 according to the values for  $pK_a$  of the arsenic species (Table 1). Since the pH of the groundwater used was between 7 and 8, the water was acidified with 1M HCl. Flow rates between 2 and 22 mL/min were tested using varying amounts of resin.

Secondly, in order to find the optimum pH range for the separation of As(III) and As(V), the flow rate was fixed at the optimum value determined from previous experiments. For the purpose of testing at different pH, As(III) and As(V) stock solutions were acidified with 1M HCl and basified with 1M NaOH in groundwater. The pH range tested was between 2 and 11.

The efficiency of the ion exchange method used was evaluated by testing As(III) and As(V) mixed in different ratios in groundwater. Both As(III) and As(V) were spiked into groundwater to make a total concentration of approximately 100  $\mu\text{g/L}$ . The flow rate used was 2.6 mL/min and the pH was set at 4.6 and these values were obtained from the previous flow rate and pH tests.

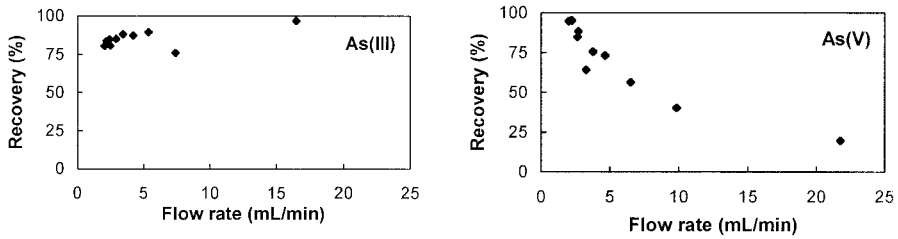
In order to investigate the stability of arsenic species in unpreserved samples, groundwater samples were collected in 2L polyethylene bottles from five private wells in Genesee County in Michigan. No headspace was found in the bottles. The concentrations of total arsenic and arsenic species were measured at different times as follows.

1. Immediately after sampling (on site)
2. After storing in refrigerator for 3 days without acidification
3. After storing in refrigerator for 13 days without acidification

Arsenic species were separated using the same method described above.

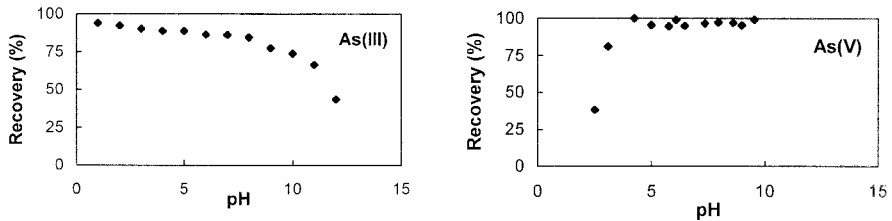
## RESULTS AND DISCUSSION

First, in order to find the optimum flow rate for the separation of As(III) and As(V), pH was fixed and various flow rates were tested. The results are shown in Figure 2. The flow rate did not affect the elution of As(III), but affected the collection of As(V) by resin in a column. If the flow rate is higher than 2.7 mL/min, there is not enough time for the anion exchange resin to capture As(V) as the water sample passes through the column. The optimum flow rate in groundwater was found to be 2-2.7 mL/min.



**Figure 2.** Determination of optimum flow rate for the speciation

Second, for the purpose of finding the optimum pH range for the separation of As(III) and As(V), the flow rate was fixed from the results of previous flow rate tests and various pH solutions were tested. The results are shown in Figure 3. The optimum pH was lower than 7 for As(III) and higher than 4 for As(V). Therefore, the optimum pH range for the separation of As(III) and As(V) was from 4 to 7.



**Figure 3.** Determination of optimum pH for the speciation

The efficiency of the ion exchange method used was tested with As(III) and As(V) mixed solutions in different ratios. The tests were done in groundwater. The optimum pH and flow rate from the previous tests were used. The results are shown in Table 2. The percent recoveries of total arsenic, As(III), and As(V) species were over 90 %. The results indicate that the methodology developed is very efficient for the speciation of arsenic in groundwater.

At pH of about 4-7, As(III) exists in solution as a neutral species, and As(V) exists primarily as an anionic species. Thus, in this pH range, As(III) species in the acid adjusted water sample flows through the anion exchange resin, while the negatively charged As(V) species is efficiently retained on the resin. As a more acidic solution (pH<1.0) enters the anion exchange resin bed, As(V) is neutralized and eluted. The separation of the inorganic arsenic species is rationalized on the basis of their acid dissociation constants.

**Table 2.** Efficiency of the ion exchange method in groundwater<sup>a</sup>

Mixed ratios		Recovery(%)		
As(III) <sup>b</sup>	As(V) <sup>b</sup>	Total	As(III)	As(V)
100	0	104	90	
80	20	102	92	119
60	40	101	97	114
50	50	104	93	110
40	60	106	96	109
20	80	105	95	102
0	100	102		97

a, pH=4.64, flow rate=2.6 mL/min

b, unit = µg/L

Neither arsenic species changed its oxidation state during the experiment as the efficiency of the methodology was verified. Some authors have reported that the oxidation reaction occurs quickly, and that environmental samples must be analyzed within a few hours of collection, or significant amounts of As(III) would be converted to As(V) (Glaubig and Goldberg 1988; Haswell et al. 1985). In this respect, the ion exchange method is an efficient field method for measuring the redox-sensitive arsenic species.

As shown in Table 3, in fresh groundwater, 82-95% of the arsenic species was in the form of As(III). After 3 days of storing the samples in a refrigerator, 25-30 % of the As(III) was oxidized to As(V). In addition, the water color changed to light yellow, dark brown particulates were found in the bottom of the bottle, and the total dissolved arsenic concentration decreased. After 13 days of storing, more As(III) was oxidized to As(V) and the total dissolved arsenic concentration decreased even more. However, the rate of oxidation was less than that observed after 3 days. The results show that it is important to separate the arsenic species at the sampling sites immediately after collecting well water in order to obtain reliable results.

The ion exchange method is good for field work because the speciation results were reliable, the required equipment was portable, and the experiment could be done simply and quickly. In addition, preservation of the sample was unnecessary.

**Table 3.** Stability of arsenic species in groundwater samples

Sample	On site		After 3 days		After 13 days	
	As(T) <sup>a</sup>	As(III)(%)	As(T)	As(III)(%)	As(T)	As(III)(%)
1	65	87	47	48	36	44
2	62	82	50	59	50	49
3	63	93	54	60	59	54
4	43	95	38	74	30	78
5	79	86	71	70	65	76

a, total dissolved arsenic concentration (unit =  $\mu\text{g/L}$ )

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