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Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Arsenic Speciation in Natural-Water Samples Using Laboratory and Field Methods

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Water-Resources Investigations Report 02-4144

U.S. Department of the Interior
U.S. Geological Survey

Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Arsenic Speciation in Natural-Water Samples Using Laboratory and Field Methods

By John R. Garbarino, Anthony J. Bednar, and Mark R. Burkhardt

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CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
	Length	
centimeter (cm)	3.94×10^{-1}	inch
micrometer (µm)	3.94×10^{-5}	inch
millimeter (mm)	3.94×10^{-2}	inch
nanometer (nm)	3.94×10^{-8}	inch
	Mass	
gram (g)	3.53×10^{-2}	ounce, avoirdupois
microgram (µg)	3.53×10^{-8}	ounce, avoirdupois
milligram (mg)	3.53×10^{-5}	ounce, avoirdupois
picogram (pg)	3.53×10^{-14}	ounce, avoirdupois
	Volume	
liter (L)	2.64×10^{-1}	gallon
microliter (µL)	2.64×10^{-7}	gallon
milliliter (mL)	2.64×10^{-4}	gallon

Degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) by using the following equation:

$$°F = 9/5\ (°C) + 32.$$

ABBREVIATED WATER-QUALITY UNITS

mg-As/L	milligrams of arsenic per liter
mg/L	milligram per liter
µg/L	microgram per liter
µS/cm	microsiemens per centimeter at 25 degrees Celsius

ABBREVIATIONS AND ACRONYMS

AAS	atomic absorption spectrometry
As(III)	arsenite
As(V)	arsenate
AMD	acid mine drainage
ASTM	American Society for Testing and Materials
CAS	Chemical Abstract Service registry number
DMA	dimethylarsinate
EDTA	ethylenediaminetetraacetic acid
Hz	hertz
ICP–MS	inductively coupled plasma–mass spectrometry
M	moles per liter
m*M*	millimoles per liter
MDL(s)	method detection limit(s)
MMA	monomethylarsonate
m/z	mass-to-charge ratio

NWQL	National Water Quality Laboratory
s	seconds
SRWS(s)	U.S. Geological Survey Standard Reference Water Sample(s)
USGS	U.S. Geological Survey
~	approximately
±	plus or minus
<	less than
>	greater than

GLOSSARY

MDL—The method detection limit (MDL) is defined as the minimum concentration of an element that can be measured and reported with 99-percent confidence that the element concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the element of interest (U.S. Environmental Protection Agency, 2000).

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Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Arsenic Speciation in Natural-Water Samples Using Laboratory and Field Methods

By John R. Garbarino, Anthony J. Bednar, and Mark R. Burkhardt

ABSTRACT

Analytical methods for the determination of arsenite [As(III)], arsenate [As(V)], dimethylarsinate (DMA), monomethylarsonate (MMA), and roxarsone in filtered natural-water samples are described. Various analytical methods can be used for the determination, depending on the arsenic species being determined. Arsenic concentration is determined by using inductively coupled plasma–mass spectrometry (ICP–MS) as an arsenic-specific detector for all methods. Laboratory-speciation methods are described that use an ion chromatographic column to separate the arsenic species; the column length, column packing, and mobile phase are dependent on the species of interest. Regardless of the separation technique, the arsenic species are introduced into the plasma by either pneumatic nebulization or arsine generation. Analysis times range from 2 to 8 minutes and method detection limits range from 0.1 to 0.6 microgram-arsenic per liter (μg-As/L), 10 to 60 picograms absolute (for a 100-microliter injection), depending on the arsenic species determined and the analytical method used. A field-speciation method also is described that uses a strong anion exchange cartridge to separate As(III) from As(V) in the field. As(III) in the eluate and As(V) in the cartridge extract are determined by direct nebulization ICP–MS. Methylated arsenic species that also are retained on the cartridge will positively bias As(V) results without further laboratory separations. The method detection limit for field speciation is 0.3 μg-As/L.

The distribution of arsenic species must be preserved in the field to eliminate changes caused by photochemical oxidation or metal oxyhydroxide precipitation. Preservation techniques, such as refrigeration, the addition of acids, or the addition of ethylenediaminetetraacetic acid (EDTA) and the effects of ambient light were tested. Of the preservatives evaluated, EDTA was found to work best with the laboratory- and field-speciation methods for all sample matrices tested. Storing the samples in opaque polyethylene bottles eliminated the effects of photochemical oxidation. The percentage change in As(III):As(V) ratios for an EDTA-preserved acid mine drainage (AMD) sample and ground-water sample during a 3-month period was –5 percent and +3 percent, respectively.

The bias and variability of the methods were evaluated by comparing results for total arsenic and As(III), As(V), DMA, and MMA concentrations in ground water, AMD, and surface water. Seventy-one ground-water, 10 AMD, and 24 surface-water samples were analyzed. Concentrations in ground-water samples reached 720 μg-As/L for As(III) and 1,080 μg-As/L for As(V); AMD samples reached 12,800 μg-As/L for As(III) and 7,050 μg-As/L for As(V); and surface-water samples reached 5 μg-As/L for As(III) and As(V). Inorganic arsenic species distribution in the samples ranged from 0 to 90 percent As(III). DMA and MMA were present only in surface-water samples from agricultural areas where the

herbicide monosodium methylarsonate was applied; concentrations never exceeded 6 µg-As/L.

Statistical analyses indicated that the difference between the As(III) and As(V) concentrations for samples preserved with EDTA in opaque bottles and field-speciation results were analytically insignificant at the 95-percent confidence interval. There was no significant difference among the methods tested for total arsenic concentration. Percentage recovery for field samples spiked at 50 µg-As/L and analyzed by the laboratory-speciation method (n=2) ranged from 82 to 100 percent for As(III), 97 to 102 percent for As(V), 90 to 104 percent for DMA, and 81 to 96 percent for MMA; recoveries for samples spiked at 100 µg-As/L and analyzed by the field-speciation method ranged from 102 to 107 percent for As(III) and 105 to 106 percent for As(V). Laboratory-speciation results for Environment Canada reference material SLRS-2 closely matched reported concentrations. Laboratory-speciation method variability at 0.5 µg-As/L was 8 to 13 percent (n=7) for all four arsenic species in reagent water. The variability for the field-speciation method at 1 µg-As/L was 3 to 4 percent and at 10 µg-As/L was 0.7 to 1 percent for As(III) and As(V), respectively.

INTRODUCTION

The presence of arsenic and its potential toxicity in the environment require the measurement of individual inorganic and organic arsenic species. The toxicity of each species (in the forms present in most natural water) varies in the series as arsenite [H_3AsO_3, As(III)] > arsenate [$H_2AsO_4^-$, As(V)] > dimethylarsinate [$(CH_3)_2HAsO_2$, DMA] > monomethylarsonate [$(CH_3)HAsO_3^-$, MMA] (Roehl and others, 1992; Neff, 1997; Pantsar-Kallio and Manninen, 1997). Researchers, however, recently have reported that some methylated metabolites of trivalent arsenic are highly reactive and damage DNA in cultured human cells (Mass and others, 2001). Humans and animals can be exposed to arsenic species by drinking-water supplies, surface water and ground water, foodstuffs, and growth additives. In addition to natural sources of arsenic, alkylarsenicals and arylarsenicals used in agriculture and the poultry industry can be introduced to the environment. For example, alkylarsenicals, such as monosodium methylarsenate, are used as a nonselective defoliant herbicide, and disodium methylarsenate is used as a selective post-emergence herbicide. Methylated arsenic species also can appear as metabolites from arsenic-mediated biological activity (Le and others, 1996; Nimbal and others, 1996; Pergantis and others, 1997). The arylarsenical 3-amino-4-hydroxyphenylarsonic acid (roxarsone) is a supplement in poultry feed that promotes growth by controlling intestinal parasites. Most of the roxarsone is excreted unchanged (Morrison, 1969). The arsenic-containing poultry manure is commonly applied to agricultural fields as fertilizer where the arsenic might become mobilized.

Measurement of individual arsenic species recently has been recognized as important for identifying sources of human, plant, and animal arsenic exposure. Arsenic species have been measured in human urine, marine and terrestrial flora and fauna samples, and in drinking water. Analytical methods used for arsenic speciation in water have been described by Cullen and Reimer (1989), Gonzalez Soto and others (1996), Burguera and Burguera (1997), Dean and others (1997), Nakahara (1997), Benramdane and others (1999), and by Matschullat (2000). Methods that can be used for arsenic speciation include gas chromatography, liquid chromatography coupled with atomic absorption spectrometry (AAS), cold vapor trapping with AAS, ion chromatography coupled with inductively coupled plasma–mass spectrometry (ICP–MS),

and micellular liquid chromatography using ICP–MS detection. Species measured in most studies include As(III), As(V), MMA, and DMA; some include the nontoxic, biologically derived alkylarsenic compounds, such as arsenocholine, arsenobetaine, and organoarsenic sugars.

This report describes laboratory-speciation and field-speciation methods that are optimized for the determination of As(III), As(V), MMA, DMA, and the arylarsenical roxarsone in filtered natural-water samples. Arsenocholine, arsenobetaine, and organoarsenic sugars were not determined because they have short half-lives in the hydrologic environment owing to their biological activity, and therefore, are not thought to contribute substantially to the arsenic budget in natural hydrologic systems. The laboratory-speciation methods described use ion chromatographic separation of the arsenic species and ICP–MS as an arsenic specific detector. As the arsenic species elute from the column, the mobile phase either is introduced directly into a pneumatic cross-flow nebulizer or into a arsine generator. The temporal signals corresponding to the arsenic species are identified and quantified by comparing peak retention times and peak areas to corresponding data from known arsenic standards that contain the desired species.

The field-speciation method uses a cartridge containing strong anion exchange material to separate As(III) and As(V) in the field. The As(III) in the eluate and the As(V) in the cartridge extract are analyzed directly using nebulization ICP–MS. When DMA or MMA are present in a sample, they are retained on the cartridge with As(V). Differentiation between As(V) and other anionic arsenic species in the extract require additional laboratory separations.

All arsenic-speciation methods require some type of protocol to preserve the arsenic speciation of the sample. Crecelius and others (1986) investigated different storage temperatures and the addition of hydrochloric acid or ascorbic acid as possible preservation protocols, however, quick-freezing the sample with liquid nitrogen was recommended to preserve As(III) and As(V) speciation in water samples. Hall and others (1999) reported that storing samples at 5°C preserved As(III) and As(V) speciation in water samples for about 30 days, whereas using 0.1 percent nitric or hydrochloric acid altered the arsenic species distribution. Other studies have shown that EDTA preserved arsenic speciation distributions in three ground-water samples for up to 14 days (Gallagher and others, 2001). Exclusion of light and the addition of hydrochloric acid, nitric acid, sulfuric acid, or EDTA were evaluated as possible preservation techniques in this report.

This report describes the following:

- Laboratory-speciation methods for the determination of As(III), As(V), DMA, MMA, and roxarsone in natural water.
- A field-speciation method for the separation of As(III) and As(V) in natural-water samples in the field.
- Different arsenic speciation preservation techniques.
- The bias and variability of results for ground-water, surface-water, acid mine drainage, and reference-material samples.
- The advantages and disadvantages of the speciation methods.

The methods described were developed by the U.S. Geological Survey (USGS) for use at the National Water Quality Laboratory (NWQL). These methods do not supplement or replace any other USGS arsenic speciation methods. The new methods were implemented at NWQL in June 2002.

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ANALYTICAL METHODS

Lab and parameter codes for laboratory speciation and field speciation are listed in the following table for As(III), As(V), MMA, and DMA. Lab and parameter codes have not been assigned to roxarsone because currently (2002) it is only determined by special request. The method code, however, includes all arsenic species addressed in this report.

Field arsenic speciation, solid-phase extraction, graphite furnace–atomic absorption spectrometry detection, dissolved, I-1190-02

[All species are measured in micrograms-arsenic per liter]

Species	Lab code	Parameter and method code
H_3AsO_3, arsenite [As(III)]	2738	62452A
$H_2AsO_4^-$, arsenate [As(V)] plus possibly other anionic arsenic species	2739	62453A

Laboratory arsenic speciation, phosphate mobile phase, arsine generation, ICP–MS detection, dissolved, I-2191-02

[All species are measured in micrograms-arsenic per liter]

Species	Lab code	Parameter and method code
H_3AsO_3, arsenite [As(III)]	2734	62452B
$H_2AsO_4^-$, arsenate [As(V)]	2735	62453B
$(CH_3)HAsO_3^-$, monomethylarsonate (MMA)	2736	62454B
$(CH_3)_2HAsO_2$, dimethylarsinate (DMA)	2737	62455B

Laboratory arsenic speciation, nitric acid mobile phase, ICP–MS detection, dissolved, I-2193-02

[All species are measured in micrograms-arsenic per liter]

Species	Lab code	Parameter and method code
H_3AsO_3, arsenite [As(III)]	2740	62452D
$H_2AsO_4^-$, arsenate [As(V)]	2741	62453D
$(CH_3)HAsO_3^-$, monomethylarsonate (MMA)	2742	62454D
$(CH_3)_2HAsO_2$, dimethylarsinate (DMA)	2743	62455D

Laboratory arsenic speciation, malonate/acetate mobile phase, ICP–MS detection, dissolved, I-2192-02

[All species are measured in micrograms-arsenic per liter]

Species	Lab code	Parameter and method code
H_3AsO_3, arsenite [As(III)]	2744	62452C
$H_2AsO_4^-$, arsenate [As(V)]	2745	62453C

Application

Methods described in this report can be used to determine As(III), As(V), DMA, and MMA in natural water. Adding EDTA to filtered samples in opaque polyethylene bottles preserves the distribution of arsenic species for up to 3 months. The typical analytical ranges extend from the method detection limits (MDL) to either 100 (for arsine generation) or 1,000 (for nebulization) micrograms-arsenic per liter (µg-As/L) for the methods described. MDLs range from 0.1 to 0.6 µg-As/L, 10 to 60 picograms absolute (for a 100-microliter injection), depending on the arsenic species determined and the analytical method used.

Arsenic-Speciation Methods

Method selection depends on which arsenic species will be determined and the required sensitivity. The most commonly measured species, As(III), As(V), MMA, and DMA, are determined by using a laboratory-speciation method. Moreover, 3-nitro-4-hydroxyphenylarsonic acid (roxarsone) and related compounds also can be determined. When samples are known to contain only As(III) and As(V) species, the short-column laboratory-speciation or field-speciation method can be used.

Laboratory-Speciation Methods. Different laboratory-speciation methods can be used to analyze the field-preserved sample. They differ in column length, column packing, and mobile phases (see tables 1a–c). All use lithium as an injector standard to detect injector malfunctions. The method listed in table 1a is based on methods described by Chen and others (1992) and Rubio and others (1993) for the determination of As(III), As(V), MMA, and DMA. The method uses a phosphate buffer to separate the species in about 7 minutes. Using arsine generation to introduce the analytes into the ICP–MS prevents salt build-up on the cones, eliminates chloride interferences, and improves the method detection limit.

Phosphate buffers previously have been used as the mobile phase to chromatographically separate arsenic species. A gradient of 20 millimolar (m*M*) and 100 m*M* phosphate buffers was used in methods described in the literature (Rubio and others, 1993; Demesmay and others, 1994; Guerin and others, 1997; Palacios and others, 1997). The subject method was optimized with a gradient using 38 m*M* and 75 m*M* phosphate buffer (see table 1a). A typical chromatogram for a 10-µg-As/L standard containing all four arsenic species obtained using the gradient phosphate mobile phase and arsine generation is shown in figure 1.

The conditions listed in table 1b include modifications of a method first described by Jackson and others (2000) for the determination of As(III), As(V), MMA, DMA, and roxarsone in about 8 minutes (see fig. 2). The nitric acid mobile phase effluent can be introduced by nebulization or arsine generation. Arsine, however, cannot be generated from arylarsenicals, such as roxarsone, without using an ultraviolet photoreactor prior to introducing the reduction agent.

Table 1a. Laboratory arsenic-speciation method for the determination of arsenite, arsenate, monomethylarsonate, and dimethylarsinate in filtered natural water

[mm, millimeters; °C, degrees Celsius; m*M*, millimoles per liter; mL/min, milliliters per minute; min, minute; kPa, kilopascal; lb/in^2, pounds per square inch; µL, microliters; r/min, revolutions per minute; L/min, liters per minute]

Chromatographic parameters	
Analytical column	Hamilton PRP-X100, 250 mm by 4.1 mm
Guard column	Phenomenex SecurityGuard SAX, 4 mm by 3 mm
Column temperature	33°C
Mobile phase, gradient	38–75 m*M* phosphate buffer, pH 5.7
Mobile phase flow rate	1.0 mL/min
Gradient program	• 0–1 min, 38 m*M* phosphate buffer • 1–4 min, 75 m*M* phosphate buffer • 4 min to end, 38 m*M* phosphate buffer
Nominal column pressure	4.7 x 10^3 kPa (680 lb/in^2)
Typical injection volume	100 µL
Total elution time	7 min
Sample introduction by arsine generation	
Peristaltic pump	16 r/min
Sodium borohyhride/sodium hydroxide flow rate, orange/orange pump tube	0.9 mL/min
L-Cysteine flow rate, orange/white pump tube	0.5 mL/min
Nitric acid flow rate, orange/white pump tube	0.5 mL/min
Waste flow rate, purple/orange pump tube	3.5 mL/min
Reduction reactor temperature	95°C
Arsine generation reactor temperature	5°C
Argon carrier gas-flow rate	0.8 L/min

Table 1b. Laboratory arsenic-speciation method for the determination of arsenite, arsenate, monomethylarsonate, dimethylarsinate, and roxarsone in filtered natural water

[Introduction of eluate to the inductively coupled plasma–mass spectrometer by either nebulization or arsine generation. mm, millimeters; °C, degrees Celsius; m*M*, millimoles per liter; %, percent; mL/min, milliliters per minute; min, minute; kPa, kilopascal; lb/in^2, pounds per square inch; µL, microliters]

Chromatographic parameters	
Analytical column	Dionex AS7, 4 mm by 250 mm
Guard column	Dionex AG7, 4 mm by 50 mm
Column temperature	33°C
Mobile phase, gradient	2.5–50 m*M* nitric acid in 0.5% methanol
Mobile phase flow rate	1.0 mL/min
Gradient program	• 0–3 min, 2.5 m*M* nitric acid • 3–6 min, 50 m*M* nitric acid • 6 min to end, 2.5 m*M* nitric acid
Nominal column pressure	1.2 x 10^4 kPa (1,800 lb/in^2)
Typical injection volume	100 µL
Total elution time	8 min

Table 1c. Laboratory arsenic-speciation method for the determination of arsenite and arsenate in filtered natural water

[Introduction of eluate to the inductively coupled plasma–mass spectrometer by either nebulization or arsine generation. mm, millimeters; °C, degrees Celsius; m*M*, millimoles per liter; mL/min, milliliters per minute; min, minute; kPa, kilopascal; lb/in^2, pounds per square inch; µL, microliters; min, minute]

Chromatographic parameters	
Analytical column	User packed SAX[1], 4 mm by 50 mm
Guard column	PhenomenexSecurity Guard SAX, 4 mm by 3 mm
Column temperature	33°C
Mobile phase, isocratic	12.5 m*M* malonate and 17.5 m*M* acetate, pH 4.8
Mobile phase flow rate	1.0 mL/min
Nominal column pressure	2.1 x 10^3 kPa (300 lb/in^2)
Typical injection volume	100 µL
Total elution time	2 min

[1]Supelclean LC–SAX quaternary amine, chloride counter ion, strong anion exchange packing.

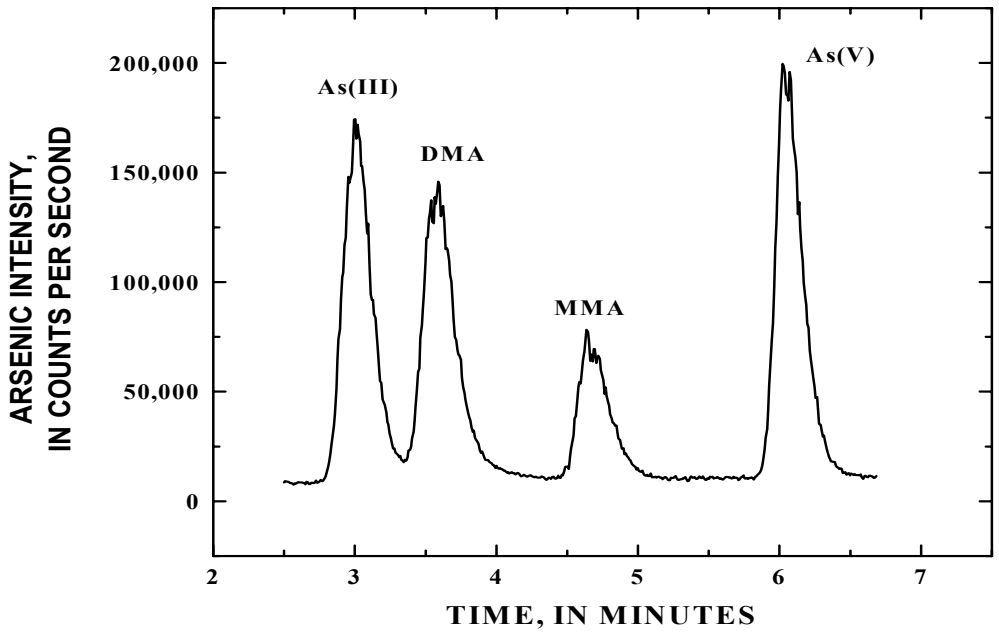

Figure 1. A typical chromatogram using the PRP-X100 column, a gradient phosphate mobile phase, and arsine introduction. The peaks represent a 100-microliter injection of a standard containing 10 microgram-arsenic per liter of arsenite [As(III)], dimethylarsinate (DMA), monomethylarsonate (MMA), and arsenate [As(V)].

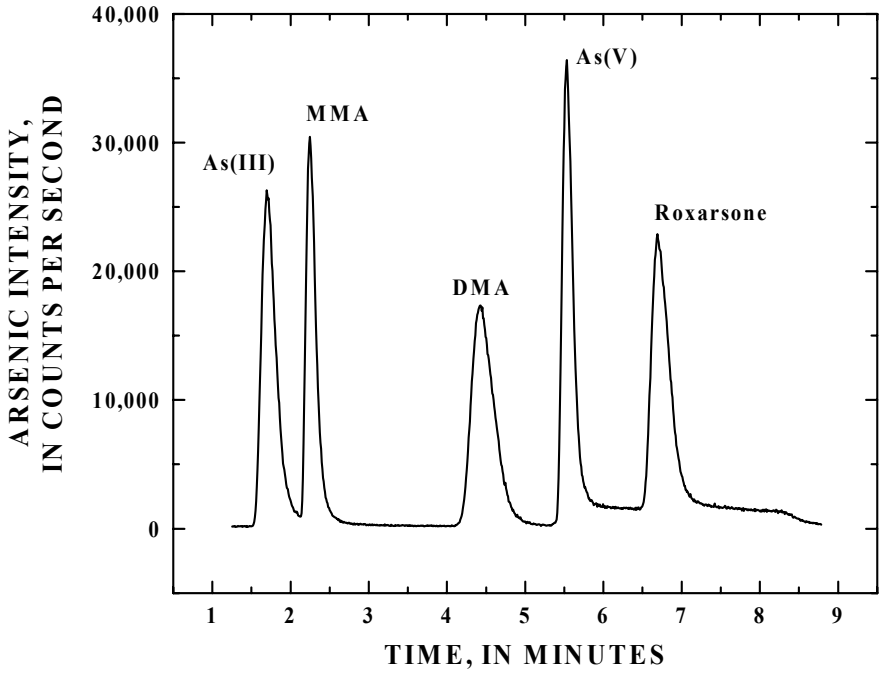

Figure 2. A typical chromatogram using the AS7 column, a gradient nitric acid mobile phase, and nebulizer introduction. The peaks represent a 100-microliter injection of a standard containing 10 micrograms-arsenic per liter of arsenite [As(III)], dimethylarsinate (DMA), monomethylarsonate (MMA), arsenate [As(V)], and roxarsone.

The As(III) and As(V) species can be separated rapidly by using a 50-mm column with strong anion exchange packing (see table 1c). A malonate/acetate mobile phase separates the species in about 3 minutes, as shown in the top graph of figure 3. However, DMA and MMA are unresolved and eluted concurrently with As(III) and As(V), respectively (see fig.4). When the presence of DMA or MMA is indicated, either method I-2191-02 or I-2193-02 can be used to quantitate the arsenic present. Roxarsone, moreover, can be separated from As(III) and As(V) by adding 2 percent (by volume) of methanol to the mobile phase (see bottom graph of fig. 3). A small piece of metallic silver was added to the storage vessel containing the malonate/acetate mobile phase to curtail microbial activity.

The linear dynamic range extends to about 1,000 µg-As/L for each species when using a 100-microliter (µL) sample-injection volume and nebulization to about 100 µg-As/L for each species when using arsine generation. The linear dynamic range can be extended when the analog stage of the detector is calibrated, otherwise samples that have arsenic concentrations that exceed these concentrations either must be diluted or a smaller sample volume must be injected. The method detection limits listed in table 2 were calculated using the U.S. Environmental Protection Agency's (2000) definition.

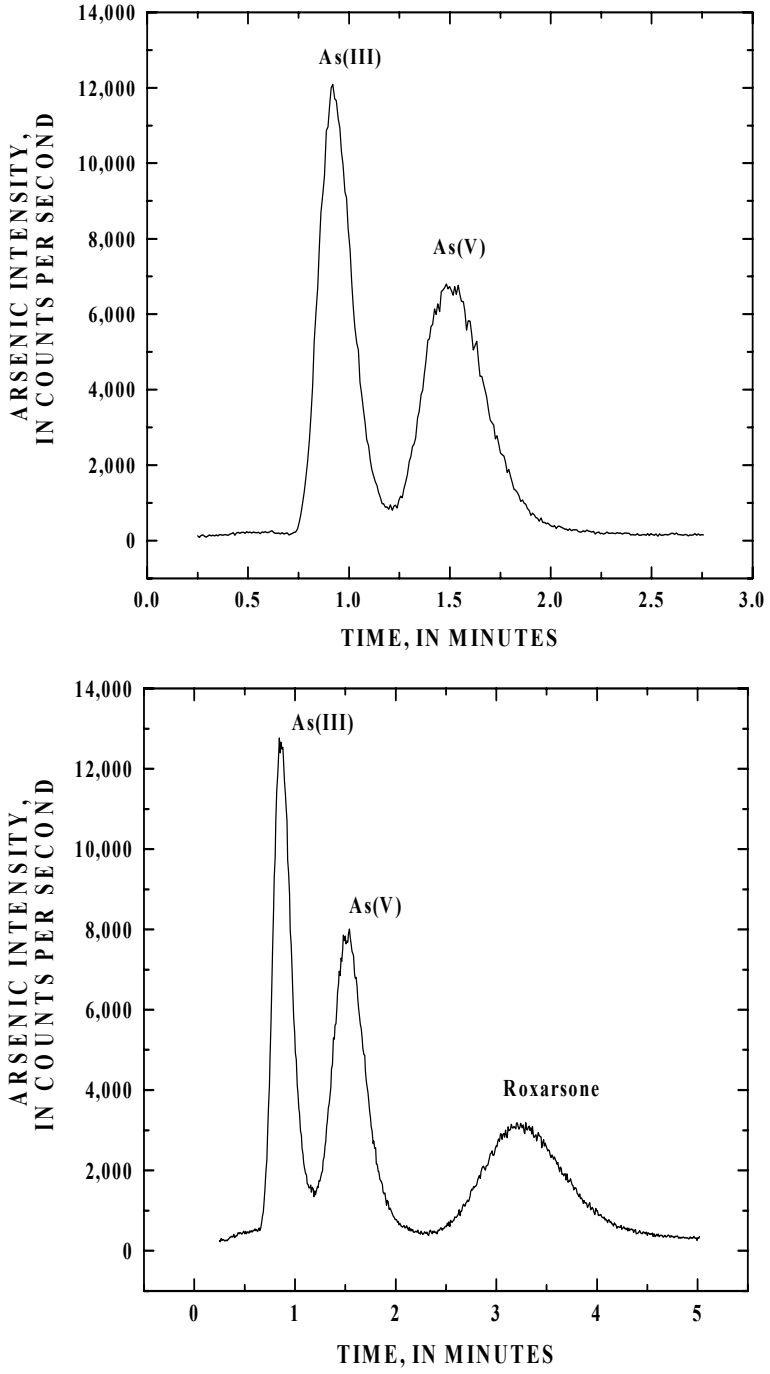

Figure 3. Typical chromatograms using the short LC-SAX column, an isocratic malonate/acetate mobile phase, and nebulizer introduction. The peaks represent a 100-microliter injection of a standard containing 10 micrograms-arsenic per liter of arsenite [As(III)], arsenate [As(V)], and roxarsone.

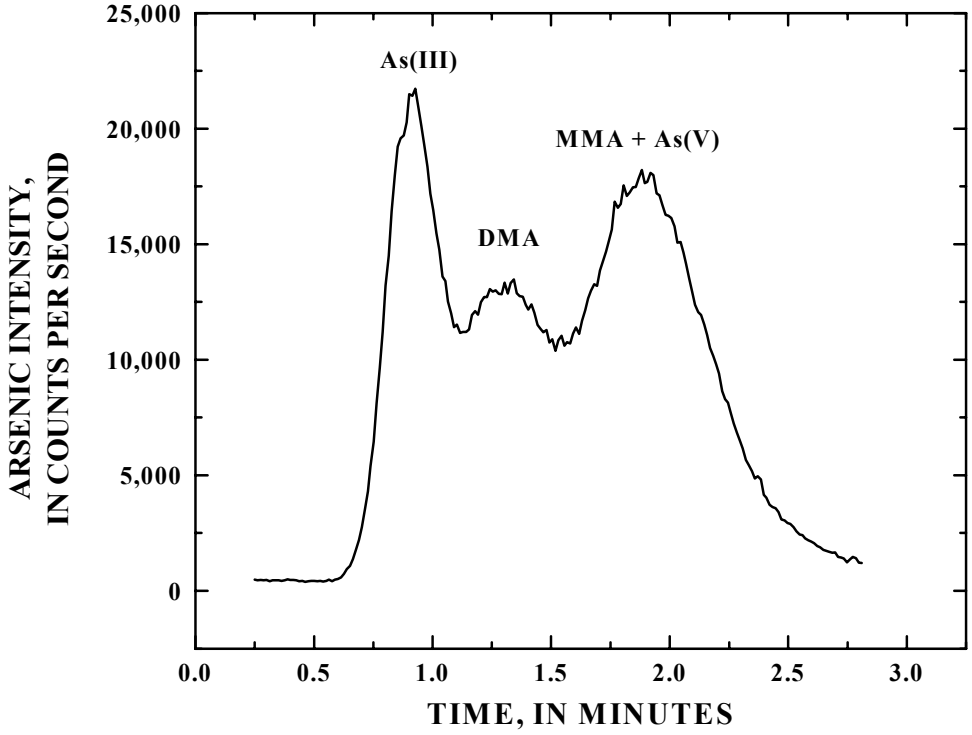

Figure 4. Methylated arsenic species are not resolved from the inorganic arsenic species when using the short-column laboratory method (I-2192-02). Dimethylarsinate (DMA) is not resolved from arsenite [As(III)] and monomethylarsonate (MMA); MMA is not resolved from arsenate [As(V)].

Field-Speciation Method. Ficklin (1983) first described a field method using a strong anion exchange resin for the separation of As(III) and As(V). This method was found to give highly variable results because of gravity feed and channeling within the cartridge (Miller and others, 2000). More recently, Le and others (2000) used a commercially available strong anion exchange cartridge for field speciation. A modification of the method of Le and others (2000) was used to obtain all the field-speciation results. A field-speciation kit consisting of a strong anion exchange cartridge (Supelco, Bellefonte, Penn.; LC-SAX, 3-mL cartridge barrel, 500-mg packing, part number 57017), a plastic 10-mL syringe, and two plastic 15-mL capped centrifuge tubes, one containing the EDTA preservative is used. The LC-SAX cartridge is conditioned with 2 mL of methanol followed by 10 mL of reagent water before use (see table 3). The exchange material can be in the chloride form (as received) or converted to the acetate form (preferred for acid mine drainage) by using 1.7 *M* acetic acid and reagent water. The capacity of the cartridge is reported to be about 0.1 milliequivalent (Supelco, oral commun., 2001).

Table 2. Short-term method detection limits using inductively coupled plasma–mass spectrometry as an arsenic-specific detector

[Based on a 100-microliter injection volume; µg-As/L, micrograms-arsenic per liter; pg, picograms; As(III), arsenite; As(V), arsenate; MMA, monomethylarsonate; DMA, dimethylarsinate; nd; not determined, na; not applicable]

Method	Short-term method detection limits	
	(µg-As/L)	(pg)
***Laboratory speciation*:**		
Long column; phosphate mobile phase; arsine generation; Method I-2191-02		
As(III)	0.1	10
As(V)	.2	20
MMA	.1	10
DMA	.1	10
Long column; nitric acid mobile phase; nebulization; Method I-2193-02		
As(III)	.3	30
As(V)	.3	30
MMA	.2	20
DMA	.2	20
Short column; malonate/acetate mobile phase; nebulization; Method I-2192-02		
As(III)	.6	60
As(V)	.6	60
MMA	nd	na
DMA	nd	na
***Field speciation*:**[1]		
Direct nebulization; Method I-1190-02		
As(III) and As(V)	.3	na

[1]The method detection limit is about 2 µg–As/L when graphite furnace–atomic absorption spectrometry is used.

Table 3. Field arsenic-speciation method for the determination of arsenite and arsenate plus alkyl arsenicals in filtered natural water

[Solid-phase extraction cartridge can be in either the chloride form or acetate form; Analysis of elutriate and extract by either graphite furnace–atomic absorption spectrometry or inductively coupled plasma–mass spectrometry; mL, milliliters; mg, milligrams; *M*, moles per liter; meq; milliequivalent; As(III), arsenite; As(V), arsenate; s, second]

Speciation parameters	
Solid-phase extraction cartridge	Supelco LC-SAX, 3-mL size, 500-mg packing
Cartridge conditioning, chloride form	2-mL methanol; 10-mL deionized water
Cartridge conditioning, acetate form	10-mL 1.7 *M* acetic acid; 10-mL deionized water
Cartridge capacity	0.1 meq
Typical sample volume	10 mL
As(III)	Elutriate fraction
As(V) plus alkyl-arsenic species, if present	Extraction of cartridge using 10 mL of 0.16 *M* nitric acid
Elution and extraction flow rate	1–2 drops/s
Separation of As(V) from alkyl-arsenic species in the extract	Requires additional laboratory separation

Arsenic species are separated in the field by using a syringe to elute 10 mL of EDTA-preserved sample through the cartridge at a rate of 1 to 2 drops per second. Uncharged arsenic species [primarily As(III)] elute from the cartridge, whereas charged species [As(V), MMA, DMA, and others] are retained on the cartridge. The cartridge and elutriate are retained for laboratory arsenic determination. The charged arsenic species are stripped from the cartridge in the laboratory with 10 mL of 0.16 *M* nitric acid. The extract and elutriate are analyzed for total arsenic using direct nebulization ICP–MS (Garbarino, 1999) or graphite furnace–AAS (Jones and Garbarino, 1999). The short-term MDL for ICP–MS is 0.3 µg-As/L regardless of the species (see table 2).

Interferences

Chemical and spectral interferences can affect the accuracy of determining arsenic species unless appropriate procedures are followed. Chemical interferences can affect speciation and analytical methods. Speciation methods can be affected by cations, such as iron, manganese, or aluminum, or by anions, such as sulfate or carbonate, which often compose the sample matrix. Approaches used to mitigate such interferences differ depending on whether laboratory- or field-speciation methods are being used. Selected analytical methods measuring arsenic also are affected by the chemistry of the sample matrix. For example, high matrix concentrations can affect sample atomization in graphite furnace–atomic absorption spectrometry, organoarsenic compounds and complexes can bias arsine generation, and isobaric and molecular ions can affect arsenic determinations by ICP–MS.

Interferences from dissolved iron, manganese, or aluminum can affect the laboratory- and field-speciation methods. These metal cations are problematic in matrices with low redox potential (Eh) and dissolved oxygen concentration, conditions that usually are more common in ground water than in surface water. When ground water is pumped to the surface during sampling, it interacts with atmospheric oxygen to precipitate iron and manganese oxyhydroxides, which provide sorption sites for dissolved arsenic species (Raven and others, 1998) that might negatively bias arsenic speciation results. Formation of the precipitate is minimized by either decreasing the pH to stabilize metal cations or by complexation of the metal cations. Results indicate that EDTA works best to preserve the arsenic speciation for a wide range of sample matrices. In addition to sequestering interfering metal cations, EDTA also buffers the sample solution. Cartridges from the field speciation of selected ground-water samples that were not preserved with enough EDTA showed colored bands most likely associated with Fe or Mn oxyhydroxides. Corresponding laboratory-speciation results for such samples gave slightly higher As(V) concentrations, indicating that a fraction of the As(V) was bound to the oxide bands during the field-speciation procedure.

The oxidation of As(III) to As(V) by photolytically produced free radicals also can affect the determination of arsenic species. The rate of photochemical oxidation is dependent on the radiation wavelength and flux, pH, and sample-matrix composition. Hug and others (2001) have shown that As(III) is oxidized within hours by free radicals formed by solar radiation. Moreover, present experiments have shown that in a matrix having 3 mg/L nitrate, greater than 50 percent of the As(III) is converted to As(V) in less than 3 hours, a rate about five times faster than a control having no nitrate. Such behavior is supported by Sharpless and Linden (2001), who have shown that nitrate can be reduced photolytically to nitrite. Other increases in the rate of As(III) oxidation have been observed when iron (Fe^{3+}) or natural organic matter was present. Opaque polyethylene sample bottles are used to

eliminate the effect of photochemical oxidation by omitting light exposure.

Field-speciation results also can be affected by sample-matrix composition. Positively biased As(V) concentrations are possible when samples contain other anionic arsenic species. Charged arsenic species, including MMA and DMA, are retained on the LC–SAX cartridge with As(V). If quantitation of MMA and DMA is required, or if high concentrations are suspected, further laboratory separations of the cartridge extract are required to access accurately the arsenic species concentrations. For example, when a sample containing only 0.9 µg-As/L of As(V) was eluted through a cartridge, analysis of the cartridge extract gave 2.5 µg-As/L of apparent As(V). Further analysis of the extract using the laboratory-speciation method (see table 1a) gave 0.89 µg-As/L for As(V), 0.92 µg-As/L for MMA, and 0.83 µg-As/L for DMA, for a total arsenic concentration of 2.64 µg/L, a total within 4 percent of the apparent As(V) concentration. Methylated arsenic compounds are used extensively as herbicides, and, therefore, can be present in surface water or ground water that drains agricultural areas.

Other potential problems inherent to the field-speciation method are anions, such as sulfate, that compete with charged arsenic species for the exchange sites of the strong anion exchange packing in the LC–SAX cartridge. When the exchange capacity is exceeded, As(V) is not retained fully on the cartridge and elutes with the fraction that contains As(III). The effects of three different sample matrices containing high sulfate concentrations on the LC-SAX cartridge field-speciation method are shown in figure 5. Each test matrix had about 500 µg-As/L as As(V) in 2,000 mg/L Na_2SO_4, 2,000 mg/L Na_2SO_4 plus 1 mg/L Fe^{3+}, or AMD. The cartridges did not retain As(V) whenever the exchange capacity was exceeded (see 1X dilution in fig. 5). As a result, the As(V) eluted as apparent As(III). All the arsenic, however, was recovered as As(V) when the matrices were diluted by a factor of 100. One disadvantage of matrix dilution is that the analyte concentrations also are diluted. The exchange capacity has not been found to be a limitation for most surface- and ground-water samples. AMD samples, however, often require dilution prior to field speciation. The water matrix must be characterized prior to field speciation to ensure that the exchange capacity will not be exceeded. Concomitant anions are much less of a concern in laboratory speciation because small sample volumes are injected so that column capacity is not exceeded and the retention times for concomitant anions do not coincide with arsenic species.

Spectral interference from argon-chloride molecular ion at m/z 75 when using ICP–MS to determine arsenic has been documented and suitable correction methods have been established (Tan and Horlick, 1986). The interference correction for $^{40}Ar^{35}Cl^{+}$ is accurate for chloride concentrations of at least 5,000 mg/L (Garbarino, 1999). Field or the laboratory chromatographic separation also minimizes the effects from chloride interference. Nevertheless, chloride interference correction usually is used because late-eluting arsenic species might not be fully resolved from chloride in some samples.

Interferences have been reported for arsine generation reactions. Possible interferents include other hydride-forming elements and selected transition metals (Pierce and Brown, 1976; Brindle and Le, 1990; Barth and others, 1992; Chen and others, 1992). Various potential interferents were tested to determine their effect. No interferences were found to substantially affect laboratory speciation when arsine generation is used. Hydride-forming anions of selenium and antimony showed no substantial interference. Chloride, nitrate, and sulfate

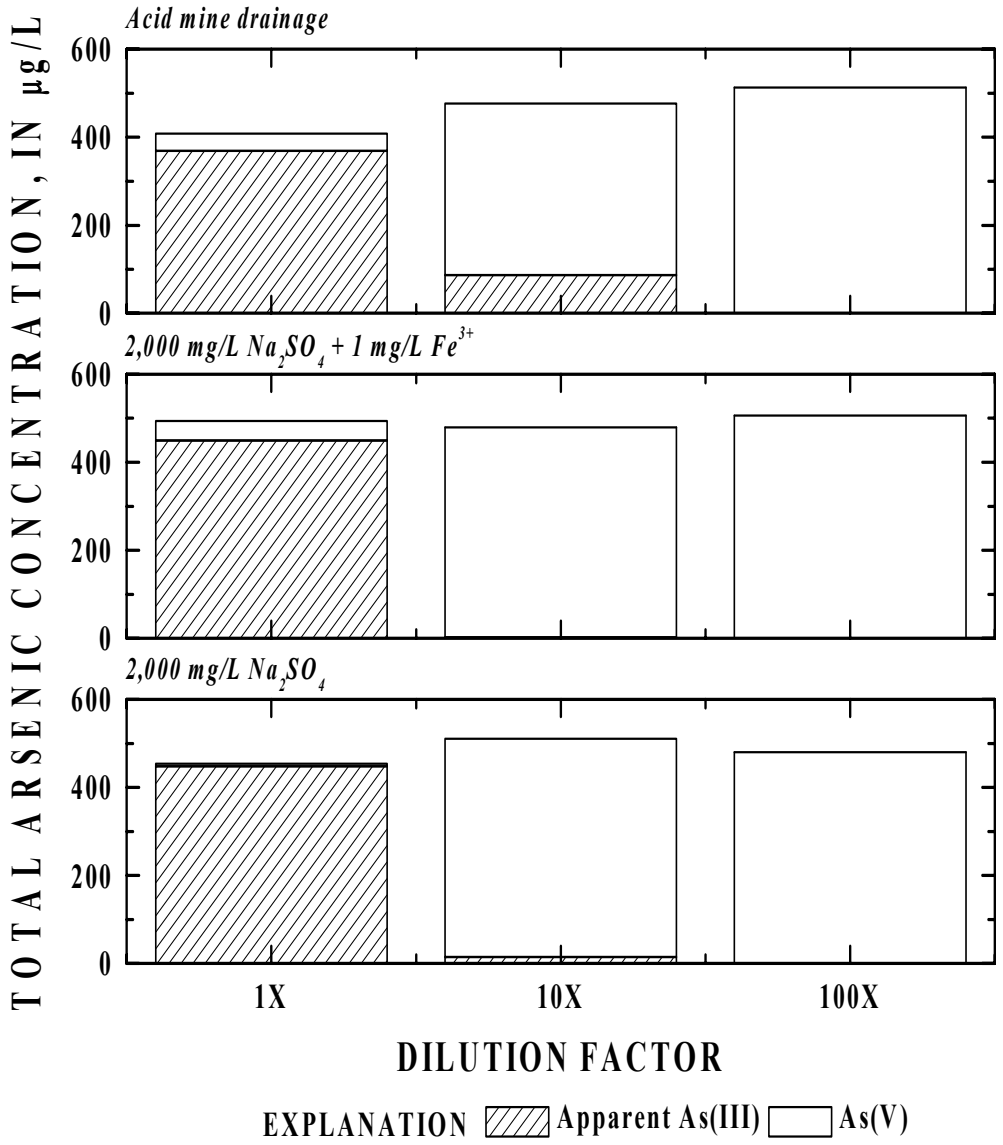

Figure 5. Stacked column charts showing the effects of three different sample matrices on the LC-SAX cartridge field-speciation method. Each test matrix has about 500 micrograms-arsenic per liter (µg/L) of As(V) in either 2,000 milligram per liter (mg/L) sodium sulfate (Na_2SO_4), 2,000 mg/L Na_2SO_4 plus 1 mg/L Fe^{3+}, or acid mine drainage (bottom to top). When the exchange capacity of the cartridge is exceeded (see the 1X dilution), As(V) is not retained resulting in apparent As(III) in the eluate. All the arsenic is recovered as As(V) when the matrices are diluted by a factor of 100.

concentrations of up to 1,000 mg/L showed no chromatographic overlap or reduction in arsenic signal.

Instrumentation

The instrumentation used for the arsenic speciation methods with corresponding operating conditions is listed in table 4. The system is composed of three major components: (1) a high-performance liquid chromatograph with an anion exchange column, (2) a sample introduction system, and (3) an arsenic-specific detector. The high-performance liquid chromatograph with an anion exchange column is not required for the field-speciation method, however, the method uses the same sample introduction system and arsenic-specific detector. The high-performance liquid chromatograph consists of a commercially available controller, fluid unit, and autosampler. The column type, column temperature, mobile-phase composition and flow rate, and injection volume are listed in tables 1a through 1c.

Column effluent from the laboratory-speciation methods can be introduced into the ICP–MS using either nebulization or arsine generation. Direct injection of the column effluent into a pneumatic nebulizer was evaluated to determine the feasibility of using such sample introduction systems for the determination of arsenic speciation in natural-water samples. The signal-to-background ratio using arsine generation was about two times greater than pneumatic nebulization. Moreover, chloride interferences associated with ICP–MS are eliminated when using arsine generation.

Table 4. Instrumentation and operating conditions for the laboratory arsenic-speciation methods

[HPLC, high-performance liquid chromatography; readings per replicate establishes the desired analysis time; acquisition delay is the time prior to acquiring spectrometric data; L/min, liters per minute; ICP–MS, inductively coupled plasma–mass spectrometry; PE part no, Perkin-Elmer part number; cm, centimeter; mm, millimeter; id, inside diameter; °C, degrees Celsius; ms; milliseconds; m/z, mass-to-charge ratio]

HPLC	
Hewlett Packard HP 1090	
Hewlett Packard ChemStation software	
Sample Introduction	
Nebulization	
PE Sciex cross flow nebulizer flow rate	0.8 L/min
Arsine generation	
Perkin-Elmer FIAS Mercury/Hydride Chemifold (PE No. B0507957)	
Flow injection ICP–MS vapor adapter kit (PE part no. B0505540)	
Heating coil consisting of about 300 cm of fluoropolymer tubing (0.35-mm id) wound around a 3x30-cm aluminum cylinder with a heating element controlled by a Cole-Parmer temperature controller	95°C
3-dimensional reactor (PE part no. B501595)	
Cooling manifold consisting of about 4 cm of fluoropolymer tubing (0.35-mm id) threaded inside a ¼ inch (0.6 cm) Swagelock manifold cooled by a Neslab RBC-3 refrigerated circulating chiller	5°C
Detector	
PE Sciex Elan 6100 ICP–MS	
Typical dwell time	500 ms
Readings per replicate	Variable
Acquisition delay	Variable
Mass monitored	7 and 75 m/z

Excessive salt build-up on the interface cones contributed to erratic precision for nebulization when the phosphate mobile phase is used; none of the other mobile phases caused salt or carbon buildup. Chromatographic resolution and peak full width at half maximum were similar regardless of the method of sample introduction.

A commercially available arsine generation manifold (see table 4 and fig. 6) was the basis for the arsine generation system. The manifold and the arsine-generation chemistry were modified to optimize system performance. The efficiency of arsine generation depends on the valence state of arsenic; As(III) is reduced to arsine more easily than As(V), therefore, As(V) is pre-reduced to ensure arsenic is in the proper valence state for the reaction. Potassium iodide has been used routinely for the pre-reduction but arsine generation in a continuous-flow system required a much faster reaction. Chen and others (1992) reported that L-cysteine could be used to quickly pre-reduce As(V) to As(III) under mild acid conditions. Experiments that used various concentrations of L-cysteine in deionized water indicated that 2.5 percent (by weight) gave the optimal response.

Column effluent, L-cysteine, and 0.3 *M* nitric acid are mixed in a reaction coil that is heated to 95°C to aid in the conversion of As(V) to As(III) (see fig. 6). The sodium borohydride reagent is introduced into a three-dimensional reactor just prior to the second mixing coil. The heating caused water vapor to condense on cooler surfaces of the gas/liquid membrane separator and transfer lines. Such condensation resulted in episodes of noisy baselines. Consequently, a second coil cooled to 5°C with a recirculating chiller was added to eliminate the condensation (see fig. 6). The results of various experiments demonstrated that the cooling enhanced the efficiency of the gas/liquid separator and did not affect arsine generation efficiency. Such modifications improved the method detection limits, increased data quality, and provided a robust analytical system.

Column effluent from laboratory-speciation methods that do not use the phosphate mobile phase (see tables 1b and 1c) can be introduced directly into the ICP–MS through the nebulizer. A standard commercially available crossflow nebulizer (see table 4) was used to obtain all the data in this report. Laboratory-speciation methods that use nitric acid or malonate mobile phases also can use arsine generation, however, unless additional sensitivity is required (see table 2), nebulization is less problematic and eliminates the use of various reagents.

The ICP–MS is used as an arsenic-specific detector by measuring the ion intensity at m/z 75. The retention time and the chromatographic peak width determine the dwell time and readings per replicate. The sampling frequency should be at least 10 times the narrowest chromatographic peak width. For example, for a peak 10 s wide, the sampling frequency should be 1 Hz or a dwell time of about 1 s. The typical dwell times were 0.5 to 0.75 s. The number of readings per replicate was used to establish the total elution time.

Examples of typical calibration curves for arsenic species using each laboratory-speciation method and the field-speciation method are shown in figure 7. The As(V) response per unit concentration is nearly equal to that of As(III), demonstrating that the use of the heated reactor with L-cysteine pre-reduced nearly 100 percent of the As(V) (see upper graph in fig. 7). The curves also show the increase in sensitivity gained when arsine generation is used instead of direct nebulization. The lower sensitivity of the laboratory-speciation method using the

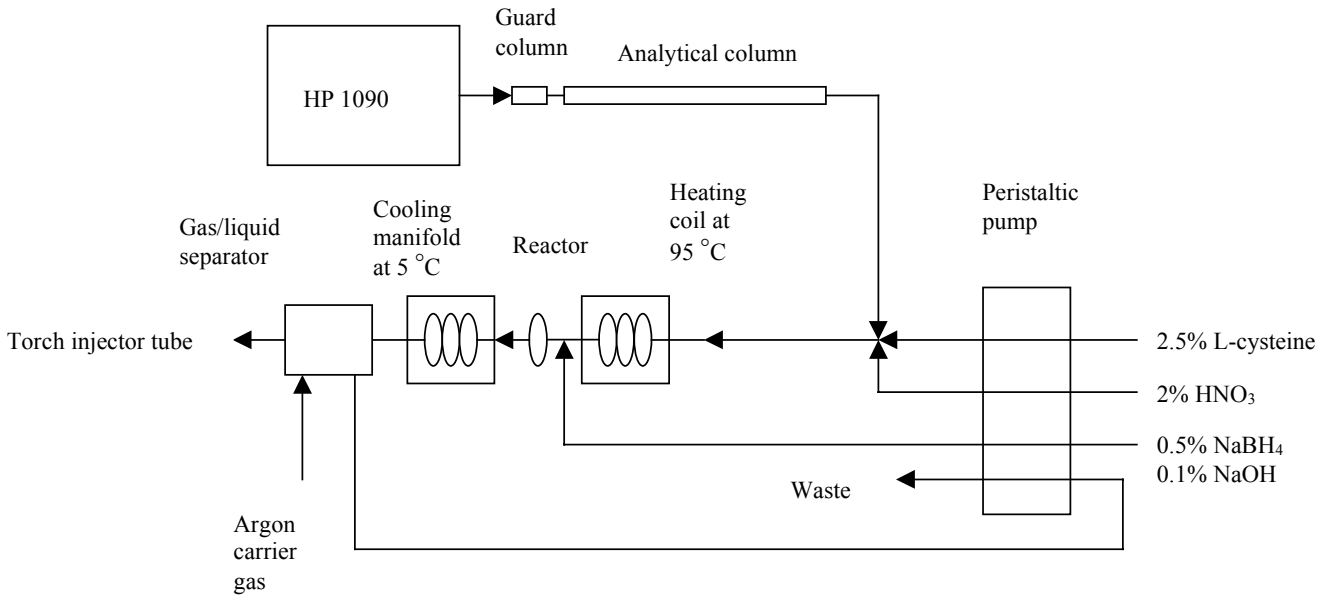

Figure 6. Ion chromatography, arsine generation, and inductively coupled plasma–mass spectrometric system. Reagent concentrations are given in weight percent (%) and temperature is in degree Celsius (°C).

malonate/acetate mobile phase (see bottom graph of fig. 7 and table 1c) presumably is a result of lower nebulization and ionization efficiency. The calibration curves are linear for all methods and had correlation coefficients of at least 0.999. Method detection limits listed in table 2 were calculated using the procedure described by the U.S. Environmental Protection Agency (2000). Refer to PE Sciex (1998), NWQL Standard Operating Procedure MD0359.0 (A.J. Bednar and J.R. Garbarino, U.S. Geological Survey, written commun., 2001), PE Sciex (1999a), and Hewlett-Packard (1986) for details of the operation and maintenance of the instrumentation used. Refer to PE Sciex (1999b) and Hewlett-Packard (1998) for details of the software used to control the instrumentation.

Sample Collection and Preservation

Samples collected for arsenic speciation require preservation to maintain the original distribution of arsenic species. Without preservation, As(III) can be oxidized to As(V) by photolytically produced free radicals, As(V) can be reduced to As(III) by microorganisms or natural organic matter, or arsenic species can coprecipitate with metal oxyhydroxides. MMA and DMA have been found to be much more stable than As(III) and As(V), however, some arylarsenicals are susceptible to degradation by way of photochemical oxidation and microbial reduction. Natural water is filtered using either a 0.45-µm-membrane syringe filter or an inline filter. Exposure of the sample to air must be minimized or eliminated when filtering

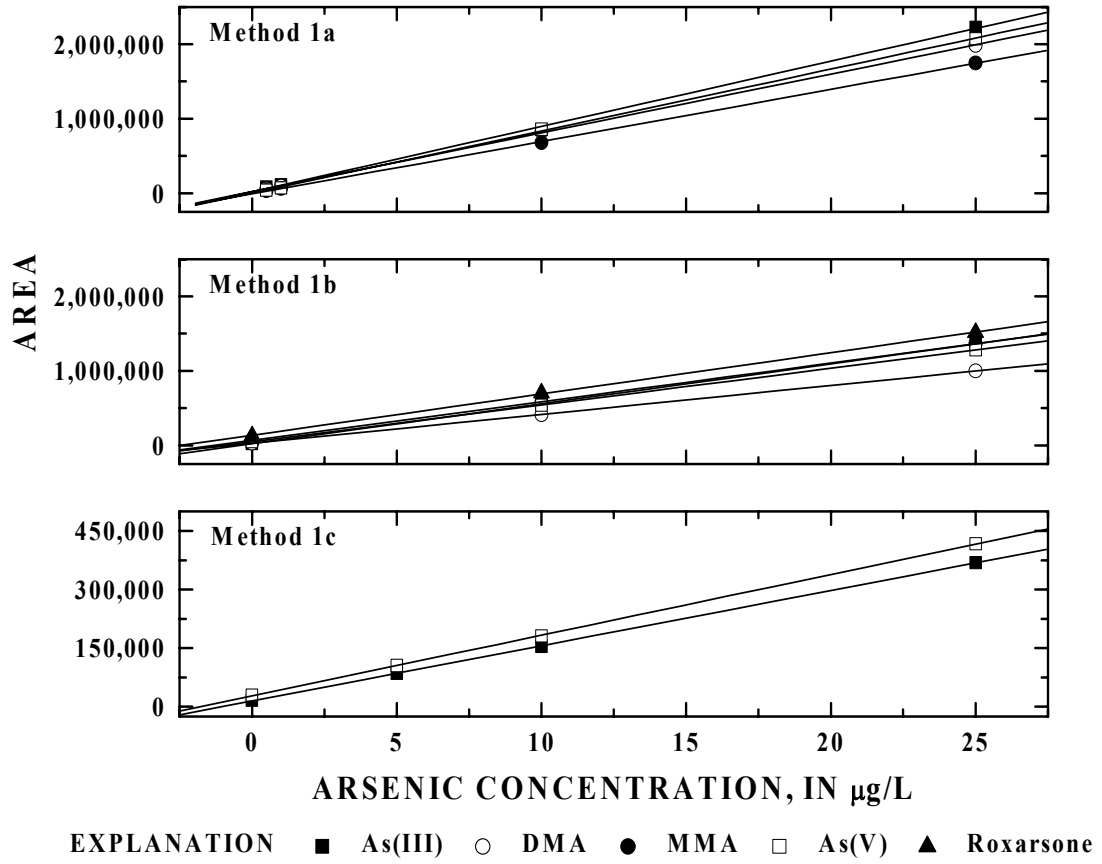

Figure 7. Calibration functions that show the relative sensitivity for arsenic species using laboratory- and field-speciation methods with inductively coupled plasma–mass spectrometric detection. The species determined are arsenite [As(III)], arsenate [As(V)], dimethylarsinate (DMA), and monomethylarsonate (MMA). Method 1a uses phosphate mobile phase with arsine generation; method 1b uses a nitric acid mobile phase with nebulization; and method 1c uses malonate/acetate mobile phase with nebulization. Arsenic concentrations are in micrograms per liter (µg/L).

ground water to prevent oxidation; the risk is minor for aerated surface water. Filtration using such conditions is not problematic because only 10 mL of filtrate is required for the analysis. EDTA is added to the filtrate to eliminate the precipitation of metal oxyhydroxides and reduce the effects of microbial activity. An opaque polyethylene bottle is used to store the preserved sample so that it is not exposed to light. The concentration of the EDTA can be varied, depending on the expected concentration of metal cations like iron, manganese, and aluminum. Only an estimate of the iron concentration is needed because iron is chelated preferentially over other major cations (for example, Ca and Mg).

The iron concentration in most ground water and acid mine drainage is less than 10 mg/L and 500 mg/L, respectively. Therefore, in this study, 100 µL of 0.125 M EDTA was added to 10 mL of natural-water filtrate, and 500 µL of 0.25 M EDTA was added to 10 mL of filtered acid mine drainage, to provide a molar excess of EDTA. Preserved samples were stored in opaque polyethylene bottles to omit light.

Standards, Mobile Phases, and Hydride Reagents

ASTM Type I reagent water (American Society for Testing and Materials, 2000, p. 10) and arsenic-free acids and reagents must be used to prepare all solutions. Reagents were obtained from J.T. Baker (Phillipsburg, N. J.), EM Science (Gibbstown, N. J.), Sigma (St. Louis, Mo.), Aldrich (Milwaukee, Wis.), or Pfaltz & Bauer (Waterbury, Conn.) chemical companies. Primary standards of 100 mg-As/L of each arsenic species were prepared by weighing 173.4 mg of sodium *meta*-arsenite ($NaAsO_2$, CAS 7784-46-5) for As(III), 240.3 mg of potassium dihydrogen arsenate (KH_2AsO_4, CAS 7784-41-0) for As(V), 216.2 mg of monosodium acid methanearsonate (CH_4AsNaO_3, CAS 2163-80-6) for MMA, 184.1 mg of dimethylarsinic acid ($C_2H_7AsO_2$, CAS 75-60-5) for DMA, or 351.2 mg of 4-hydroxy-3-nitrophenylarsonic acid ($C_6H_6AsNO_6$, CAS 121-19-7) into 1 L of reagent water. All primary standards were filtered by using a 0.2-µm membrane filter and stored in a designated fluoropolymer bottle at 4°C in the dark. The concentration and species purity of the primary standards were verified using commercially available certified reference materials for As(III) and As(V) (Spex CertiPrep, Metuchen, N. J.). At least four mixed-species calibration standards extending over the concentration range of 0 to 100 µg-As/L were prepared in 1.25 m*M* EDTA. The arsenic species distribution in calibration standards prepared in this manner were stable for three days in airtight amber glass autosampler vials.

The compositions of the mobile phases that typically are used are described as follows. The pH and molarity of every mobile phase can be increased or decreased slightly to optimize the chromatographic resolution and elution times for the analytes. All mobile phases are filtered using a 0.4-µm membrane filter prior to use. The 50-m*M* phosphate mobile phase was prepared by weighing 13.38 g of sodium phosphate monobasic monohydrate ($NaH_2PO_4 \cdot H_2O$, CAS 10049-21-5) and 0.80 g of sodium phosphate dibasic heptahydrate ($Na_2HPO_4 \cdot 7H_2O$, CAS 7782-85-6) into 2 L of reagent water before adjusting the pH to 5.75 by adding 30 percent ammonium hydroxide (NH_4OH, CAS 1336-21-6). The molarity of the phosphate mobile phase is adjusted to about 38 mM with reagent water using the proportioning valves of the mobile phase delivery system.

The 25-m*M* malonate and 35-m*M* acetate mobile phase was prepared by adding 2.60 g of malonic acid [$CH_2(CO_2H)_2$, CAS 141-82-2] and 17.5 mL of 2 *M* ammonium acetate ($NH_4CH_3CO_2$, CAS 631-61-8) to 1 L of reagent water before adjusting the pH to 4.8 with about 2.2 mL of 30 percent NH_4OH. A small piece of metallic silver was added to the storage vessel containing the malonate/acetate mobile phase to inhibit microbial activity. The molarity of the mobile phase was decreased by about 50 percent using the proportioning valves of the liquid chromatograph system to optimize the chromatographic resolution and elution times for the analytes.

The 50 and 2.5-m*M* nitric acid mobile phases were prepared by diluting 16 *M* nitric acid (HNO_3, CAS 7697-37-2) into an appropriate volume of reagent water. Methanol (CH_3OH, CAS 67-56-1) at 0.5 percent (by volume) must be added to the mobile phases whenever roxarsone is determined.

The solutions used for generating arsine were prepared as follows. The 0.5-percent (weight-to-volume or w:v) borohydride solution is prepared by dissolving 1.00 g of sodium borohydride ($NaBH_4$, CAS 16940-66-2) and 0.20 g sodium hydroxide (NaOH, CAS 1310-73-2) in 200 mL of reagent water. A 2.5 percent (w:v) L-cysteine solution for pre-reducing As(V) to As(III) is prepared by dissolving 6.25 g of L-cysteine ($HSCH_2CHNH_2CO_2H$, CAS 52-90-4) in 250 mL of reagent water. The 0.3 *M* nitric acid solution is prepared by diluting 16 *M* nitric acid into an appropriate volume of reagent water. All three solutions must be prepared daily.

The 0.250 *M* EDTA preservative is prepared by dissolving 46.5 g of EDTA disodium dihydrate ($C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$, CAS 6381-92-6) in 500 mL of reagent water. The molarity of the solution can be diluted with reagent water into a suitable range for a particular sample matrix.

The 10-mg/L lithium solution used as the injection standard for laboratory-speciation samples is prepared by dissolving 95 mg of lithium acetate ($LiC_2H_3O_2$, CAS 546-89-4) in 1 L of reagent water. Lithium is used as the injection standard because of its relatively low natural abundance, high solubility, and redox inactivity. Sample vials containing 3.96 mL of sample are spiked with 40 µL of the lithium solution. The lithium intensity at m/z 7 is monitored to identify autosampler injector malfunctions. An injector malfunction was indicated when the lithium intensity was less than 95 percent of the average expected intensity.

Quantitation

A software program, such as MassLnyx® or Graphical Analysis®, is used to calculate the area under the chromatographic peaks. Linear regression analysis is used to establish the response function from the reagent blank and a series of at least four standard solutions. Typical calibration curves for As(III), As(V), MMA, and DMA using nebulization and arsine generation sample introduction are shown in figure 7. For laboratory-speciation methods, an individual calibration curve is used for each arsenic species so that the concentration of each species is calculated directly. When field speciation is used, total arsenic is determined in sample fractions that contain different arsenic species. Various analytical techniques, for example, ICP–MS (Garbarino, 1999) or graphite furnace–atomic absorption spectrometry (Jones and Garbarino, 1999), can be used to determine total arsenic concentrations in each fraction.

Reporting of Results

The Office of Water Quality and the Quality Assurance Section of NWQL is planning to establish the number of significant figures and other reporting conventions. Nevertheless, the concentration of every arsenic species determined will be reported in micrograms per liter as arsenic.

METHOD PERFORMANCE

The bias and variability of the laboratory- and field-speciation methods were established using reference materials, laboratory solutions having known arsenic species concentrations in reagent-water matrix, and test samples from ground-water, AMD, and surface-water sites. Certified reference solutions for As(III) and As(V) are commercially available (Spex CertiPrep, Metuchen, N. J.), however, no reference solutions are available for MMA and DMA. USGS Standard Reference Water Sample (SRWS) T145 and Environment Canada riverine reference SLRS-2 were used for quality control throughout the analyses of the natural-water test samples. Total arsenic results for T145 always were less than 1 standard deviation

from the most probable value of 9.9 ± 1 µg-As/L during the analysis of test samples. For example, the experimental mean for T145 using the laboratory-speciation method described in table 1a was 9 ± 1 µg-As/L on the basis of 13 data points gathered on 13 nonconsecutive days.

The accuracy of the laboratory-speciation method also was verified using SLRS-2. The certified total arsenic concentration for SLRS-2 is 0.77±0.09 µg/L. The As(III), DMA, MMA, and As(V) concentrations in SLRS-2 were reported by Hwang and Jiang (1994) to be 0.05±0.01 µg-As/L, 0.13±0.01 µg-As/L, 0.1±0.01 µg-As/L, and 0.44±0.02 µg-As/L, respectively, for a total arsenic concentration equal to 0.72 µg/L. SLRS-2 was analyzed on 7 nonconsecutive days using the method described in table 1a to yield As(III), DMA, MMA, and As(V) concentrations of 0.05±0.01 µg-As/L, 0.08±0.01 µg-As/L, 0.10±0.01 µg-As/L, and 0.57±0.04 µg-As/L, respectively, for a total arsenic concentration equal to 0.80 µg/L. The accuracy of the results is acceptable considering the arsenic species concentrations are less than or near the calculated MDLs. The analytical variability of seven 200-µL injections of reagent water containing 0.5 µg-As/L for As(III), As(V), DMA, and MMA is shown in table 5. The average relative standard deviation was about 12 percent.

The accuracy of the field-speciation method was established by using standards of known arsenic species distribution (see table 6). Percentage recoveries for cartridge separation of a standard having 0.89 µg-As/L for As(III) and As(V) were 112 percent for As(III) and 99 percent for As(V); at 8.9 µg-As/L, As(III) recovery was 108 percent and As(V) recovery was 100 percent. The variability (n=3) in the arsenic concentration was 4 percent for As(III) and 3 percent for As(V) at 1 µg-As/L; at 10 µg-As/L, As(III) was 1 percent and As(V) was 0.7 percent.

Stabilization or preservation of the distribution of arsenic species in natural water is a major concern. Successful preservation has been shown to be matrix-composition dependent (Palacios and others, 1997). Arsenate can be reduced spontaneously to arsenite in some natural water even after a sample has been filtered to remove living organisms (Crecelius and others, 1986; Hall and others, 1999). Furthermore, dissolved organic carbon may reduce arsenic species, and the oxidation of As(III) to As(V) by hydrolxyl and dichloro free radicals photolytically produced in the presence of dissolved iron also has been reported (Emett and Khoe, 2001). Aqueous nitric, perchloric, hydrochloric, and acetic acids have been used to help stabilize As(III) and As(V) species, and stabilization was improved by storing samples at temperatures below 15°C (Portman and Riley, 1964). Quick-freezing the sample with liquid nitrogen, however, was recommended to preserve the As(III) and As(V) speciation in water samples (Crecelius and others, 1986). Storing samples at 5°C preserved As(III) and As(V) speciation in water samples for about 30 days, whereas using 0.1 percent nitric or hydrochloric acid altered the arsenic species distribution (Hall and others, 1999). Other studies have shown that EDTA preserved arsenic speciation distributions in three ground-water samples for up to 14 days (Gallagher and others, 2001). Some of these stabilization practices are either not practical for field applications, are not amenable to the analytical methodology, or have not been tested on a large number of samples with different matrix compositions.

The strategy in this study was to evaluate several preservation techniques using a reagent-water sample, with and without iron, and having a known distribution of As(III) and As(V) before testing the most promising technique on ground-water, AMD, and surface-water

Table 5. Variability of replicate determinations on 200-microliter injections of 0.5 microgram-arsenic per liter of arsenite, arsenate, dimethylarsinate (DMA), and monomethylarsonate (MMA) in reagent water

[% RSD, percent relative standard deviation]

Replicate	Arsenite	Arsenate	DMA	MMA
1	0.62	0.54	0.62	0.63
2	.44	.52	.41	.46
3	.42	.54	.46	.42
4	.48	.52	.45	.44
5	.49	.48	.48	.45
6	.50	.41	.43	.45
7	.49	.54	.46	.46
Mean	.49	.51	.47	.47
Standard deviation	.06	.04	.06	.06
% RSD	12	8	13	13

Table 6. Bias and variability of the field-speciation method using inductively coupled plasma–mass spectrometry for an arsenic specific detector

[As(III), arsenite; As(V), arsenate; µg-As/L, micrograms-arsenic per liter; *n*, number of replicates]

	Experimental	
	As(III), (µg-As/L)	**As(V), (µg-As/L)**
Bias, *n*=3		
Theoretical concentration of As(III) and As(V)		
0.89 µg-As/L	1.0	0.88
8.9 µg-As/L	9.6	8.9
	As(III), (percent)	**As(V), (percent)**
Variability, *n*=3		
Concentration of As(III) and As(V)		
1 µg-As/L	4	3
10 µg-As/L	1	0.7

samples. Methylated arsenic species were not included because these species are stable and do not require preservation (Crecelius and others, 1986). Experiments were conducted to determine the effects of ambient light, hydrochloric acid (0.06 *M*), nitric acid (0.08 *M*), sulfuric acid (0.09 *M*), and EDTA (1.25 m*M*) on the preservation of arsenic species. Clear borosilicate glass vials (1 absorbance unit at 250 nanometers, measured with respect to air) were used for light experiments, and brown borosilicate glass vials (1 absorbance unit at 550 nanometers, measured with respect to air) were used for dark experiments.

Experimental results indicate that the distribution of As(III) and As(V) is maintained for at least 120 hours (5 days) when EDTA was added (see top graph in fig. 8); exposure to ambient light was not a factor. Sulfuric acid worked nearly as well, but the distribution began to shift slightly after about 100 hours. The nitric acid preserved the distribution if samples were not exposed to light, however, if exposed to light, As(III) was oxidized to As(V) (see center graph in fig. 8). The oxidation of As(III) occurs as part of a redox couple with nitrate being reduced photolytically to nitrite in water on exposure to ultraviolet radiation (Sharpless and Linden, 2001). Hydrochloric acid shifted the distribution quickly with or without exposure to

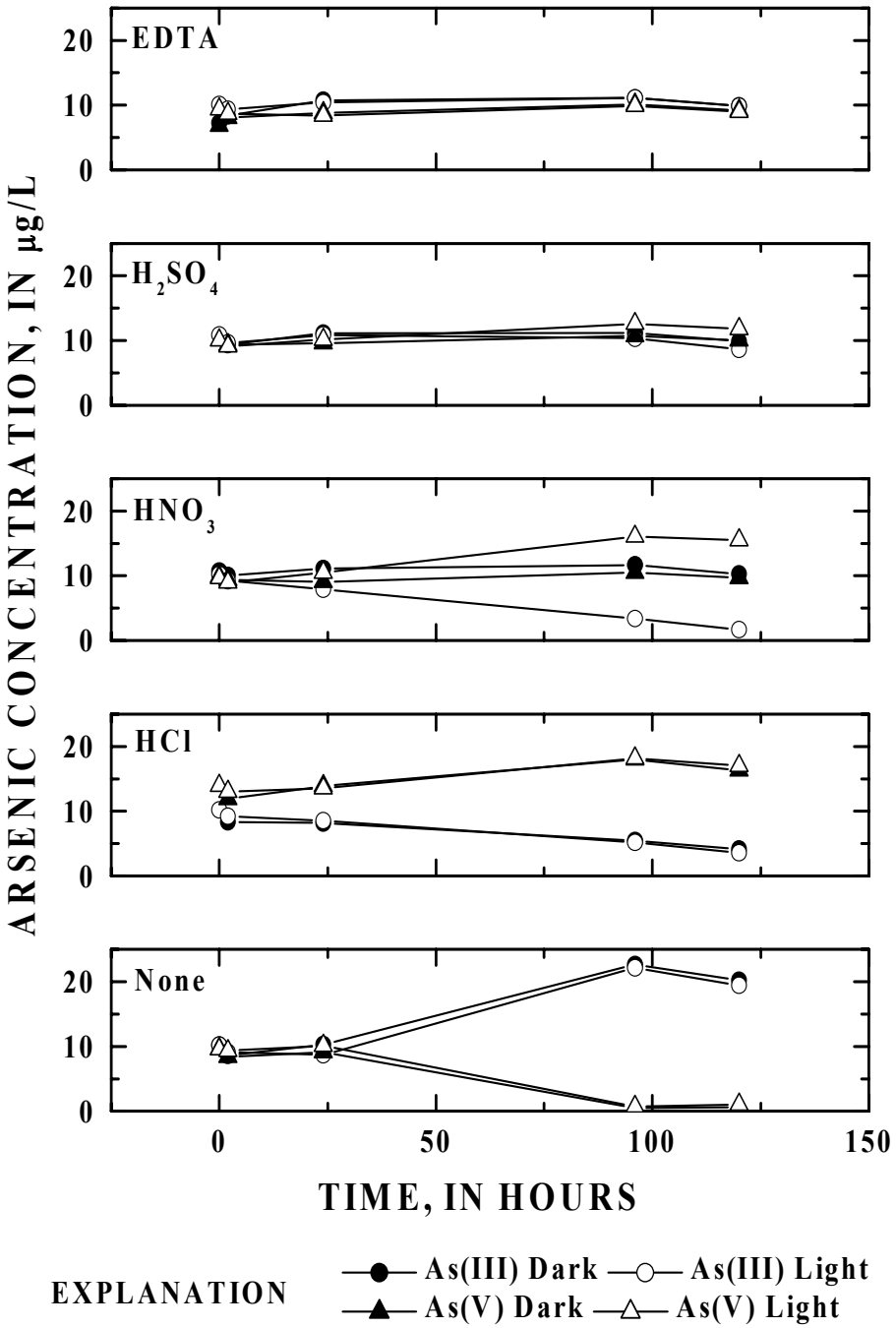

Figure 8. Ethylenediaminetetraacetic acid (EDTA), sulfuric acid (H_2SO_4), nitric acid (HNO_3), and hydrochloric acid (HCl) as preservatives for arsenic speciation and the effects of ambient light. The experimental solution initially contained an equal distribution of As(III) and As(V) in reagent water. The top graph shows that EDTA preserved the arsenic distribution for 120 hours. Arsenic concentrations are in micrograms per liter (µg/L).

light. The cause for the change in distribution is unknown but has been reported by others (Hall and others, 1999; Gallagher and others, 2001). It is possible that trace concentrations of reagent impurities, such as iron, might have affected the preservation. If no preservative is used, the distribution of the arsenic species changes within 2 days with or without light exposure. Moreover, As(V) was reduced to As(III) presumably by microbial activity (see bottom graph of fig. 8).

The results of similar experiments conducted over a longer period (14 days) with iron present (1 mg/L Fe^{3+}) are shown in figure 9. Experimental results show that EDTA again maintained the arsenic distribution (top graph in fig. 9). As with the experiments without iron, sulfuric acid worked nearly as well, and nitric acid preserved the distribution when light was omitted (second and center graph, respectively, in fig. 9). None of the other preservatives maintained the distribution for more than 24 hours. The arsenic distribution is almost shifted instantaneously from As(III) to As(V) with light exposure when hydrochloric acid is present. The oxidation of As(III) is part of a redox couple where $FeCl^{2+}$ is photolyzed to Fe(II) and a chlorine atom that is scavenged rapidly by a chloride anion to form dichlororadicals, which oxidize As(III) to As(V) by an As(IV) intermediate (Emett and Khoe, 2001); a similar mechanism also was proposed for other ionic iron species (Hug and others, 2001). Arsenate is sorbed to iron oxyhydroxides that precipitate at the pH (3 to 4) of the test solution when no preservative is present (see bottom graph in fig. 9).

Results from the laboratory experiments outlined above indicated that EDTA and opaque sample bottles combine to offer the best method for preserving the arsenic species distribution. The preservation technique was tested on samples with a wide range of sample matrices. Ground-water samples were collected for laboratory and field arsenic speciation from 60 sites in the vicinity of Fallon, Nevada, 9 sites in the Republic of Bangladesh, and 2 sites near Golden, Colorado. Acid mine drainage samples (10) were collected at sites clustered within three mineralized regions of Colorado. The Mammoth Shaft, Parole Shaft, Pumphouse Sump, Summitville, and Wetland Seep sites are within the Platoro caldera in south-central Colorado, the Koehler Tunnel and adjacent Koehler Breakdown sites are near the summit of Red Mountain Pass southeast of Ouray, Colorado, and the Argo Tunnel, Quartz Hill Tunnel and Virginia Canyon Mine sites are in the Central City mining district near Idaho Springs, Colorado.

The ranges for various chemical properties and constituents that could affect arsenic speciation if preservation was not used are listed for the test samples in table 7. Concentrations of Fe, Mn, and SO_4^{2-} in acid mine drainage samples exceeded those for ground-water samples by 3 to 4 orders of magnitude in most cases. The maximum total arsenic concentration was about 14,000 µg/L and the percentage of As(III) ranged from 0 to 90 percent for the samples tested [see fig. 10; also table 7 for the actual range of As(III) and As(V) concentrations].

Linear regression analysis and the Paired Sign Test were used to evaluate whether the laboratory-speciation results for the preserved samples were significantly different from the field-speciation results. Arsenic-speciation results for ground-water samples were evaluated separately from the acid mine drainage results because of the large difference in matrix composition, however, total arsenic results were not treated separately. The slope (1.01±0.02) and *y*-intercept (0.6±2) coefficients from the linear regression of As(III) ground-water results

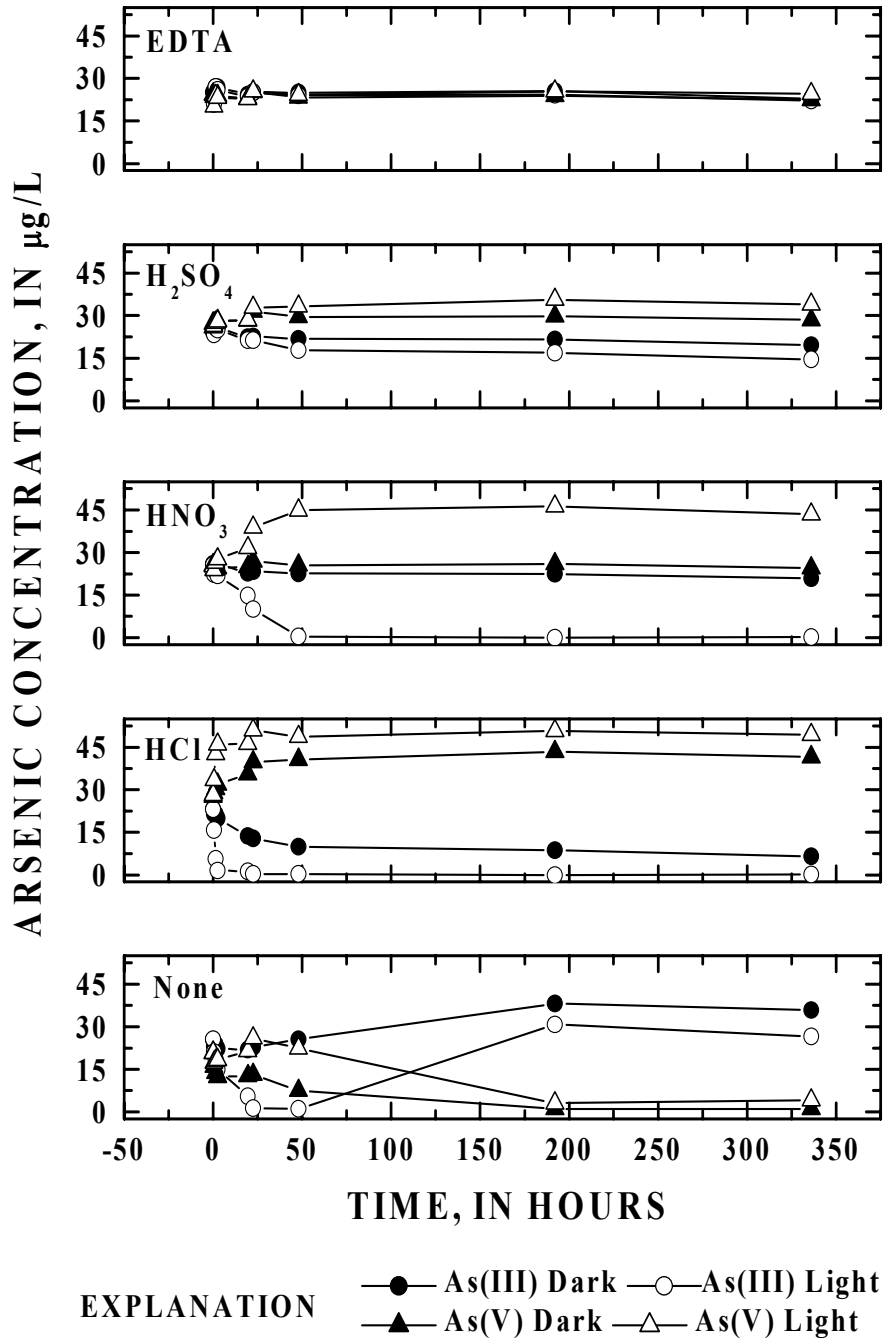

Figure 9. Ethylenediaminetetraacetic acid (EDTA), sulfuric acid (H_2SO_4), nitric acid (HNO_3), and hydrochloric acid (HCl) as preservatives for arsenic speciation in samples having iron and the effects of ambient light. The experimental solution initially contained an equal distribution of As(III) and As(V) and iron in reagent water. The top graph shows that EDTA preserved the arsenic distribution for 14 days. Arsenic concentrations are in micrograms per liter (µg/L).

Table 7. Sample sites and matrix composition for the test samples analyzed

[As(III), arsenite; As(V), arsenate; µg-As/L, microgram-arsenic per liter; pH, negative log of hydrogen ion concentration; Eh, redox potential in millivolts; Fe, iron; Mn, manganese; SO_4^{2-}, sulfate; $CaCO_3$, calcium carbonate; mg/L, milligram per liter; --, not determined; <, less than]

Sampling site	pH	Eh	As(III) [µg-As/L]		As(V) [µg-As/L]		Fe (mg/L)	Mn (mg/L)	SO_4^{2-} (mg/L)	$CaCO_3$ (mg/L)
			Range	Median	Range	Median				
Ground water										
Fallon, Nevada	6.5–9.3	--	0–300	3.1	0.1–1,080	36	<0.005–0.8	<0.003–4.2	<0.1–1,680	0.8–1,080
Peoples Republic of Bangladesh	6.5–6.9	--	4–720	92	2.5–200	20	0.1–11	0.2–2.4	<0.1–12	160–240
Golden, Colorado	--	--	7–83	--	13–220	--	<0.005–0.4	<0.003–0.034	66–78	--
Acid mine drainage			As(III) [µg-As/L]		As(V) [µg-As/L]					
Argo Tunnel	2.9	652	5		107		128	74	2,690	--
Koehler Tunnel	3.5	626	390		480		105	3.0	560	--
Koehler Breakdown	2.8	713	89		7,050		493	16	2,230	--
Mammoth Shaft	4.3	80	440		360		601	38	2,520	--
Parole Shaft	5.8	162	12,800		1,500		100	12	890	--
Pumphouse Sump	3.1	566	690		710		346	28	1,500	--
Quartz Hill Tunnel	3.0	648	15		180		639	66	4,700	--
Summitville	3.5	620	11		190		210	16	1,940	--
Virginia Canyon Mine	2.8	678	28		3,660		381	36	2,940	--
Wetland Seep	6.3	100	360		65		213	23	900	--

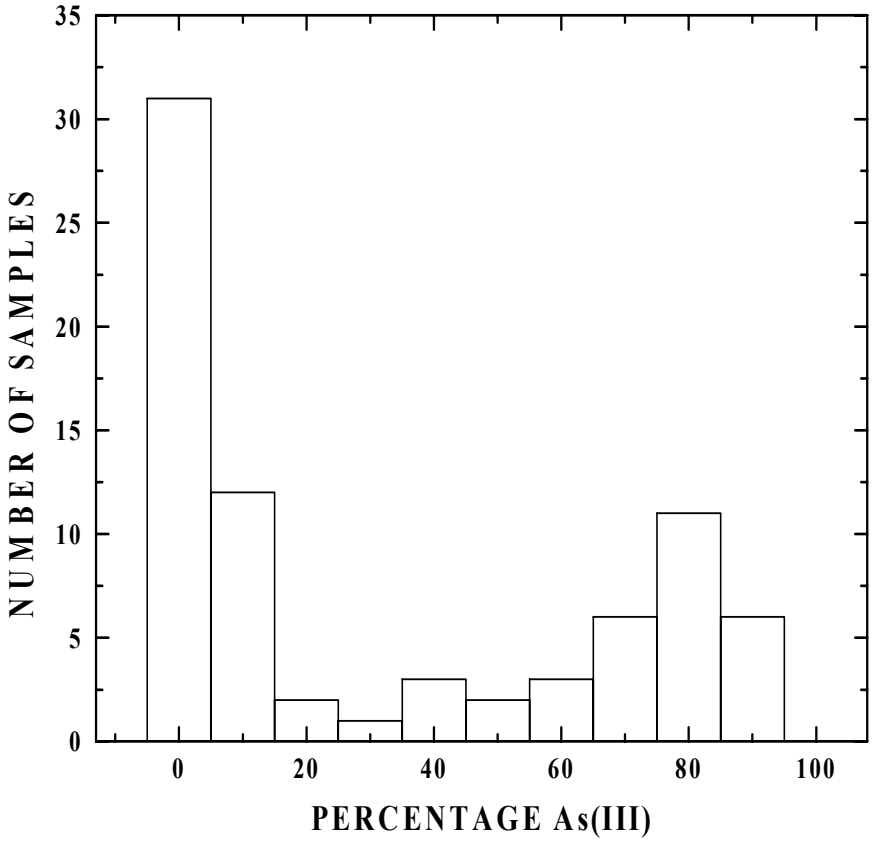

Figure 10. Distribution of As(III) percentage in ground-water and acid mine drainage samples.

indicates that there is no significant difference between the two data sets at the 95-percent confidence interval (see table 8 and top graph in fig. 11). Moreover, the *p*-value (0.0959) from the Paired Sign Test also indicated that there is no significant difference. The corresponding regression coefficients and *p*-value for As(V) suggest that the laboratory-speciation results were slightly greater than the field-speciation results at the 95-percent confidence interval (slope=1.03±0.01 (see table 8 and bottom graph in fig. 11). The systematic error might arise when As(V) is sorbed to metal oxyhydroxides precipitated at the head of the cartridge during sample processing. Precipitation would occur whenever the concentration of the EDTA preservative was less than the concentration required to complex all the iron, manganese, and aluminum cations.

The slope (1.087±0.0005) and *p*-value (0.0313) for the acid mine drainage results indicate that the laboratory speciation As(III) results were slightly greater than the field-speciation results at the 95-percent confidence interval (see table 8 and top graph in fig. 12). The bias might have resulted from As(III) oxidation during field speciation or from the 50 to 100X dilutions required for the acid mine drainage samples. However, results for As(V) are not significantly different (slope=1.0±0.2, *p*-value>0.9999)

Table 8. Statistical summary of laboratory in relation to field arsenic speciation results

[%, percent; *r*, correlation coefficient; *n*, number of replicates; As(III), arsenite; As(V), arsenate; ±, plus or minus; <, less than]

Species	Linear regression analysis at the 95% confidence interval			Paired sign test
	Slope	*y*-intercept	*r*	*p*-value
Ground-water samples, n=71				
As(III)	1.01±0.02	0.6±2	0.9981	0.0959
As(V)	1.03±0.01	4±2	0.9989	<0.0001
Acid mine drainage samples, n=10				
As(III)	1.087±0.005	22±24	0.9999	0.0313
As(V)	1.0±0.2	-200±800	0.9869	>0.9999
All samples, n=81				
As(III) plus As(V)	1.005±0.004	6±7	0.9999	<0.0001

suggesting that oxidation was not the source of the bias (see table 8 and bottom graph of fig. 12).

The slope and *y*-intercept of the graph shown in figure 13 for total arsenic, the sum of As(III) and As(V), indicates that there is no significant difference between the two methods; all the arsenic was preserved. The *p*-value (<0.001) from the Paired Sign Test suggests that the results were statistically different, however, the difference is within experimental variability and is not significant analytically (see table 8).

The preservation period for maintaining the original arsenic species distribution also was investigated. A representative ground-water and acid mine drainage sample collected in opaque polyethylene bottles and preserved with EDTA were analyzed repeatedly for about 3 months. Results in figure 14 show that the distribution of arsenic species was maintained successfully during this period. The change in the As(III):As(V) ratio was –5 percent for the Colorado Well sample and +3 percent for the Koehler Tunnel sample. The arsenic distribution in other ground-water samples from Bangladesh and Nevada with less than 10 µg/L total arsenic was stable for at least 60 d. However, the arsenic species distribution in unpreserved samples was not maintained. For example, the As(III) concentration in an EDTA preserved filtered Bangladesh ground-water sample was 720 µg-As/L compared to 95 µg-As/L in the unpreserved sample over a 1-month period, even though the total arsenic concentration in the two samples was unchanged.

Field-spike recoveries for As(III), As(V), DMA, and MMA were determined using the laboratory-speciation method on selected ground-water samples. Laboratory-speciation results for two samples spiked in the field with 50 µg-As/L of each species provided acceptable recoveries of 82 to 100 percent for As(III), 97 to 102 percent for As(V), 90 to 104 percent for DMA, and 81 to 96 percent for MMA. Percentage recoveries for a 100 µg-As/L field spike using the field-speciation method ranged from 102 to 107 percent for As(III) and 105 to 106 percent for As(V).

The comparison of the laboratory- and field-arsenic speciation results for MMA and DMA could not be made because the ground-water and AMD test samples did not contain

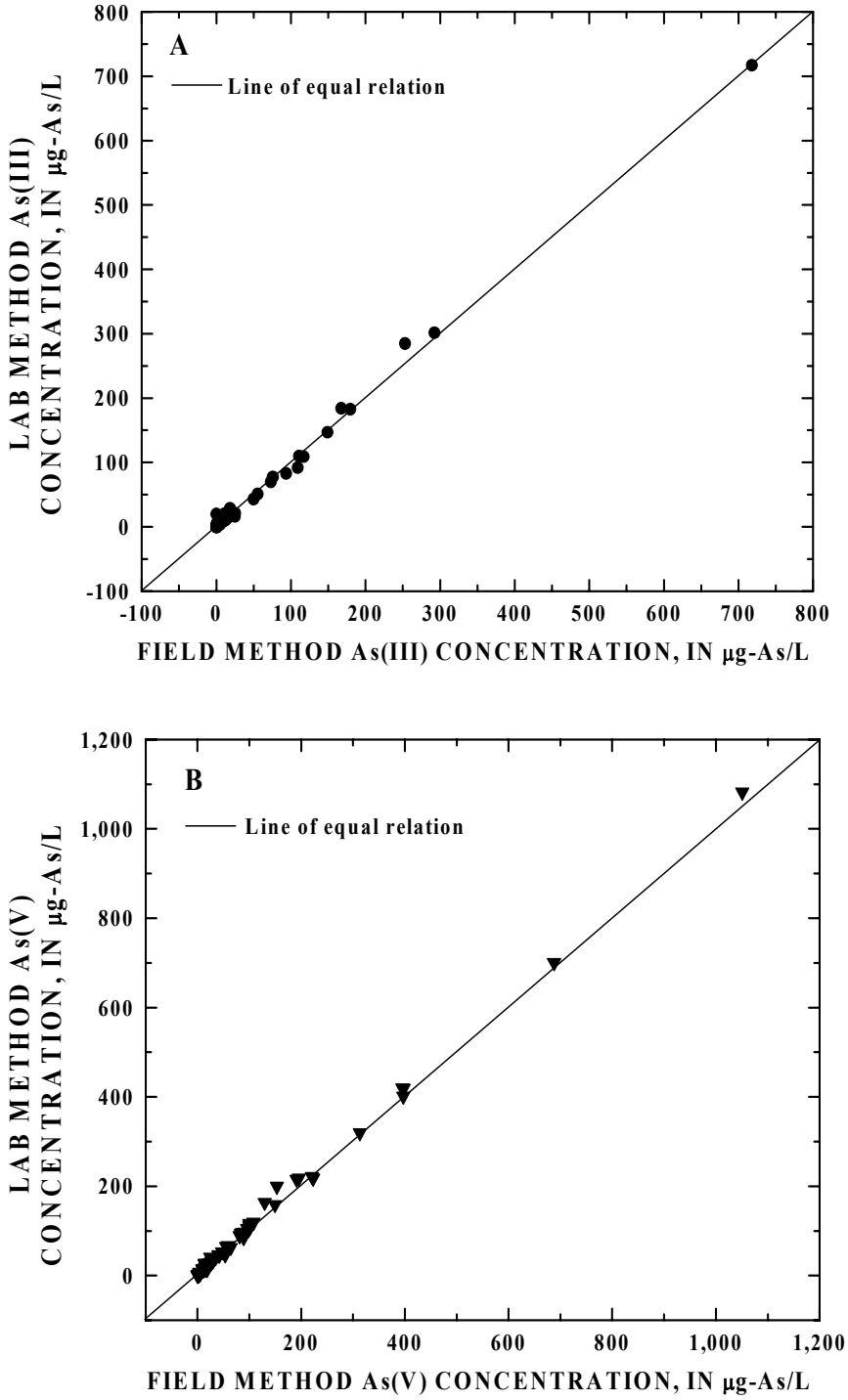

Figure 11. Linear regression analysis of laboratory and field dissolved As(III) [A] and dissolved As(V) [B] results for ground-water samples. Concentrations are in micrograms-arsenic per liter (µg-As/L).

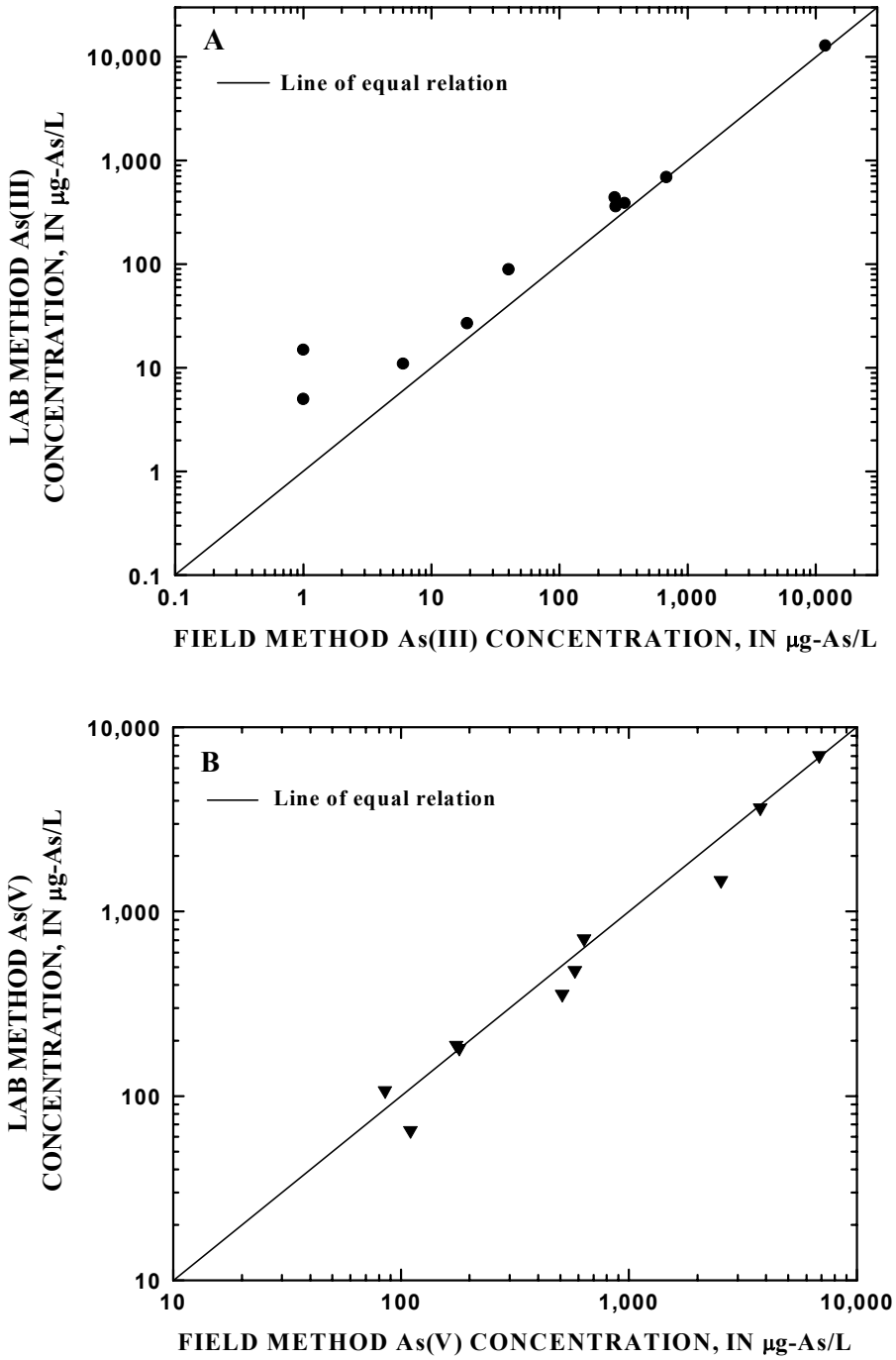

Figure 12. Linear regression analysis of laboratory and field dissolved As(III) [A] and dissolved As(V) [B] results for acid mine drainage samples. Concentrations are in micrograms-arsenic per liter (µg-As/L).

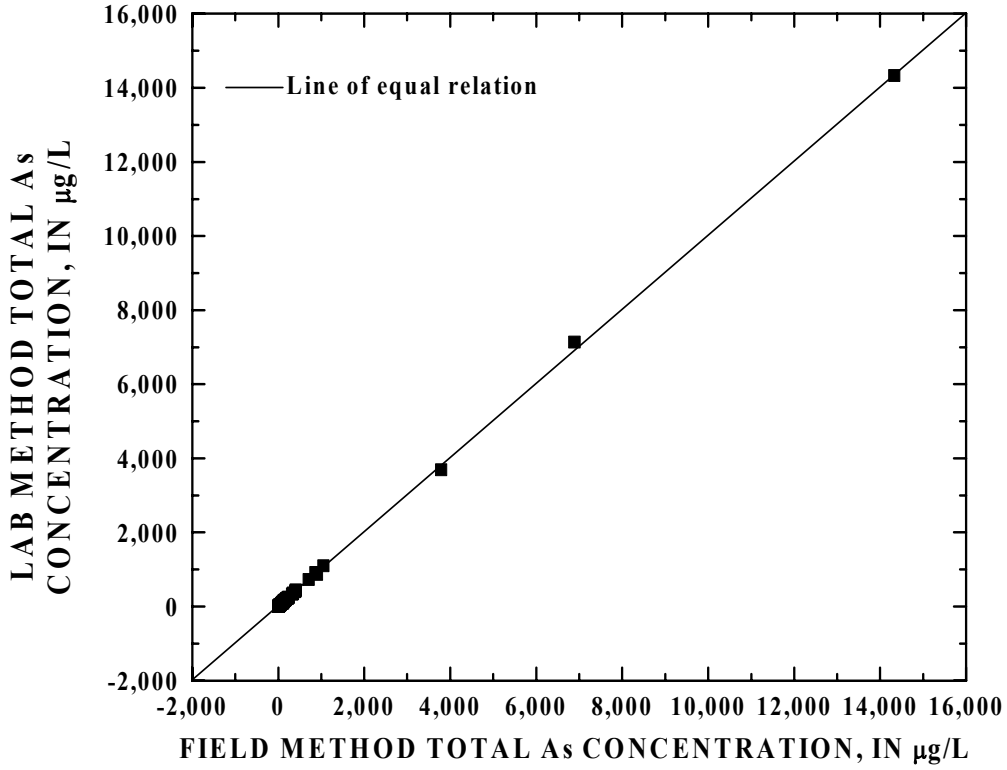

Figure 13. Linear regression analysis of laboratory and field total dissolved arsenic [As(III) plus As(V)] results for all test samples. Arsenic concentrations are in micrograms per liter (µg/L).

these species. Furthermore, MMA and DMA usually are not determined by the field-speciation method (see Interferences). Because MMA and DMA are associated with arsenic-containing herbicides, surface-water samples were collected from streams surrounding agricultural areas where such herbicides have been used historically. Unlike the ground-water and AMD test samples for As(III) and As(V) that were preserved with EDTA, these samples were refrigerated at 4°C and shipped overnight to the laboratory for analysis because MMA and DMA are stable without preservation (Crecelius and others, 1986). Moreover, blind blanks and blind duplicates were submitted and analyzed so that the accuracy of the method could be evaluated.

Twenty-four samples were collected from basins or subbasins in Mississippi draining agricultural areas where the herbicide monosodium methylarsonate (MSMA) was applied. Samples were collected at 1- or 2-week intervals from early March through the middle of September 1997. MSMA is normally applied to the fields from May through July for cocklebur control and from September to October on fallow or stale seedbeds. Samples were analyzed for MMA, DMA, As(III), and As(V) using the chromatographic separation described in table 1a coupled with arsine generation to enhance sensitivity.

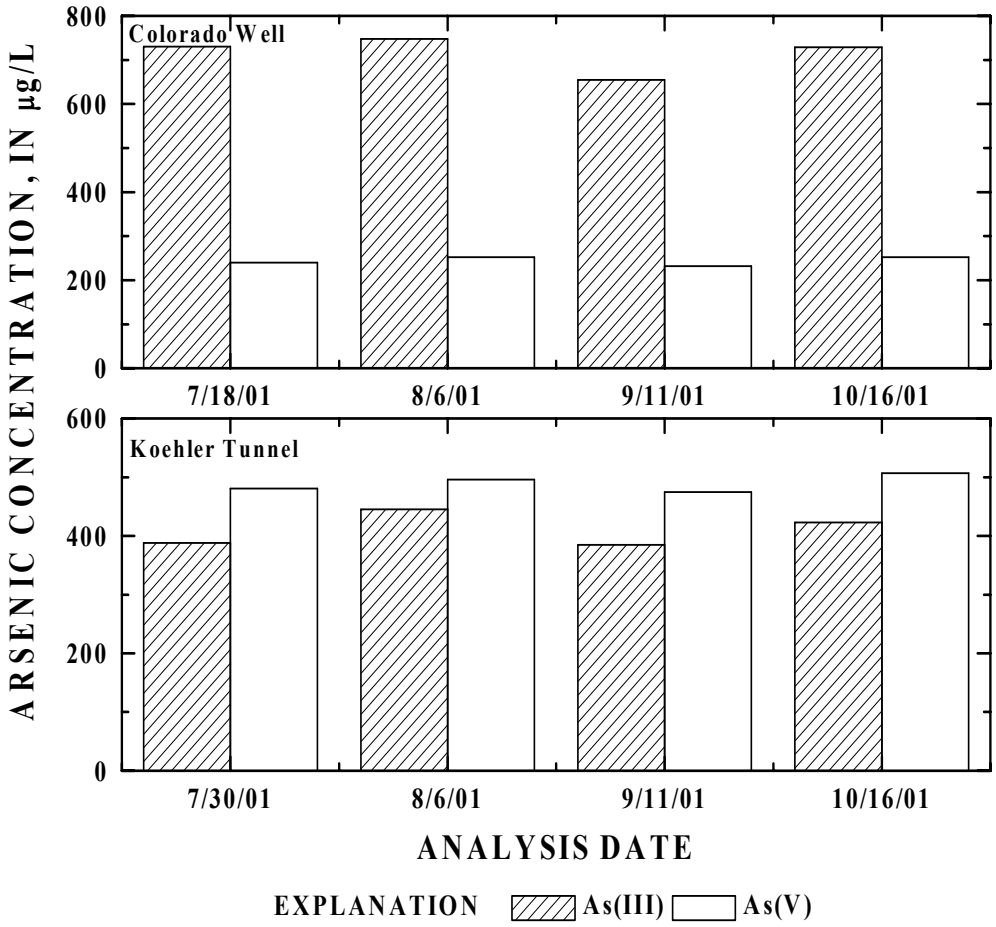

Figure 14. Preservation of arsenic species distribution for a 3-month period for a ground-water sample (Colorado Well) and an acid mine drainage sample (Koehler Tunnel). The Colorado Well and Koehler Tunnel samples were collected in opaque polyethylene bottles and preserved with EDTA on 7/18/01 and 7/27/01, respectively. Arsenic concentrations are in micrograms per liter (µg/L.

Arsenic concentrations measured in the time-series samples are shown in figures 15 and 16. The highest concentrations of MMA were measured in samples collected after the period when the application of MSMA was most likely and never exceeded 6 µg/L (see top graph in fig. 15). The data suggest that MMA either degrades quickly or is sorbed to soil components and does not persist in the environment. Except for a single occurrence at the Bogue Philia site (see second graph in fig. 15), all DMA concentrations were at or less than 0.2 µg-As/L. Concentrations of As(III) and As(V) increased later in the summer, possibly indicating alkylarsenic degradation or a secondary source of inorganic arsenic (see third and fourth graphs in figs. 15 and 16). Arsenite species predominate in samples collected at the Yazoo site for July, August, and September,

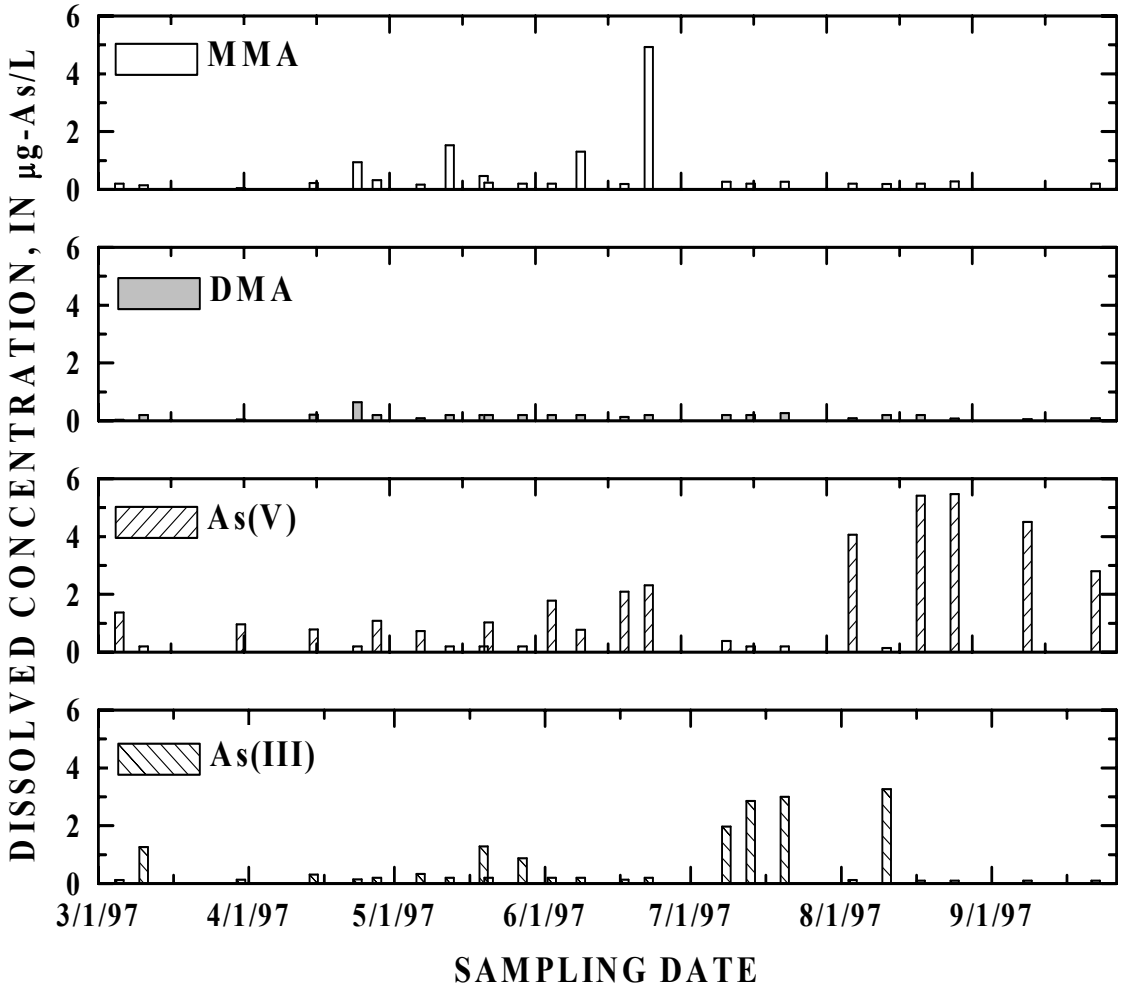

Figure 15. Dissolved arsenite [As(III)], arsenate [As(V)], dimethylarsinate (DMA), and monomethylarsonate (MMA) in samples collected from March through September 1997 at the Bogue Philia surface-water site that might have been contaminated by application of the herbicide monosodium methylarsonate. Concentrations are in micrograms-arsenic per liter (µg-As/L).

possibly indicating a stagnant, low-dissolved oxygen, reducing environment. Concentrations of As(III) and As(V) were two to three times higher in the Bogue Philia samples than in Yazoo samples. Nevertheless, total dissolved arsenic never exceeded 6 µg/L in either site.

Blind field blanks and blind duplicate samples were analyzed throughout the collection period for each site (see table 9). Duplicate results compare well except for the Bogue Philia duplicates submitted on May 7, 1997, and the Yazoo duplicates submitted on April 10, 1997. Arsenic species concentrations were less than

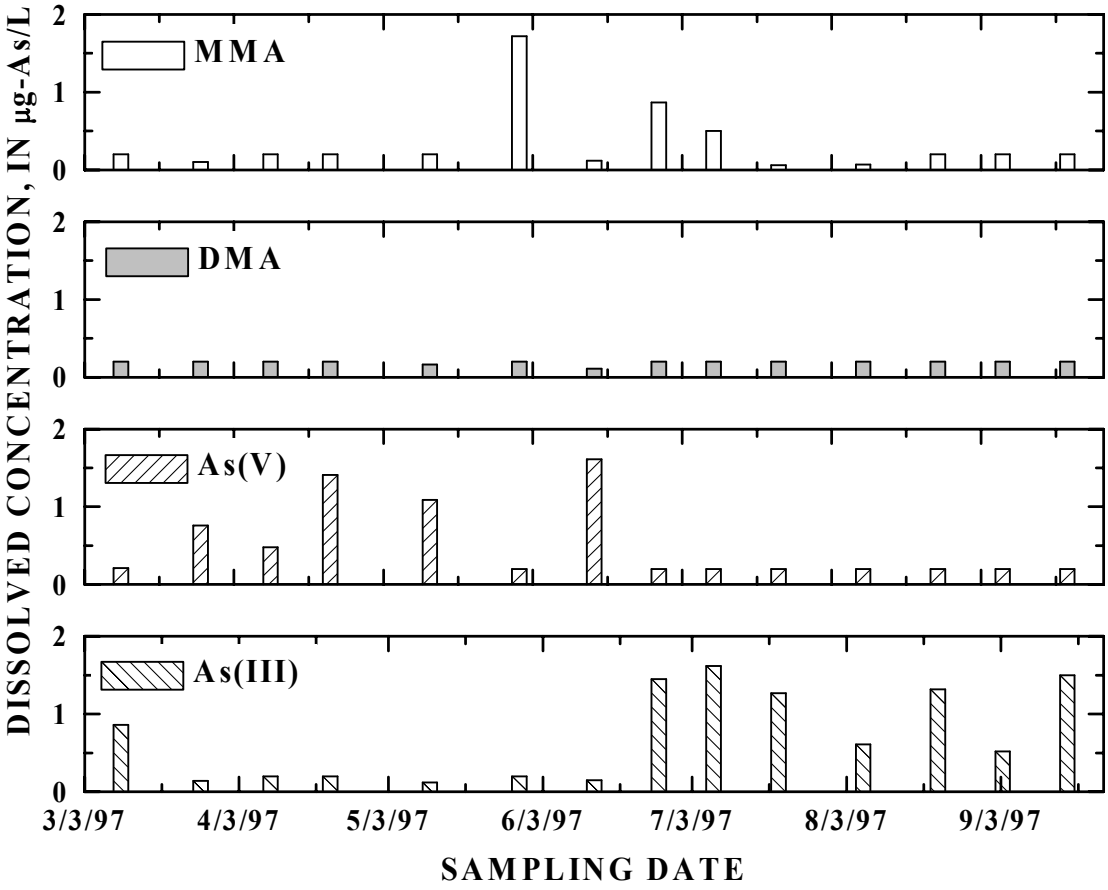

Figure 16. Dissolved arsenite [As(III)], arsenate [As(V)], dimethylarsinate (DMA), and monomethylarsonate (MMA) in samples collected from March through September 1997 at the Yazoo surface-water site that might have been contaminated by application of the herbicide monosodium methylarsonate. Concentrations are in micrograms-arsenic per liter (µg-As/L).

the method detection limits (0.1 µg-As/L) for both field blanks. The results for As(III) and As(V) in duplicate samples compared closely. The concentrations of MMA and DMA in nearly all of the duplicate samples were at the method detection limits.

SUMMARY AND CONCLUSIONS

Arsenic in the hydrologic system results from either natural phenomena or anthropogenic activities. There are several inorganic and organic arsenic species that can result from such activities. The toxicity of arsenic species is variable making it essential to distinguish between the arsenic species present. Furthermore, increasing concern about arsenic in drinking water has prompted lowering the arsenic drinking-water maximum contaminant level to 10 micrograms per liter. Methods described in this report are capable of discriminating between arsenic species and quantifying arsenic concentrations less than 1 microgram per liter. The scope of the results demonstrates the need to measure arsenite, arsenate, monomethylarsonate, and dimethylarsinate concentrations in natural

Table 9. Uncensored arsenic-speciation results for blind blanks and surface-water blind duplicate samples analyzed using ion chromatography with phosphate mobile phase and arsine generation–inductively coupled mass spectrometry

[Concentrations in micrograms-arsenic per liter; Bogue Philia and Yazoo are sites in Mississippi; As(III), arsenite; DMA, dimethylarsinate; MMA, monomethylarsonate; As(V), arsenate]

Site	Date (1997)	As(III)	DMA	MMA	As(V)
Blanks	7/22	0.2	0.2	0.06	0.1
	9/18	.2	.2	.2	.06
Bogue Philia	7/22	3.3	.2	.3	.2
		3.0	.3	.3	.2
	4/1	.1	.06	.2	.9
		.1	.04	.05	1.0
	5/7	.5	.2	3.0	.2
		.3	.1	.2	.7
	7/14	3.1	.2	.4	.2
		2.8	.2	.2	.2
	8/5	.05	.1	.2	4.3
		.1	.1	.2	4.1
	8/19	.2	.2	.2	5.5
		.1	.2	.2	5.4
Yazoo	3/12	.9	.2	.05	.2
		.9	.2	.2	.2
	4/10	.2	.2	.9	.2
		.2	.2	.2	.5
	4/22	1.3	.1	.2	.2
		1.3	.2	.06	.2
	8/8	.6	.2	.2	.2
		.6	.2	.07	.2
	9/18	1.6	.2	.2	.2
		1.5	.2	.2	.2

water. Various distributions of arsenite and arsenate were measured in ground water, surface water, and acid mine drainage. Methylated arsenic species were found only in surface water associated with agricultural use of the herbicide monosodium methylarsenate (MSMA), although ground water from the area was not collected. Arsenic-speciation measurement will provide a better understanding of the arsenic cycle in the hydrologic environment and might contribute to understanding the detrimental synergistic effects that arsenic might have with other inorganic, organic, organometallic, and biological contaminants.

The laboratory- and field-speciation methods described in this report are simple and robust methods for the determination of trace concentrations of arsenate, arsenite, monomethylarsonate, and dimethylarsinate in various sample matrices. Statistical analysis of a data set consisting of 81 ground-water and acid mine drainage samples indicated that there was no analytically significant difference

between the arsenite and arsenate results from laboratory-speciation to field-speciation methods. Percentage recovery for spiked field samples ranged from 81 to 104 percent for all four arsenic species by the laboratory-speciation method and 102 to 107 percent for arsenite and arsenate by the field-speciation method. Arsenic speciation results for reference materials closely matched concentrations determined by other studies. The laboratory-speciation method varied from 8 to 13 percent (n=7) at 0.5 µg-As/L for all four arsenic species in reagent water. Variability for the field-speciation method was from 3 to 4 percent at 1 µg-As/L and from 0.7 to 1 percent at 10 µg-As/L for As(III)and As(V). Method detection limits for the laboratory-speciation methods ranged from 0.1 to 0.6 microgram-arsenic per liter depending on whether nebulization or arsine generation is used for sample introduction and on the species being measured. Method detection limits for the field-speciation method (using ICP–MS detection) are 0.3 microgram-arsenic per liter regardless of the species.

Preservation of the distribution of arsenic species in natural water is important. The distribution of arsenite and arsenate easily can be shifted when preservation techniques are not used; monomethyl-arsonate and dimethylarsinate are stable. Changes in sample redox potential precipitate iron and manganese oxyhydroxides that sorb arsenic species. Sequestering dissolved metal cations with ethylenediaminetetraacetic acid was shown to minimize precipitate formation. The oxidation of arsenite to arsenate by photolytically produced free radicals also affected the determination of arsenic species. Opaque polyethylene sample bottles eliminated the effect of photochemical oxidation by omitting light exposure. Using these preservation measures stabilized arsenic species for up to 3 months for the sample matrices tested.

The laboratory- and field-speciation methods have the following advantages and disadvantages:

Laboratory-Speciation Methods

- **Advantages**
  1. Capable of speciating arsenite, arsenate, monomethylarsonate, and dimethylarsinate in less than 8 minutes or arsenite and arsenate in less than 3 minutes.
  2. Interferents elute at times different than arsenic species or interference can be easily corrected in real-time.
  3. Less than 200 microliters of sample typically is used for the analysis.
  4. No sample preparation is required.

- **Disadvantages**
  1. Requires specialized and expensive instrumentation, such as ion chromatographic system and inductively coupled plasma–mass spectrometer.
  2. Short-column method does not resolve methylated arsenic species.

Field-speciation method

- **Advantages**
  1. Arsenic species can be determined rapidly using inexpensive instrumentation capable of measuring arsenic.
  2. The physical separation of arsenate from arsenite in the field.

- **Disadvantages**
  1. Capable of speciating only arsenite and arsenate (unless a laboratory-speciation method also is used to quantitate the arsenate fraction).

2. Arsenate results will be biased positively when other anionic arsenic species are present in a sample.
3. Sample matrix composition can exceed cartridge capacity.
4. Strong anion exchange cartridge must be pre-conditioned or converted to the acetate form prior to sample collection.
5. Cartridge must be extracted in laboratory prior to analysis.
6. Two analytical determinations are required to quantitate arsenite and arsenate.

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