METAL INTERFERENCES AND THEIR REMOVAL PRIOR TO THE DETERMINATION OF As(T) AND As(III) IN ACID MINE WATERS BY HYDRIDE GENERATION ATOMIC ABSORPTION SPECTROMETRY

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By R. Blaine McCleskey, D. Kirk Nordstrom, and James W. Ball

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Explanation of Abbreviations

---   (not analyzed or not measured)
°C   (degrees Celsius)
AAS   (atomic absorption spectrometry)
As(III) (arsenic(III) or arsenite)
As(V) (arsenic(V) or arsenate)
As(T) (total dissolved arsenic (As(III) plus As(V))
cm   (centimeter)
conc.   (concentration)
EDL   (electrodeless discharge lamp)
FIAS   (flow injection analysis system)
g   (gas)
HCl   (hydrochloric acid)
HGAAS   (hydride generation-atomic absorption spectrometry)
HNO_3 (nitric acid)
KI   (potassium iodide)
ICP-OES   (inductively coupled plasma-optical emission spectrometry)
ISE   (ion-selective electrode)
μg/L   (micrograms per liter)
M   (moles per liter)

meq/L (milliequivalents per liter)
meq/mL   (milliequivalents per milliliter)
mg/L   (milligrams per liter)
min.   (minute)
mL   (milliliters)
mv   (millivolt)
MPV   (most probable value)
μL   (microliter)
μm   (micrometer)
μS/cm (microsiemens per centimeter at 25 degrees Celsius)
n   (number of analyses)
$NaBH_4$ (sodium borohydride)
nm   (nanometer)
RSD   (relative standard deviation)
s   (standard deviation)
SRWS (standard reference water sample)
v/v   (volume per volume)
w/v   (weight per volume)
w/w   (weight per weight)

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Abstract

Hydride generation atomic absorption spectrometry (HGAAS) is a sensitive and selective method for the determination of total arsenic (arsenic(III) plus arsenic(V)) and arsenic(III); however, it is subject to metal interferences for acid mine waters. Sodium borohydride is used to produce arsine gas, but high metal concentrations can suppress arsine production.

This report investigates interferences of sixteen metal species including aluminum, antimony(III), antimony(V), cadmium, chromium(III), chromium(IV), cobalt, copper(II), iron(III), iron(II), lead, manganese, nickel, selenium(IV), selenium(VI), and zinc ranging in concentration from 0 to 1,000 milligrams per liter and offers a method for removing interfering metal cations with cation exchange resin. The degree of interference for each metal without cation-exchange on the determination of total arsenic and arsenic(III) was evaluated by spiking synthetic samples containing arsenic(III) and arsenic(V) with the potential interfering metal. Total arsenic recoveries ranged from 92 to 102 percent for all metals tested except antimony(III) and antimony(V) which suppressed arsine formation when the antimony(III)/total arsenic molar ratio exceeded 4 or the antimony(V)/total arsenic molar ratio exceeded 2. Arsenic(III) recoveries for samples spiked with aluminum, chromium(III), cobalt, iron(II), lead, manganese, nickel, selenium(VI), and zinc ranged from 84 to 107 percent over the entire concentration range tested. Low arsenic(III) recoveries occurred when the molar ratios of metals to arsenic(III) were copper greater than 120, iron(III) greater than 70, chromium(VI) greater than 2, cadmium greater than 800, antimony(III) greater than 3, antimony(V) greater than 12, or selenium(IV) greater than 1. Low recoveries result when interfering metals compete for available sodium borohydride, causing incomplete arsine production, or when the interfering metal oxidizes arsenic(III).

Separation of interfering metal cations using cation-exchange prior to hydride-generation permits accurate arsenic(III) determinations in acid mine waters containing high concentrations of interfering metals. Stabilization of the arsenic redox species for as many as 15 months is demonstrated for samples that have been properly filtered and acidified with HCl in the field. The detection limits for the method described in this report are 0.1 micrograms per liter for total arsenic and 0.8 micrograms per liter for arsenic(III).

Introduction

Accurate determination of the redox state of dissolved As is important for interpreting its toxicity and mobility in the environment. Dissolved As can form aqueous species in several oxidation states, but in

natural waters occurs dominantly as the inorganic oxyanions As(III) and As(V). Several analytical methods use hydride generation to selectively measure As redox species, but high metal concentrations can interfere with the determination of As(T) (As(III) plus As(V)) and As(III) (Smith, 1975; Welz and Melcher, 1984; Welsch and others, 1990; Creed and others 1996; Hageman and Welsch, 1996). Accurate determination of arsenic redox species in acid mine waters is challenging because of elevated metal concentrations frequently found in this type of water (Nordstrom and Alpers, 1999). Sixteen metal species including Al, Cd, Co, Cr(III), Cr(VI), Cu(II), Fe(II), Fe(III), Mn, Ni, Pb, Sb(III), Sb(V), Se(IV), Se(VI), and Zn were evaluated as possible interferents on the determination of As(T) and As(III). Because As(III) and As(V) exist as oxyanions in solution, interfering metal cations can be removed from solution using cation-exchange while maintaining the existing As(III) and As(T) concentrations. Pre-analysis separation of Fe(III) using cation-exchange resin for the determination of As redox species by ion chromatography in iron sulfate-sulfuric acid media has been successfully performed (Tan and Dutrizac, 1985). Cyanide also has been used as a complexing agent to eliminate interferences by metals in the determination of As using hydride-generation (Jamoussi and others, 1996). Interferences usually associated with atomic absorption analysis are negligible because arsine ($AsH_3(g)$) is separated from the sample matrix.

Results of accurate and precise analytical methods can be invalidated by deteriorated samples. Proper filtration and preservation are critical for maintaining the existing As(III)/As(T) ratio prior to analyses. Wing and others (1987) observed that filtration (0.1-μm or 0.45-μm), acidification with HCl, and storage in the dark at 4°C effectively preserved the As redox species for up to 8 months in ground waters collected near Fallon, Nev. Except for Fe(III) and hydrogen sulfide (H_2S), laboratory studies demonstrate that rates of oxidation of As(III) and reduction of As(V) in aqueous solution with redox agents common to natural waters are slow (Cherry and others, 1979). Filtering the sample removes colloidal material and bacteria that can affect the dissolved As(III)/As(T) ratio (Gihring and others, 2001; Wilkie and Hering, 1998). Acidification prevents precipitation of Fe hydroxides that can coprecipitate or adsorb As (Gao and others, 1988; Wilkie and Hering, 1996). Excluding light inhibits potential photochemical reactions (Emett and Khoe, 2001; Hug and others, 2001) and storing the samples at 4°C slows chemical reactions.

To address the need for more accurate determinations of As(T) and As(III) by hydride generation atomic absorption spectrometry (HGAAS), the U.S. Geological Survey (USGS) evaluated metal interferences and their removal in acid mine waters. This report (1) describes sample collection, preservation, and analytical procedures for the accurate determination of As(T) and As(III) using HGAAS; (2) identifies metals and the concentration at which each interferes in the determination of As(T) and As(III); (3) demonstrates that Cu(II) and Fe(III), both of which interfere in the determination of As(III) by HGAAS, can be removed from solutions using cation-exchange while maintaining existing As(III)/As(T) ratios; (4) applies the method to acid mine waters collected from the Summitville Mine, Colo.; Penn Mine, Calif.; and Richmond Mine, Calif.; and (5) presents As redox species time stability data for 45 surface- and ground-water samples collected during 1999-2002 from Yellowstone National Park, Wyo.; Questa Mine site, N. Mex.; Summitville Mine site, Colo.; Richmond Mine, Calif.; Penn Mine, Calif.; Ester Dome, Alaska; Fallon, Nev.; Mojave Desert, Calif.; and Kamchatka, Russia.

Methods of Investigation

Sample Collection and Preservation

Water samples collected in the field were pumped from the source through a 0.1 μm tortuous-path filter, acidified to pH less than 2 with hydrochloric acid (typically 2 mL 6-M HCl per 250 mL sample), and stored in acid-washed opaque bottles at 4°C (To and others, 1999).

Reagents

All reagents were of purity at least equal to the reagent-grade standards of the American Chemical Society. Double-distilled water and re-distilled or trace metal grade acids were used in all preparations. The following reagents were used for the As(T) and As(III) HGAAS procedure: 10 percent (w/v) KI from Aldrich; 10 percent (w/v) L-Ascorbic Acid from Aldrich; NaOH from Fisher; $NaBH_4$ from Fisher; trace metal grade HCl from Fisher, Assay w/w 35 to 38 percent; 1,000 mg/L As(III) from High Purity Standards; 1,000 mg/L As(V) from High Purity Standards; and cation-exchange resin, AG 50W-X8, 20-50 mesh, H^+ form from Bio-Rad.

The following single-element standards (1 to 10,000 mg/L) were prepared for interference studies: $CuSO_4 \cdot 5H_2O$ was used to prepare Cu(II); $FeSO_4 \cdot 7H_2O$ was used to prepare Fe(II); $Fe_2(SO_4)_3$ was used to prepare Fe(III); $Zn(NO_3)_2 \cdot 6H_2O$ was used to prepare Zn(II); $MnSO_4 \cdot H_2O$ was used to prepare Mn(II); $Al(NO_3)_3 \cdot 9H_2O$ was used to prepare Al(III); $Ni(SO_4) \cdot 6H_2O$ was used to prepare Ni(II); $CrCl_3 \cdot 6H_2O$ was used to prepare Cr(III); $K_2Cr_2O_7$ was used to prepare Cr(VI); $CoCl_2 \cdot 6H_2O$ was used to prepare Co(II); Cd powder was used to prepare Cd(II); $NaSeO_4$ was used to prepare Se(VI); Sb_2O_3 was used to prepare Sb(III); $SbCl_5$ was used to prepare Sb(V); and Pb metal was used to prepare Pb. The Se(IV) standard was prepared by adding an equal volume of concentrated HCl to a portion of Se(VI) standard and heating at 90°C for 20 minutes.

Analytical Apparatus

An atomic absorption spectrophotometer (Perkin-Elmer (PE) – AAnalyst 300) with an electrically heated quartz cell having a path length of 15-cm inline with a flow injection analysis system (FIAS; PE – FIAS 100), an autosampler (PE – AS90), and an arsenic electrodeless discharge lamp (EDL) attached to an EDL power supply (PE – EDL System 2) were used. The following spectrometer parameters were used: EDL current: 380 mv; wavelength: 193.7 nm; slit: 0.7 nm. Peak height was used for data processing. The following FIAS parameters were used: carrier gas: Ar; cell temperature: 900°C; sample loop: 500 μL; carrier solution: 10 percent (v/v) HCl; reducing agent: 0.25 percent (As(T)) or 0.03 percent (As(III)) $NaBH_4$ in 0.05 percent NaOH; carrier solution flow rate: 10 mL/min; reductant flow rate: 5 mL/min. Sodium borohydride was prepared daily and filtered through a 0.45 μm polyvinylidene fluoride filter membrane using a vacuum pump.

Analytical Procedures

Hydride formation occurs when As(III) in an acidic solution reacts with $NaBH_4$ according to the following reaction:

$$3NaBH_4 + 4H_3AsO_3 \rightarrow 4AsH_3(g) + 3H_3BO_3 + 3NaOH \quad (1)$$
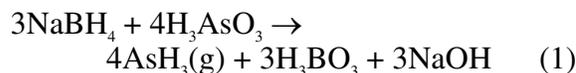
For the determination of As(T), As(V) is pre-reduced to As(III) using KI and L-ascorbic acid.

All water samples and standards were prepared in 25-mL volumetric flasks. The

method detection limits of the HGAAS analytical procedure used at the USGS National Research Laboratory in Boulder, Colo., are 0.1 µg/L for As(T) and 0.8 µg/L for As(III).

Determination of Arsenic(T)

(1) A solution containing 10 percent (w/v) KI and 10 percent (w/v) L-ascorbic acid was prepared.
(2) To each 25-mL volumetric flask, 5 mL concentrated HCl and 2.5 mL of the KI–L-ascorbic acid solution prepared from step 1 were added.
(3) The As(III) standard stock solution was used to prepare standards ranging in concentration from 0 to 10 µg/L As.
(4) To demonstrate completeness of reduction, synthetic samples containing varying As(III)/As(V) ratios were prepared.
(5) A volume of sample (up to 16.5 mL) that will yield 1 to 10 µg/L As(T) when diluted to volume was transferred to a 25-mL volumetric flask.
(6) Appropriate spike-recovery samples were prepared by adding both As(III) and As(V) to selected samples to demonstrate reduction of As(V) and $AsH_3(g)$ production.
(7) The HGAAS analyses were performed a minimum of 30 minutes after sample preparation.

Determination of Arsenic(III)

(1) Twenty-five mL of concentrated HCl was added to each 25-mL volumetric flask.
(2) As(III) standards ranging in concentration from 0 to 20 µg/L were prepared.
(3) To demonstrate that As(V) was not reduced, synthetic samples were prepared containing several As(III)/As(V) ratios.
(4) A volume of sample (up to 24.75 mL) that will yield 2 to 20 µg/L As(III) when

diluted to volume was transferred to a 25-mL volumetric flask.
(5) Appropriate spike-recovery samples were prepared by adding both As(III) and As(V) to demonstrate that As(V) is not reduced and that adequate $AsH_3(g)$ production occurs.
(6) The HGAAS analysis was performed immediately.

Removal of Interfering Metals Prior to Arsenic(III) Determination

For samples having a Cu(II)/As(III) molar ratio greater than 120, Fe(III)/As(III) molar ratio greater than 70, Cd/As(III) molar ratio greater than 800, or for samples with low As(III) spike recoveries, the sample was mixed with cation-exchange resin (AG 50W-X8, 20-50 mesh, H^+ form) to remove interfering metals prior to determination of As(III). The following procedure was used to remove interfering metals and regenerate the resin:

(1) Approximately 100 grams dry resin was transferred to a 250-mL polyethylene bottle. The resin was washed 2 times with 100 mL 2-M HCl followed by 5 washes with distilled water. The excess water was decanted.
(2) The resin was dried in an oven at 100°C.
(3) To a 50-mL polyethylene bottle, 12.5 grams dried resin and 25 mL sample were added. The mixture was periodically shaken for 30 minutes.
(4) The sample was separated from the resin by decanting it into an acid-washed 15-mL polyethylene bottle. This sample was used to determine the As(III) concentration.

Results and Discussion

Selective Reduction of Arsenic(III)

During the As(III) determination, As(V) can be reduced to $AsH_3(g)$ by the $NaBH_4$ reductant causing an overestimation of As(III) concentration. At a constant carrier concentration and FIAS flow rate, increasing the $NaBH_4$ concentration increases the sensitivity of the As(III) determination (fig. 1); however, when the $NaBH_4$ concentration exceeds 0.0625 percent, As(V) is reduced, causing an overestimation of As(III) concentration (fig. 2). To ensure selective reduction of As(III), the $NaBH_4$ concentration is maintained at 0.03 percent for the As(III) determination for analyses described in this report.
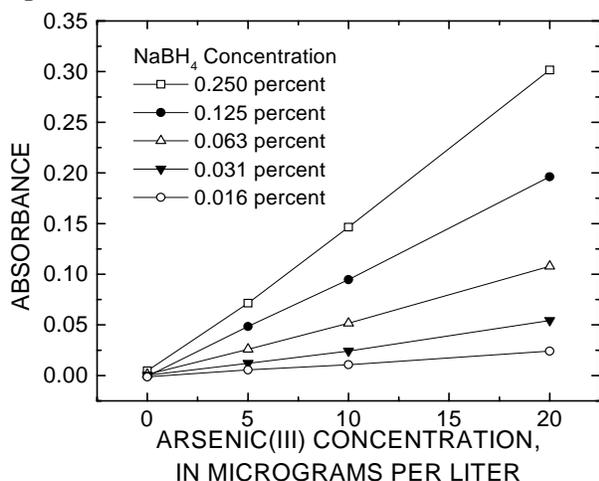
**Figure 1.** Effect of $NaBH_4$ concentration on the calibration curve in solutions containing only As(III)

Potential Metal Interferences on the Determination of Arsenic(T)

Sixteen metal species including Al, Cd, Co, Cr(III), Cr(VI), Cu(II), Fe(III), Fe(II), Mn, Ni, Pb, Sb(III), Sb(V), Se(IV), Se(VI),
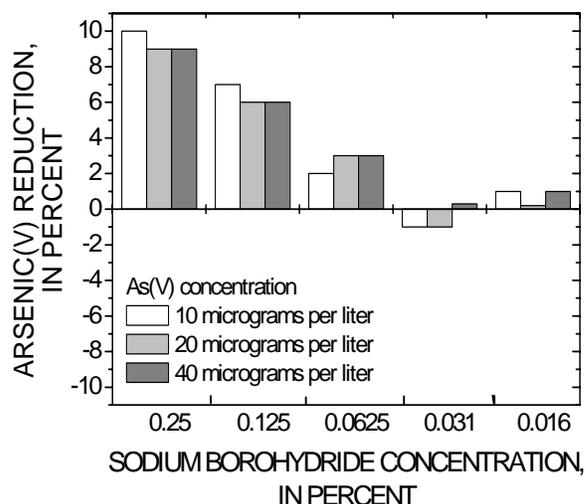
Figure 2. Effect of $NaBH_4$ concentration on the reduction of As(V) to As(III) in solutions containing 10 μg/L As(III) and varying As(V) concentrations.

And Zn were evaluated as possible interferents on the determination of As(T). The interference of each metal was evaluated by spiking synthetic samples containing 6 μg/L As(III) and 6 μg/L As(V) with 0.002 to 1,000 mg/L of the potential interfering metal and then determining the As(T) concentration using the HGAAS procedure (without cation exchange treatment). Arsenic(T) recoveries ranged from 92 to 102 percent for individual solutions spiked with Al, Cd, Co, Cr(VI), Cr(III), Cu(II), Fe(II), Fe(III), Mn, Ni, or Zn (fig. 3). For solutions spiked with a combination of metals including Al, Cd, Co, Cr(III), Cr(VI), Cu(II), Fe(II), Fe(III), Mn, Ni, and Zn, each up to a concentration of 500 mg/L, As(T) recoveries ranged from 97 to 102 percent. Dissolved Cu(II) was reduced to Cu metal during the pre-reduction step. The precipitated metal is visible at Cu concentrations greater than 100 mg/L and the liquid phase was decanted and analyzed with little change in As(T) concentration. Antimony(III) and Sb(V) were the only hydride-forming species found to interfere with the formation of $AsH_3(g)$ (fig. 4). Antimony(III) and Sb(V) substantially suppressed $AsH_3(g)$ formation by reacting
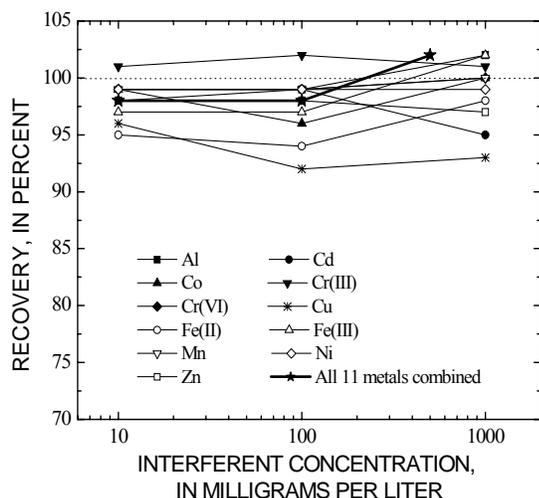
Figure 3. As(T) determinations in the presence of potential interfering metals.
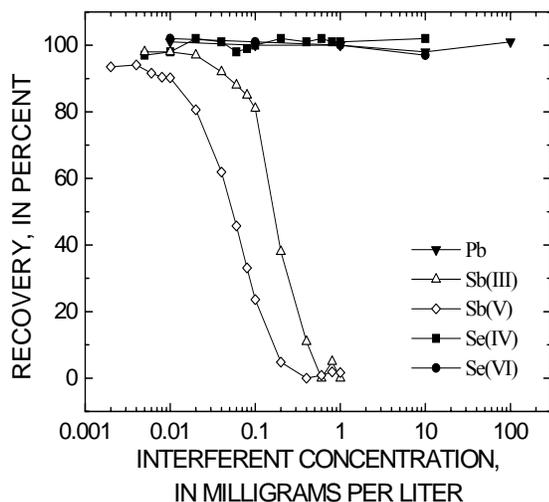
Figure 4. As(T) determinations in the presence of hydride-forming metals.

with the $NaBH_4$ when the Sb(III)/As(T) molar ratio exceeded 4 or the Sb(V)/As(T) molar ratio exceeded 2. In most waters, concentrations of Sb(III) and Sb(V) are much lower than As(T) concentrations and are likely to be diluted (As(T) less than 10 µg/L) to a concentration that will not interfere with the As(T) determination. Alkali and alkaline earth elements do not interfere with the As(T) determination (Smith, 1975).

Potential Metal Interferences on the Determination of Arsenic(III)

The interference of 16 metal species on the determination of As(III) was tested by spiking synthetic samples containing 10 µg/L As(III) and 10 µg/L As(V) with 0.0001 to 1,000 mg/L Al, Cd, Co, Cr(III), Cr(VI), Cu(II), Fe(III), Fe(II), Mn, Ni, Pb, Sb(III), Sb(V), Se(IV), Se(VI), and Zn and determining the As(III) co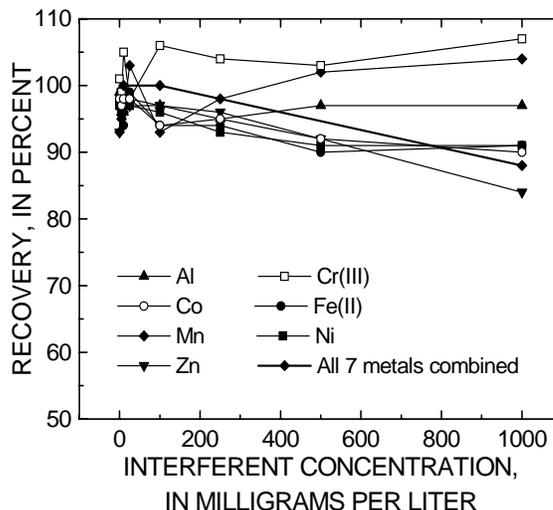ncentration using the HGAAS procedure (without cation-exchange treatment). Arsenic(III) recoveries for samples spiked with Al, Co, Cr(III), Fe(II), Mn, Ni, and Zn ranged from 84 to 107 percent over the entire concentration range tested (fig. 5).

Figure 5. As(III) determinations in the presence of potential interfering metals.

Low As(III) recoveries occurred when Cd exceeded 25 mg/L, Cr(VI) exceeded 0.03 mg/L, Cu(II) exceeded 2.0 mg/L, or Fe(III) exceeded 1.0 mg/L. Cadmium and Cu(II) are likely reduced by $NaBH_4$ in the FIAS reaction chamber and, consequently, arsine production is limited by the available $NaBH_4$. Chromium(VI) and Fe(III) inhibit arsine production by either competing with As(III) for the available $NaBH_4$ or oxidizing As(III) to As(V). Arsenic(III) is quickly oxidized as

Fe(III) undergoes photoreduction (Emett and Khoe, 2001). These synthetic samples were prepared in clear volumetric flasks and exposed to light. Therefore, the low As(III) recovery in the presence of only Fe(III) may be due to photochemical reactions with Fe(III) prior to the As(III) determination. However, when Fe(II) concentrations were twice the concentration of Fe(III), low As(III) recoveries occurred only when Fe(III) exceeded 10 mg/L (fig. 6). Iron(II) relieves the interference from Fe(III), within a limited Fe(III) concentration range, by reacting with free radicals generated as Fe(III) undergoes photoreduction (Emett and Khoe, 2001).
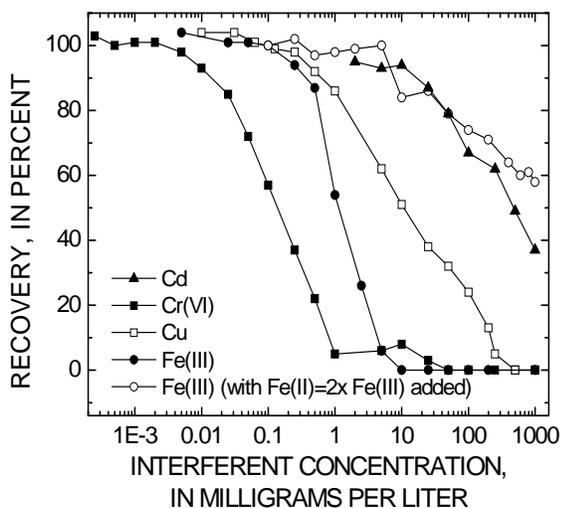
Figure 6. As(III) determinations in the presence of interfering metals.

Among the hydride-forming metals, Sb(III) at concentrations greater than 0.1 mg/L, Sb(V) greater than 0.4 mg/L, and Se(IV) greater than 0.02 mg/L interfered with As(III) determinations, whereas Pb and Se(VI) did not (fig. 7). Antimony(III), Sb(V), and Se(IV) suppress $AsH_3(g)$ production by reacting with the available $NaBH_4$. An additive effect of interfering metals on the determination of As(III) was demonstrated by adding increasing amounts of Fe(III) to a solution containing 0.5 mg/L Cu and 10 μg/L As(III) (fig. 8). Low As(III) recoveries occurred when the molar ratios of metals to As(III)

were: Cu(II) greater than 120, Fe(III) greater than 70, Cr(VI) greater than 2, Cd greater than 800, Sb(III) greater than 3, Sb(V) greater than 12, or Se(IV) greater than 1. The sample could not be diluted to an As(III) concentration (As(III) less than 20 μg/L) below which these interferences were absent.
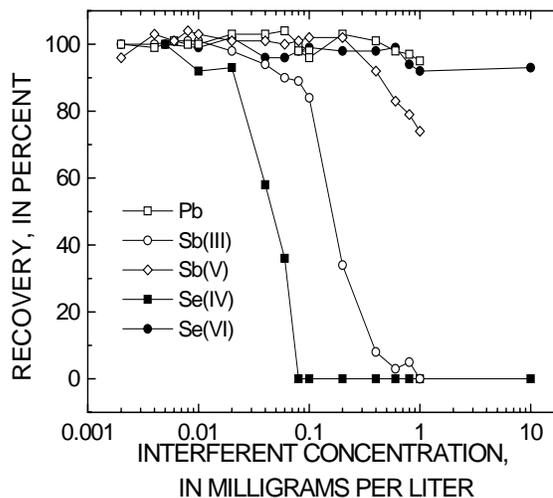
Figure 7. As(III) determinations in the presence of hydride-forming metals.
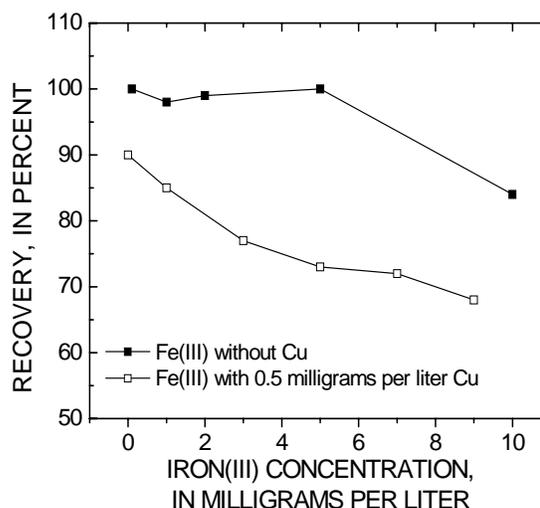
Figure 8. Additive interference in the determination of As(III) in a solution containing 10 micrograms per liter As(III) and 5 milligrams per liter Cu(II).

Copper(II) and Fe(III) are of primary concern because water generated from acid mine

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drainage potentially contains high concentrations of Cu(II) and Fe(III).

Cation Exchange Separation of Iron(III) and Copper

Interfering metals can be removed using cation-exchange resin prior to the determination of As(III). The relative selectivity for AG 50W-X8 cation-exchange resin is 2.95 for Cd, 2.9 for Cu(II), and 1.0 for H^+ (Bio-Rad, 2003). Therefore, as long as the capacity of the resin (1.7 millieqivalents (meq) per mL of resin) is not exceeded, Cd and Cu(II) are expected to be removed from solution. The relative selectivity for Fe(III) is not published in the AG 50W instruction manual.

Laboratory experiments done for this report demonstrated that AG 50W-X8 cation-exchange resin in the H^+ form removed large amounts of Cu(II) and Fe(III) while maintaining the existing As(III)/As(T) ratio (table 1). When the As(III) concentration is high relative to that of the interfering metal, the sample may be diluted before analysis to a Cd, Cu(II), Cr(VI), Fe(III), Sb(III), or Se(IV) concentration that does not interfere with the As(III) determination. Chromium(VI) and the Se and Sb oxyanions will not be removed by cation exchange.

Accuracy and Time Stability of Arsenic Redox Species in Acid Mine Waters

Accuracy of Arsenic(T) Determinations

Acid mine water may contain up to 31 major metal species with concentrations that can vary over several orders of magnitude (Nordstrom and Alpers, 1999). Consequently, interferences are likely during As redox determinations by HGAAS for acid mine waters. Samples of water collected from the Reynolds Adit and a monitoring well near the Chandler Adit on the Summitville Mine site,

the Richmond Mine, and the Penn Mine were analyzed for many dissolved constituents including As(T) and As(III). Concentrations of potential interfering metals for these samples are listed in Table 2. The samples contain elevated concentrations of metals, as determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES) and colorimetric determinations for Fe redox species (To and others, 1999).

Accuracy of the As(T) method was evaluated by performing a standard addition on samples collected from the Summitville Mine, Colo. (Reynolds Adit and a monitoring well near Chandler Adit); the Richmond Mine, Calif.; and the Penn Mine, Calif. Spike recoveries for the samples ranged from 96 to 101 percent (fig. 9). Twenty samples from the Summitville Mine site, 6 from the Richmond Mine, and 3 from the Penn Mine were analyzed by ICP-OES for As(T). Concentrations compared well with As(T) concentrations determined by hydride generation (fig. 10). All As(T) determinations were performed without cation-exchange separation. As another measurement of accuracy for As(T) determinations, USGS standard reference water samples (SRWS) AMW4, T143, T155, and T159 (Farrar, 2000) were analyzed as unknowns along with the acid mine water samples. Measured concentrations compare well to the most probable values (MPV) (table 3).

Table 1. Cation exchange separation of Cu and Fe(III)

[mg/L, milligrams per liter; %, percent; ---, not measured; > greater than]

Initial Sample Concentration, mg/L					% Recovery		% Removal	
As(III)	As(V)	Cu	Fe(III)	Fe(II)	As(III)	As(T)	Cu	Fe(T)
0.010	0.010	---	---	---	96	99	---	---
0.010	0.010	25	---	---	96	97	>99	---
0.010	0.010	---	100	200	99	102	---	>99
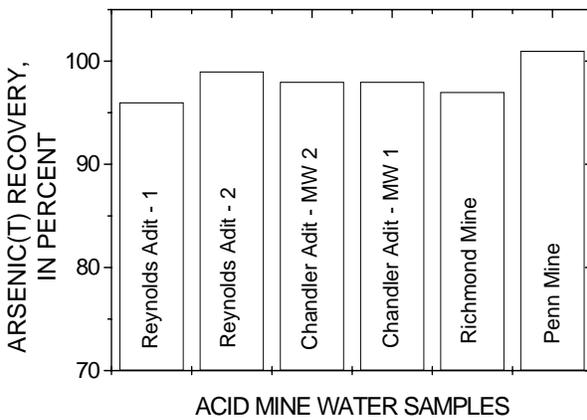
Figure 9. Spike recovery determinations of As(T) using hydride generation atomic absorption spectrometry.
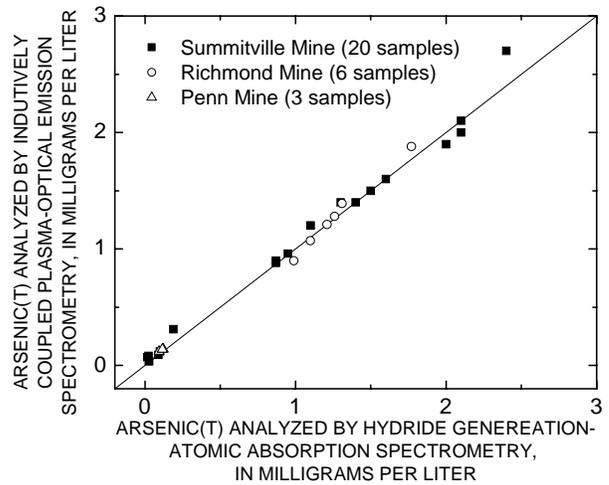
Figure 10. As(T) determinations by inductively coupled plasma-optical emission spectrometry and hydride generation atomic absorption spectrometry for 20 samples collected from Summitville Mine, Colo., 6 samples collected from Richmond Mine, Calif., and 3 samples collected from the Penn Mine, Calif.

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Table 2. Composition of acid mine water samples collected from Summitville Mine, Colo.; Richmond Mine, Calif.; and Penn Mine, Calif.

[As(T), As(III) plus As(V); HGAAS, hydride generation atomic absorption spectrometry; ICP-OES, inductively coupled plasma-optical emission spectrometry; ISE, ion-selective electrode; mg/L, milligrams per liter]

Constituent mg/L	Technique	Chandler Adit Monitoring Well	Reynolds Adit	Richmond Mine	Penn Mine
pH	ISE	2.7	2.8	0.9	3.2
As(T)	ICP-OES	2.6	2.1	33	0.14
As(T)	HGAAS	2.4	2.1	35	0.12
Al	ICP-OES	170	270	1,300	5.0
Cd	ICP-OES	0.088	0.52	14	0.023
Co	ICP-OES	0.50	1.1	0.47	0.048
Cr	ICP-OES	0.13	0.088	0.27	0.070
Cu	ICP-OES	31	130	350	<0.01
Mn	ICP-OES	13	39	16	8.2
Ni	ICP-OES	0.73	1.7	1.4	0.044
Pb	ICP-OES	0.19	1.1	4.1	0.022
Zn	ICP-OES	80	35	2,100	12
Fe(II)	Colorimetric	246	707	20,700	551
Fe(III)	Colorimetric by difference	205	54	1,300	4.0

Table 3. As(T) determinations in U.S. Geological Survey standard reference water samples

[µg/L, micrograms per liter; n, number of analyses; s, standard deviation; SRWS, standard reference water samples; MPV, most probable value; %RSD, percent relative standard deviation]

SRWS	n	As(T), µg/L	s	%RSD	MPV, µg/L
AMW4	25	170	4	2	168
T143	13	15	1	6	15.2
T155	6	33	1	2	32.9
T159	23	27	1	3	28.4

Accuracy of Arsenic(III) Determinations

Accuracy of As(III) determinations, both with and without cation exchange, was estimated by spiking samples collected from the Summitville Mine (Reynolds Adit and Chandler Adit), the Richmond Mine, and the Penn Mine with As(III). Iron(III) and Cu(II) interfere with the determination of As(III) in samples collected from Summitville, but not with the Richmond or Penn Mine samples (fig 11). Spike recoveries for Summitville Mine samples not separated by cation exchange were 44 to 53 percent, whereas recoveries for the same samples separated by cation exchange were 102 to 103 percent. The Richmond and Penn Mine samples were not separated with cation exchange resin because the ratios of Fe(III) and Cu(II) to As(III) were low enough that samples could be diluted to Fe(III) and Cu(II) concentrations that did not interfere with the determination. The As(III) concentrations were underestimated in the Summitville Mine samples not separated by cation exchange (fig. 12). No USGS standard reference water sample exists for As redox species.
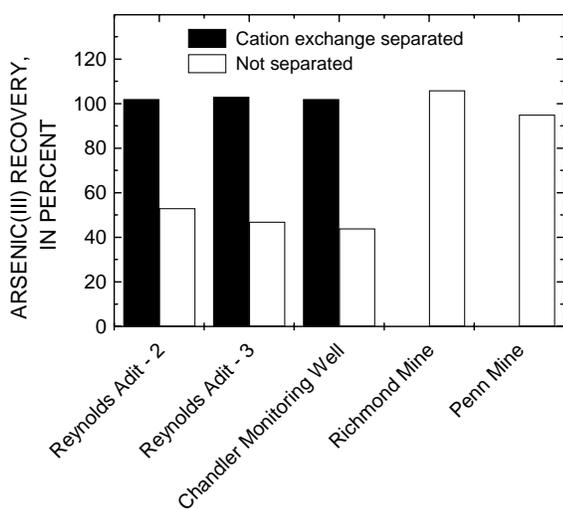

Figure 11. Spike recovery determinations using hydride generation atomic absorption spectrometry for As(III) in samples separated by cation exchange and not separated.
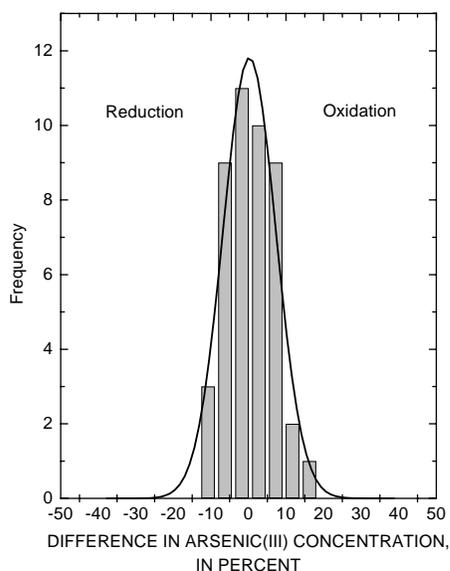
Time Stability of Arsenic Redox Species

The time stability of As(III) was monitored in 45 surface and ground water samples from Yellowstone National Park, Wyo.; Questa Mine site, N. Mex., Summitville Mine site, Colo., Richmond Mine, Calif., Penn Mine, Calif., Ester Dome, Alaska, Fallon, Nev., Mojave Desert, Calif., and Kamchatka, Russia. Samples were filtered through a 0.1-μm membrane, acidified to pH <2 with HCl, and stored in opaque bottles at 4°C. Samples were reanalyzed as many as 15 months after the initial determination. The samples containing Cu(II) or Fe(III) concentrations that interfered with the As(III) determination were separated using cation exchange. The change in As(III) is represented by plotting percent difference in As(III) concentration as a function of the initial As(III)/As(T) ratio. The equation used to calculate percent difference (Δ%) is:

$$\Delta\% = \frac{(\text{Initial As(III) conc.} - \text{Final As(III) conc.}) \times 100}{\text{Initial As(III) conc.}} \quad (2)$$
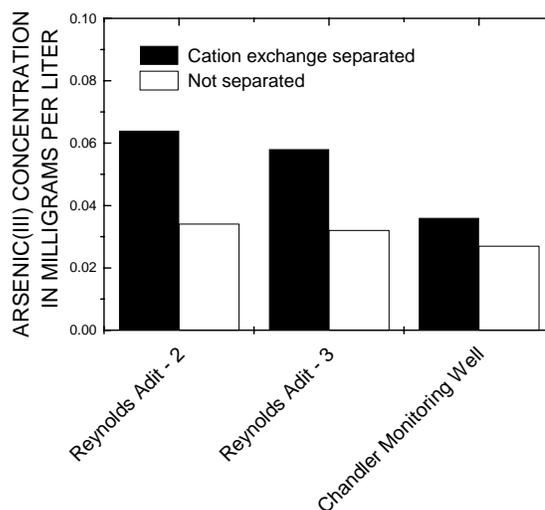
Figure 12. As(III) determinations using hydride generation atomic absorption spectrometry for samples collected from the Summitville Mine.

The As(T) concentration ranged from 0.006 to 33 mg/L and the initial As(III)/As(T) ratio ranged from 0.01 to 1.0 (fig. 13). The curved line is a Gaussian Fit. The average percent difference ($\Delta\%$) for all samples was 0.2 with a standard deviation of 7.

Figure 13. Time stability of As(III) for 45 surface and ground water samples from Yellowstone National Park, Wyo.; Questa Mine site, N. Mex.; Summitville Mine site, Colo.; Richmond Mine, Calif.; Penn Mine, Calif.; Ester Dome, Alaska; Fallon, Nev.; Mojave Desert, Calif.; and Kamchatka, Russia reanalyzed 3 to 15 months after the initial determination. The curved line is a Gaussian Fit.

Summary

Hydride generation atomic absorption spectrometry (HGAAS) is a sensitive and selective method for the determination of As(T) and arsenic(III); however, it is subject to metal interferences for acid mine waters. Antimony(III) and Sb(V) interfere with the HGAAS As(T) determination when the molar ratios of Sb(III) and Sb(V) exceed 4 and 2, respectively. Low As(III) recoveries occurred when the molar ratios of metals to As(III) were: Cu(II) greater than 120, Fe(III) greater than 70, Cr(VI) greater than 2, Cd greater than 800, Sb(III) greater than 3, Sb(V) greater than 12, or Se(IV) greater than 1. Samples could not be diluted to an As(III) concentration (As(III) less than 20 µg/L) below which these interferences were absent. Copper(II) and Fe(III) are of primary concern because water generated from acid mine drainage potentially contains high concentrations of Cu(II) and Fe(III). Separation of Fe(III) and Cu(II) from the sample while maintaining the existing As(III)/As(T) ratio can be achieved using cation exchange.

Some acid mine waters contain high Fe(III) and Cu(II) and accurate measurements of As(III) is problematic without removing the Fe(III) and Cu(II) prior to hydride generation. Proper sample collection and preservation are critical to maintain the existing As(III/V) ratio prior to the analysis. Filtering samples through a 0.1 µm filter, acidifying with HCl to a pH less than 2, and storing in an opaque bottle at 4°C inhibits changes in the As(III)/As(T) ratios for up to 15 months after sample collection.

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