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# Preserving the Distribution of Inorganic Arsenic Species in Groundwater and Acid Mine Drainage Samples

A. J. BEDNAR,[†,‡] J. R. GARBARINO,[*,†] J. F. RANVILLE,[‡] AND T. R. WILDEMAN[‡]

*U.S. Geological Survey, P.O. Box 25046 MS407, Denver Federal Center, Denver, Colorado 80225-0046, and Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado 80401*

The distribution of inorganic arsenic species must be preserved in the field to eliminate changes caused by metal oxyhydroxide precipitation, photochemical oxidation, and redox reactions. Arsenic species sorb to iron and manganese oxyhydroxide precipitates, and arsenite can be oxidized to arsenate by photolytically produced free radicals in many sample matrices. Several preservatives were evaluated to minimize metal oxyhydroxide precipitation, such as inorganic acids and ethylenediaminetetraacetic acid (EDTA). EDTA was found to work best for all sample matrices tested. Storing samples in opaque polyethylene bottles eliminated the effects of photochemical reactions.

The preservation technique was tested on 71 groundwater and six acid mine drainage samples. Concentrations in groundwater samples reached 720 $\mu$g-As/L for arsenite and 1080 $\mu$g-As/L for arsenate, and acid mine drainage samples reached 13 000 $\mu$g-As/L for arsenite and 3700 $\mu$g-As/L for arsenate. The arsenic species distribution in the samples ranged from 0 to 90% arsenite. The stability of the preservation technique was established by comparing laboratory arsenic speciation results for samples preserved in the field to results for subsamples speciated onsite. Statistical analyses indicated that the difference between arsenite and arsenate concentrations for samples preserved with EDTA in opaque bottles and field speciation results were analytically insignificant. The percentage change in arsenite:arsenate ratios for a preserved acid mine drainage sample and groundwater sample during a 3-month period was −5 and +3%, respectively.

## Introduction

The occurrence of arsenic and its potential toxicity in the environment requires the measurement of individual aqueous inorganic and organic arsenic species. Arsenite [$H_3AsO_3$ or As(III)] is the most toxic inorganic arsenic species followed by arsenate [$H_2AsO_4^-$ or As(V)] (*1*−*3*). Researchers recently have reported, however, that some methylated metabolites of As(III) are highly reactive and damage DNA in cultured human cells (*4*).

Stabilization or preservation of the distribution of inorganic arsenic species in natural water is a major concern. Methylated arsenic species, such as monomethylarsonate and dimethylarsinate, have been found to be much more stable (*5*). Successful preservation has been shown to be dependent on matrix composition (*6*). Arsenate can be reduced to arsenite in some natural water even after a sample has been filtered to remove living organisms (*5*, *7*). Furthermore, some forms of natural organic matter can reduce As(V) to As(III), while other forms can photolytically oxidize As(III) to As(V) (*8*, *9*).

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 (*10*). Different storage temperatures and the addition of hydrochloric acid or ascorbic acid also have been investigated as possible preservation techniques; in addition, quick-freezing the sample with liquid nitrogen was recommended to preserve the As(III) and As(V) speciation in surface-water samples (*5*). Storing samples at 5 °C preserved As(III) and As(V) speciation in water samples for about 30 d, while using 0.1% nitric or hydrochloric acid altered the arsenic species distribution (*7*). Other studies have shown that EDTA preserved arsenic speciation distributions in three groundwater samples for up to 14 d (*11*). Some of these stabilization practices are not practical for field applications, are not amenable to analytical methodology, or have not been tested on a large number of samples with different matrix compositions.

In this article, the authors describe a technique that preserves arsenic species distribution in natural-water samples. Precipitation of metal oxyhydroxides that result from shifts in redox potential or pH and oxidation of As(III) by photolytically produced free radicals are processes that are controlled by the preservation technique. Several different reagents were evaluated for stabilizing metal cations, and opaque bottles were used to eliminate the formation of photochemical free radicals. The technique was tested on samples that have a wide range of matrix compositions collected from groundwater and acid mine drainage sites. The accuracy of maintaining the arsenic species distribution in preserved samples was determined by using results from onsite field speciation and subsequent comparison to laboratory results. The preservation technique also could be applied to surface-water samples containing methylated arsenic species if different chromatographic methods are used (*12*).

## Experimental Section

**Calibration Standards.** ASTM Type I reagent water (*13*) and arsenic-free acids and reagents must be used to prepare all solutions. Reagents were obtained from J. T. Baker (Phillipsburg, NJ) and EM Science (Gibbstown, NJ) chemical companies. Primary standards of 100 mg-As/L of each arsenic species were prepared by weighing 173.4 mg of sodium m-arsenite ($NaAsO_2$, CAS 7784-46-5) for As(III) and 240.3 mg of potassium dihydrogen arsenate ($KH_2AsO_4$, CAS 7784-41-0) for As(V). All primary standards were filtered by using a 0.2-$\mu$m 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, NJ). At least three mixed-species calibration standards were prepared in 1.25 mM EDTA extending over the concentration range of 0−100 $\mu$g/L. The arsenic species distribution in calibration standards prepared in this manner were stable for several days in airtight amber glass autosampler vials.

* Corresponding author phone: (303)236-3945; fax: (303)236-3499; e-mail: jrgarb@usgs.gov.

† U.S. Geological Survey.

‡ Colorado School of Mines.

**TABLE 1. Arsenic Speciation Methods for the Determination of Arsenite and Arsenate in Filtered Natural Water**

| laboratory speciation method | |
|---|---|
| analytical column | user packed SAX 4 mm × 50 mm |
| guard column | Phenomenex SecurityGuard SAX 4 mm by 3 mm |
| column temperature | 25 °C |
| mobile phase, isocratic | 12.5 mM malonate and 17.5 mM acetate, pH 4.8 |
| mobile phase flow rate | 1.0 mL/min |
| nominal pressure | $2.1 \times 10^3$ kPa (300 lb/in$^2$) |
| typical injection volume | 100 $\mu$L |
| nominal As(III) retention time | 0.95 min |
| nominal As(V) retention time | 1.50 min |

| field speciation method | |
|---|---|
| solid-phase extraction cartridge | Supelco LC-SAX |
| cartridge conditioning chloride form | 2 mL of methanol; 10 mL of deionized water |
| cartridge conditioning acetate form | 10 mL of 1.7 M acetic acid; 10 mL of deionized water |
| cartridge capacity | 0.2 mequiv/g |
| typical sample volume | 10 mL |
| As(III) | Elutriate |
| As(V) plus other charged arsenic species extracted from LC-SAX cartridge | 10 mL of 0.16 M nitric acid |
| elution and extraction flow rate | 1−2 drops/s |

**Sample Collection and Preservation.** All samples were filtered using either a 0.45-$\mu$m membrane syringe filter or an inline filter. Exposure of the sample to air was minimized when filtering the samples to reduce the possibility of oxidation. Filtration using such conditions was not problematic because only 10 mL of filtrate was required for the analysis. EDTA was added to the filtrate to chelate metal cations, buffer the sample pH, and reduce microbial activity. The 0.250 M EDTA preservative was 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 concentration of the EDTA can be varied depending on the expected concentration of Fe, Mn, and other divalent metal cations. Generally, only an estimate of the Fe concentration is needed because Fe is preferentially chelated over other major cations (e.g. Ca and Mg), and Fe oxyhydroxide precipitation is the main concern. The Fe concentration in most groundwater and acid mine drainage is less than 10 mg/L and 500 mg/L, respectively. Therefore in this study, 100 $\mu$L of 0.125 M EDTA was added to 10 mL of groundwater filtrate, and 500 $\mu$L of 0.250 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.

**Laboratory Speciation Method.** Preserved samples were analyzed using a liquid chromatograph with an anion exchange column to separate the arsenic species, a cross-flow nebulizer for sample introduction, and an inductively coupled plasma-mass spectrometer (ICP-MS) as an arsenic-specific detector (*12*). The liquid chromatograph was composed of a Waters 600-MS system controller and fluid unit and a Waters 700 Satellite WISP autosampler under Waters Millenium software control. A Waters in-line degasser was used to purge the mobile phase. The column, mobile-phase composition and flow rate, and typical injection volume are listed in Table 1. A user-prepared 4-mm by 50-mm column packed with Supleco LC-SAX strong anion-exchange resin was used to rapidly separate As(III) and As(V). The malonate and acetate mobile phase isocratically separated the species in less than 3 min.

The 25 mM malonate and 35 mM 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 ($NH_4$-$CH_3CO_2$, CAS 631-61-8) to 1 L of reagent water before adjusting the pH to 4.8 with about 2.2 mL of 30% ammonium hydroxide. The mobile phase was filtered using a 0.4-$\mu$m membrane filter prior to use. 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% using the proportioning valves of the liquid chromatograph system to optimize the chromatographic resolution and elution times for the analytes.

The ICP-MS was used as an arsenic-specific detector by measuring the ion intensity at $m/z$ 75. A PE Sciex Elan 6100 ICP-MS was operated at 1100 W and data were acquired using a 750 ms dwell time and 180 readings per replicate. Column effluent was introduced into the ICP-MS with a PE Sciex cross-flow nebulizer. The retention times and the chromatographic peak width determined the dwell time and readings per replicate used.

Spiking lithium into every autosampler vial provided a method for identifying autosampler injector malfunctions. Lithium was used as the injection standard because of its low natural abundance, high solubility, and redox inactivity. The lithium ion intensity was measured at $m/z$ 7. A 10-mg/L lithium solution was prepared by dissolving 95 mg of lithium acetate ($LiC_2H_3O_2$, CAS 546-89-4) in 1 L of reagent water. Sample vials containing 3.96 mL of sample were spiked with 40 $\mu$L of the lithium solution. Injector malfunction was indicated whenever the lithium intensity was less than 95% of the average expected intensity.

A software program, such as Graphical Analysis, was used to calculate the area under the chromatographic peaks. Linear regression analysis established the response function from the reagent blank and the series of standard solutions. The linear dynamic range extends to about 1000 $\mu$g/L for each species when using a 100-$\mu$L injection volume and pulse-counting detection. The chloride interference on arsenic using ICP-MS was corrected by using standard procedures (*14*). Excessive carbon or salt buildup on the interface cones was not found to be a problem after several days of operation. The method detection limit was 0.6 $\mu$g-As/L (or 60 pg for a 100-$\mu$L injection) for As(III) and As(V) as calculated using the U.S. Environmental Protection Agency's procedure (*15*).

**Field Speciation Method.** A field speciation method was used to provide benchmark arsenic speciation results for comparison to results from the preservation technique (see Table 1). The field speciation method used a cartridge containing a strong anion-exchange resin (Supelco, Bellefonte, PA; LC-SAX, 3-mL cartridge barrel, 500-mg packing, part number 57017) to separate the arsenic species (*16*). The exchange material can be in the chloride form (as received) or converted to the acetate form by washing with 1.7 M acetic acid and reagent water. The acetate form was preferred when speciating acid mine drainage samples because of its high buffering capacity. The exchange capacity of the cartridge is reported to be about 0.1 mequiv (Supelco).

Arsenic species are separated in the field by using a syringe to elute 10 mL of EDTA-preserved sample through the cartridge. Uncharged arsenic species [primarily As(III)] remain in the sample solution and elute from the cartridge, while charged species [As(V)and others] are retained on the cartridge. The charged arsenic species are stripped from the cartridge in the laboratory using 10 mL of 0.16 M nitric acid. The extract and elutriate were analyzed for total arsenic using ICP-MS (*14*). EDTA must be added to the sample filtrate prior to cartridge extraction to prevent metal oxyhydroxide precipitation and redox reactions; the concentration of EDTA was consistent with that used for the laboratory speciation method. It is important that a molar excess of EDTA is present in the filtrate to sequester all the Fe and Mn cations, otherwise

the corresponding oxyhydroxides will precipitate at the head of the cartridge and provide sorption sites that will negatively bias As(V) results and to a lesser extent the As(III) results.

Potential problems inherent to the field speciation method arise when the exchange capacity of the cartridge is exceeded because of high concomitant anion concentrations (such as sulfate) or when other arsenic species (such as monomethylarsonate and dimethylarsinate) are retained on the cartridge with As(V). Whenever the exchange capacity is exceeded, As(V) is not fully retained on the cartridge and elutes with the fraction that contains As(III). Therefore, samples with high anion concentrations must be diluted or a larger capacity cartridge must be used; however, matrix dilution can be a disadvantage because the analyte concentrations also are diluted. The exchange capacity was not a limitation for most groundwater samples tested; however, acid mine drainage samples often exceeded the capacity and required a 1:50 dilution. Monomethylarsonate and dimethylarsinate were not present in either the groundwater or acid mine drainage samples. However, groundwater and surface-water samples collected from agricultural areas impacted by arsenic-containing herbicides have been found to contain methylated arsenic species (*12*).

## Results and Discussion

Dissolved iron and manganese can affect arsenic speciation results in anoxic groundwater samples and in acid mine drainage samples with high iron concentration. When groundwater that is pumped to the surface during sampling interacts with atmospheric oxygen, iron and manganese oxyhydroxides precipitate and provide sorption sites for dissolved arsenic species (*17*). The oxidation of As(III) to As(V) by photochemical free radicals also is possible at a rate that is dependent on the radiation wavelength and flux, pH, and sample-matrix composition; As(III) is oxidized within hours of exposure to solar radiation in iron-containing water (*8*). Both these processes can affect the arsenic species distribution if they are not controlled.

The strategy of the present authors 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 groundwater and acid mine drainage samples. 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 mM) on the preservation of inorganic arsenic species. All experiments were conducted at room temperature (about 20 °C). Clear borosilicate glass vials (1 absorbance unit at 250 nm, measured with respect to air) were used for light experiments, and brown borosilicate glass vials (1 absorbance unit at 550 nm, 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 120 h (5 d) when EDTA was added (see top panel in Figure 1); exposure to ambient light was not a factor. Sulfuric acid worked nearly as well; however, the distribution began to shift slightly after about 100 h. Nitric acid preserved the distribution if samples were not exposed to light; however, if exposed to ambient light, As(III) was oxidized to As(V) (see center panel in Figure 1). The oxidation of As(III) occurs as part of a redox couple with nitrate being photolytically reduced to nitrite in water on exposure to ultraviolet radiation (*18*). Hydrochloric acid shifted the distribution quickly with or without exposure to light. The cause for the change in distribution is unknown but has been reported by others (*7, 11*). 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 d with or without light exposure. Moreover, As(V) was reduced to

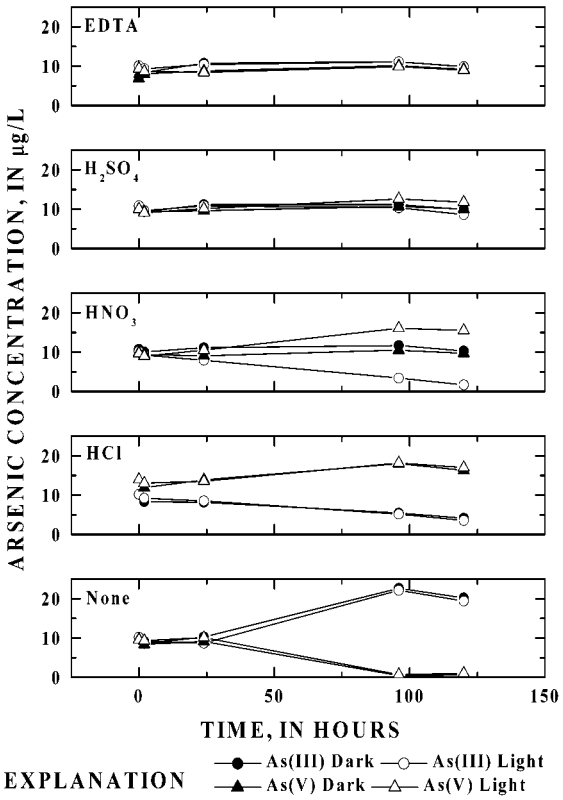


**FIGURE 1. Graphs showing EDTA, $H_2SO_4$, $HNO_3$, and HCl as preservatives and the effects of ambient light for arsenic speciation in test samples. The test solution initially contained an equal distribution of As(III) and As(V) at 10 µg-As/L in reagent water.**

As(III) presumably by microbial activity (see bottom panel of Figure 1).

The results of similar experiments conducted over a longer time (14 d as compared to 5 d) with $Fe^{3+}$ present (1 mg/L) are shown in Figure 2. Experimental results show that EDTA again maintained the arsenic distribution (top panel in Figure 2). As with the experiments without $Fe^{3+}$, sulfuric acid worked nearly as well, and nitric acid preserved the distribution when light was omitted (second and center panel, respectively, in Figure 2). None of the other preservatives maintained the distribution for more than 24 h. The arsenic distribution is shifted almost 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) via an As(IV) intermediate (*9*); a similar mechanism also was proposed for other ionic iron species (*8*). As(V) is sorbed to iron oxyhydroxides that precipitate at pH 3−4 in the test solution when no preservative is present (see bottom panel in Figure 2).

Results from the laboratory experiments outlined above indicated that EDTA and opaque sample bottles combine to offer the best technique for preserving the arsenic species distribution. The accuracy of the benchmark field speciation method was established using standards of known arsenic species distribution. Percentage recoveries for cartridge separation of a standard that had 0.89 µg/L as As for As(III) and As(V) were 112% for As(III) and 99% for As(V); at 8.9 µg/L as As for As(III) and As(V) recoveries were 108% for As(III) and 100% for As(V). The variability ($n = 3$) in the arsenic distribution was 4% and 3% at 1 µg/L as As and 1% and 0.7% at 10 µg/L as As, for As(III) and As(V), respectively.

The preservation technique was tested on samples with a wide range of sample matrices. Groundwater samples were

**TABLE 2. Sample Sites and Matrix Composition**

| sampling site | pH | Eh | As(III) [$\mu$g-As/L] range | As(III) median | As(V) [$\mu$g-As/L] range | As(V) median | Fe (mg/L) | Mn (mg/L) | $SO_4^{2-}$ (mg/L) | $CaCO_3$ (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|
| **Groundwater** | | | | | | | | | | |
| Fallon, NV | 6.5–9.3 | | 0–300 | 3.1 | 0.1–1080 | 36 | <0.005–0.8 | <0.003–4.2 | <0.1–1680 | 0.8–1080 |
| 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, CO | | | 7–83 | | 13–220 | | <0.005–0.4 | <0.003–0.034 | 66–78 | |
| **Acid Mine Drainage** | | | | | | | | | | |
| Virginia Canyon Mine | 2.8 | 678 | 27 | | 3660 | | 381 | 36 | 2940 | |
| Quartz Hill Tunnel | 3.0 | 648 | 15 | | 180 | | 639 | 66 | 4700 | |
| Koehler Tunnel | 3.5 | 626 | 390 | | 480 | | 105 | 3.0 | 560 | |
| Koehler Breakdown | 2.8 | 713 | 89 | | 7050 | | 493 | 16 | 2230 | |
| Summitville | 3.5 | 620 | 11 | | 190 | | 210 | 16 | 1940 | |
| Platoro | 5.8 | 162 | 12 800 | | 1500 | | 100 | 12 | 890 | |

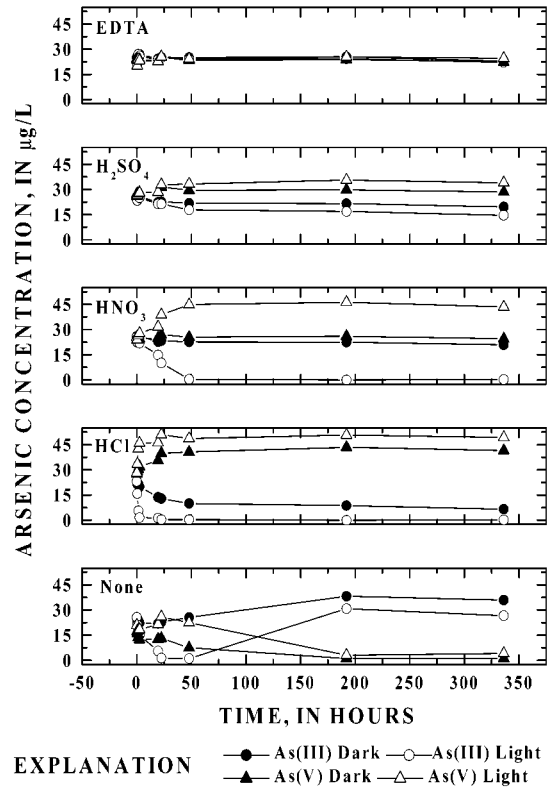


**FIGURE 2. Graphs showing EDTA, $H_2SO_4$, $HNO_3$, and HCl as preservatives and the effects of ambient light for arsenic speciation in test samples having iron. The test solution initially contained an equal distribution of As(III) and As(V) at 20 $\mu$g-As/L and 1 mg/L of $Fe^{3+}$ in reagent water.**

collected for laboratory and field arsenic speciation from 60 sites in the vicinity of Fallon, Nevada, 9 sites in the Peoples Republic of Bangladesh, and 2 sites near Golden, Colorado. Acid mine drainage samples were collected at sites clustered within three mineralized regions of Colorado. The Summitville and Platoro 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, CO, and the Quartz Hill Tunnel and Virginia Canyon Mine sites are in the Central City mining district near Idaho Springs, CO.

The ranges for several chemical properties and constituents that could affect arsenic speciation if preservation was not used are listed for the test samples in Table 2. Concentrations of Fe, Mn, and $SO_4^{2-}$ in acid mine drainage samples exceeded those for groundwater samples by several orders

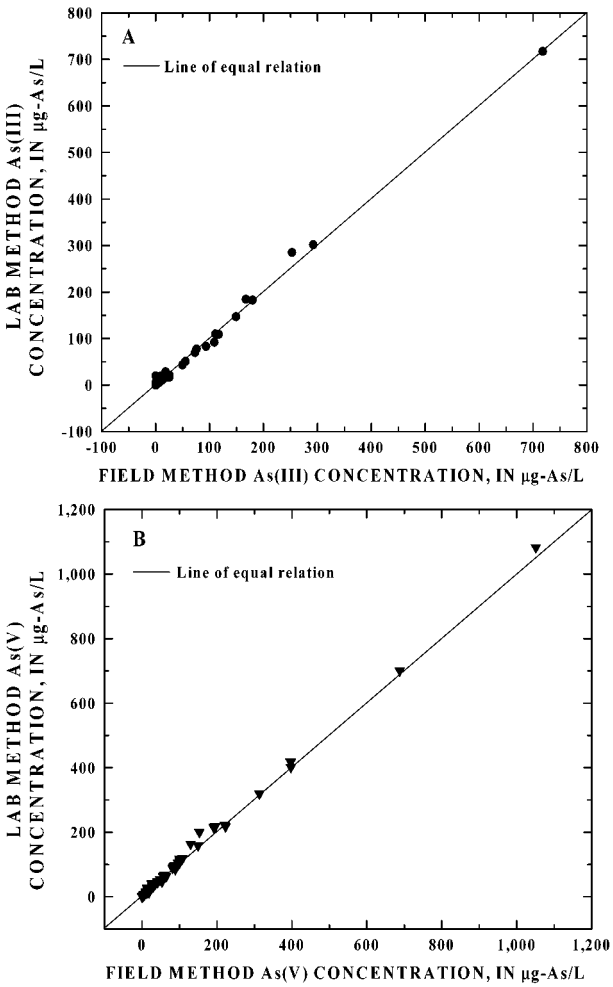


**FIGURE 3. Relation between As(III) concentration (A) and As(V) concentration (B) determined in groundwater samples by laboratory and field methods results.**

of magnitude in most cases. The maximum total arsenic concentration was about 14 000 $\mu$g/L. The percentage of As(III) in the test samples was distributed as follows: 31 at <5%; 12 at 5–15%; 7 at 20–45%; 10 at 50–75%; 11 at 75–85%; and 6 at >85% (see Table 2 for 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

**TABLE 3. Statistical Summary of Laboratory versus Field Arsenic Speciation Results**

| species | linear regression analysis at the 95% confidence interval: slope | y-intercept | r | paired sign test p-value |
|---|---|---|---|---|
| | | **Groundwater 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 = 6** | | |
| 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 = 77** | | |
| As(III) plus As(V) | 1.005 ± 0.004 | 6 ± 7 | 0.9999 | <0.0001 |

groundwater 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) groundwater results indicate that there is no significant difference between the two data sets at the 95% confidence interval (see top panel in Figure 3a and Table 3). The p-value (0.0959) from the Paired Sign Test also implies 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% confidence interval (see bottom panel in Figure 3b and Table 3). 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 too low to sequester all of the iron and manganese 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% confidence interval (see top panel in Figure 4a and Table 3). The bias might have resulted from As(III) oxidation during field speciation or from the large dilution 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), thus suggesting that oxidation was not the source of the bias (see bottom panel of Figure 4b and Table 3).

The slope and y-intercept of the graph shown in Figure 5 for total arsenic, the sum of As(III) and As(V), indicate 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 analytically significant (see Table 3).

The preservation period for maintaining the original arsenic species distribution also was investigated. A representative groundwater and acid mine drainage sample collected in opaque polyethylene bottles and preserved with EDTA were analyzed repeatedly for about 3 months. Results in Figure 6 show that the distribution of arsenic species was successfully maintained during this period. The change in the As(III):As(V) ratio was −5% for the Colorado Well sample and +3% for the Koehler Tunnel sample. The arsenic distribution in other groundwater samples from Bangladesh and Nevada that had 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 groundwater 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.

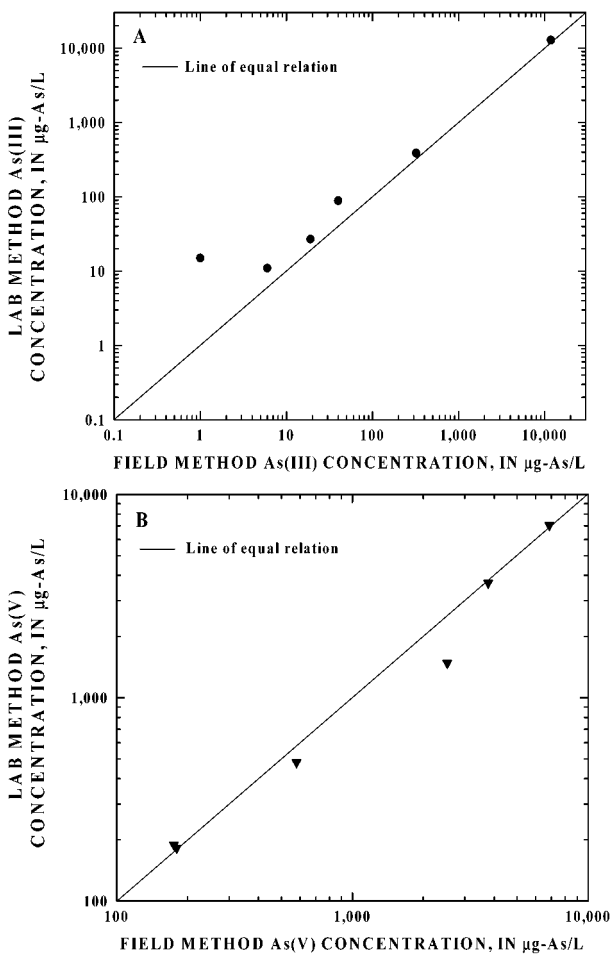


**FIGURE 4. Relation between As(III) concentration (A) and As(V) concentration (B) determined in acid mine drainage samples by laboratory and field methods.**

Preservation of the distribution of arsenic species in natural water is important. The distribution of As(III) and As(V) can easily be shifted when preservation techniques are not used. Changes in sample Eh or pH can precipitate iron and manganese oxyhydroxides that sorb arsenic species differentially to negatively bias results. Sequestering dissolved metal cations with EDTA was shown to minimize precipitate formation and redox reactions. The oxidation of As(III) to As(V) by photolytically produced free radicals also affects the accuracy of arsenic speciation. Opaque polyethylene sample bottles eliminated the effect of photooxidation by omitting light exposure. Combining these preservation measures stabilized arsenic species distribution for up to 3 months for the sample matrices tested.

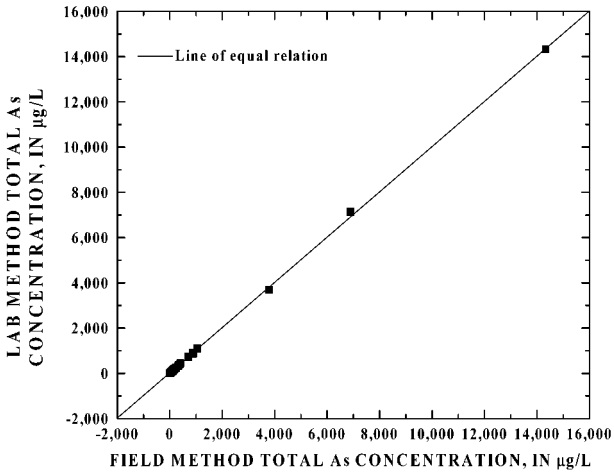


**FIGURE 5. Relation between As(III) plus As(V) concentration determined in all test samples by laboratory and field methods.**

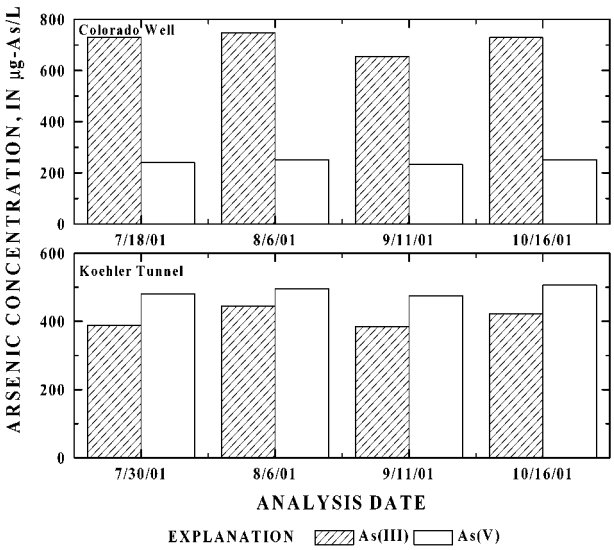


**FIGURE 6. Column chart showing the preservation of arsenic species distribution over a 3-month period for a groundwater sample (Colorado Well) and an acid mine drainage sample (Koehler Tunnel). The Colorado Well and Koehler Tunnel samples were collected in opaque polyethylene bottles and preserved with EDTA on 7/18/01 and 7/27/01, respectively.**

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