

CATION-EXCHANGE SEPARATION OF INTERFERING METALS FROM ACID MINE WATERS FOR ACCURATE DETERMINATION OF TOTAL ARSENIC AND ARSENIC(III) BY HYDRIDE GENERATION-ATOMIC ABSORPTION SPECTROMETRY

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INTRODUCTION

Accurate and precise determination of inorganic As (III/V) redox species is important in the interpretation of its toxicity and mobility in acid mine waters. Several analytical methods use arsine generation to separate arsenic species but high metal concentrations can suppress arsine production (Creed and others 1996). The potential inhibition of arsine formation by eleven metal species including Cu, Fe(III), Fe(II), Al, Cd, Mn, Zn, Co, Ni, Cr(III), and Cr(VI) ranging in concentration from 0-1000 mg/L was investigated with a flow injection analysis system (FIAS) and detection by atomic absorption spectrometry. Interfering metal cation species can be removed with cation exchange resin while maintaining existing As(III)/As(T) ratios (As(T)=As(III+V)). The pre-analysis separation of Fe(III) using cation exchange resin for the determination of As redox species using ion chromatography in iron sulfate-sulfuric acid media has been successfully performed in the past (Tan and Dutrizac, 1985). Oxidation of As(III) by Fe(III) was also investigated.

EXPERIMENTAL

Samples collected in the field are immediately filtered through a 0.1 μm tortuous-path filter, acidified to pH of about 1.3 with hydrochloric acid (2 mL 6 M HCl per 250 mL sample), and stored in acid-washed opaque bottles at 4°C.

The hydride generation determination of As(T) involves pre-reduction of As(V) by preparing the sample in a solution of 1% (w/v) KI - 1% (w/v) L-ascorbic acid and 24% (v/v) concentrated HCl (Creed and others 1996). The determination of As(III) requires the sample to be in 1% (v/v) concentrated HCl. Prior to determination of As(III), batch cation exchange separation using AG 50W-X8 cation exchange resin (20-50 mesh, Na form) is needed for samples having concentrations of Cu > 0.5 mg/L, Fe(III) > 0.5 mg/L, or Cd > 10 mg/L in the sample diluted for As(III) determination.

The carrier solution is 10% (v/v) HCl and the reducing agent is NaBH₄ at 0.25% (w/v) for As(T) or 0.03% (w/v) for As(III) in 0.05% NaOH. NaBH₄ is prepared fresh daily and filtered through a 0.45 μm filter membrane using a vacuum pump. The method detection limits are 0.0001 mg/L for As(T) and 0.0002 mg/L for As(III).

RESULTS AND DISCUSSION

Potential Interferences in the Determination of As(T) and As(III)

Acid mine water may contain at least 31 major species with concentrations that can vary more than several orders of magnitude (Nordstrom and Alpers, 1999). Eleven metal species common to acid mine waters including Cu, Fe(III), Fe(II), Al, Cd, Mn, Zn, Co, Ni, Cr(III), and Cr(VI) have been evaluated for interfering with the determination of As species. The degree of interference for each metal in the determination of As(T) was evaluated by spiking a synthetic sample containing 6 $\mu\text{g/L}$ As(III) and 6 $\mu\text{g/L}$ As(V) with 10, 100, and 1000 mg/L of the potential interfering metal. The As(T) recoveries ranged from 92-102% for all metals tested (Fig.1). The expected range of recovery for synthetic samples without any potential interfering metals is 95-105%. Dissolved Cu was reduced to Cu metal and precipitated during the pre-reduction step. The liquid phase was decanted and analyzed with minimal loss of As(T).

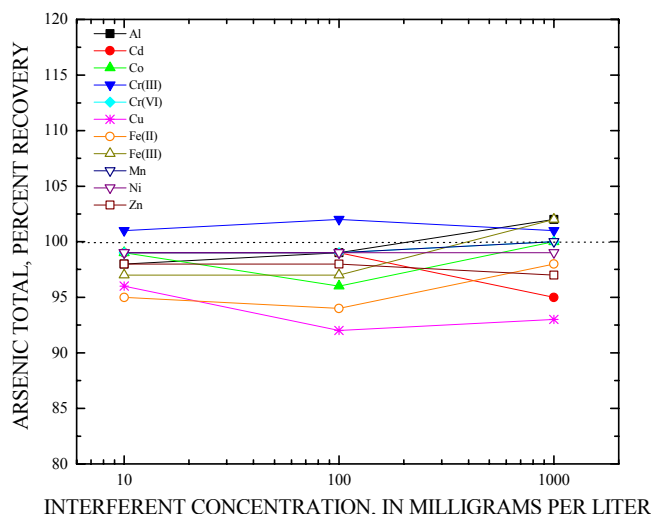


Figure 1. As(T) determinations in the presence of potential interfering metal.

The degree of interference for each metal in the determination of As(III) was tested by spiking a synthetic sample containing 10 µg/L As(III) and 10 µg/L As(V) with 0-1000 mg/L of the potential interfering metal. The As(III) recoveries for samples spiked with Fe(II), Al, Mn, Zn, Co, Ni, and Cr(III) ranged from 84-107% over the entire concentration range tested. Poor As(III) recoveries occurred when Cu exceeded 0.5 mg/L, Fe(III) exceeded 0.5 mg/L, Cr(VI) exceeded 0.01 mg/L, or Cd exceeded 10 mg/L. However, when Fe(II) concentrations were twice the concentration of Fe(III), poor As(III) recoveries occurred only when Fe(III) exceeded 10 mg/L (Fig. 2). Apparently, Fe(II) relieves the interference from Fe(III) within a limited range. The poor recoveries are the result of hindered arsine production and/or oxidation of As(III) by the interfering metal.

When the As(III) concentration is high relative to the interfering metal, the interfering metal may be diluted prior to analysis to a level that does not interfere with the As(III) determination. Concentrations of Cu and Fe(III) are frequently very high in acid mine waters. Batch cation exchange separations using AG 50W-X8 cation exchange resin (20-50 mesh, Na form) using 12.5 g dry resin per 25 mL sample removes sufficient Cu and Fe(III) while maintaining the existing As(III)/As(T) ratio (Table 1). Chromate (Cr(VI)) is not expected to be removed via cation exchange.

Table 1. Recovery of As(III) and As(T) and removal efficiency of Cu and Fe(III) following cation exchange.

---Initial Sample Composition, mg/L---					% Recovery		% Removal	
As(III)	As(V)	Cu	Fe(III)	Fe(II)	As(III)	As(T)	Cu	Fe(III)
0.010	0.010	---	---	---	96	99	---	---
0.010	0.010	25	---	---	96	97	>99	---
0.010	0.010	---	100	200	99	102	---	>99

Oxidation of As(III)

When testing removal of interfering metals from synthetic solutions via cation exchange and subsequent analysis of As(III), it appeared that Fe(III) quickly oxidizes As(III), while Cu did not. However, the oxidation of As(III) by Fe(III) is inhibited by Fe(II). Borho and Wilderer (1997) used Fe(II) as a preservative for As redox species in ground waters containing high Fe(III). Acid mine water from Summitville, CO did not appear to oxidize As(III) as demonstrated by good recoveries over a 23 hour period (Fig. 3).

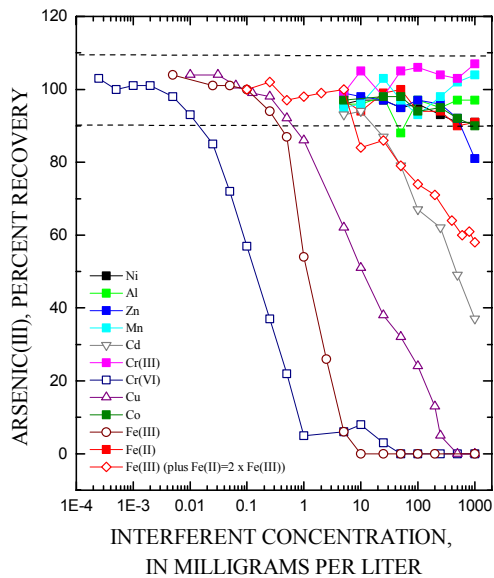


Figure 2. As(III) recovery in synthetic samples containing potential interfering metals.

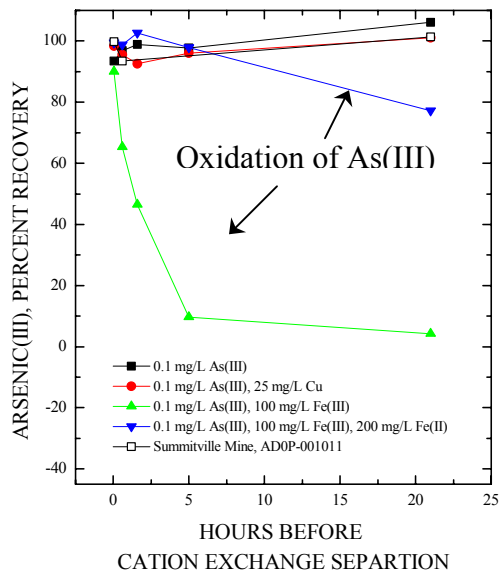


Figure 3. As(III) recovery in samples containing potential interfering metals following cation exchange.

Accuracy of As(T) Measurements in Acid Mine Waters from Summitville

The accuracy of the As(T) method was estimated by performing spike recoveries on samples collected from Reynolds Adit and a monitoring well near Chandler Adit, at the Summitville Mine site. Recoveries were 96-99% (Table 2). The samples contained elevated concentrations of transition metals determined using inductively couple plasma-atomic emission spectroscopy and colorimetric determinations for iron redox species (Stookey, 1970) (Table 3).

Table 2. As(T) spike recovery determinations (without cation exchange).

Sample ID	As(V) added	As(V) Recovered	
	mg/L	mg/L	%
Reynolds Adit - 1	0.004	0.0038	96
Reynolds Adit - 2	0.004	0.0040	99
Chandler Monitoring Well - 1	0.004	0.0039	98
Chandler Monitoring Well - 2	0.004	0.0039	98

Accuracy of As(III) Measurements in Acid Mine Waters from Summitville

The accuracy of As(III) analyses in samples collected from the Summitville Mine site was estimated by performing spike recoveries on samples with and without cation exchange (Table 4). Recoveries were 100-103% in samples undergoing cation exchange and 44-53% in samples without cation exchange. Arsine production was hindered in the untreated samples resulting in an under-estimation of As(III) (Table 5). To ensure that the separation maintained the existing As(III)/As(T) ratio, sample AD0P-091900 was also spiked with As(III) and As(V) prior to cation exchange separation. The recoveries were 90% for As(III) and 94% for As(T).

Table 3. Composition of samples collected from the Summitville Mine site.

Constituent, mg/L	Technique	Chandler Monitoring Well - 2	Reynolds Adit - 2
As(T)	ICP-AES / HG	2.6 / 2.4	2.1 / 2.1
Al	ICP-AES	170	270
Cd	ICP-AES	0.088	0.52
Co	ICP-AES	0.5	1.1
Cr	ICP-AES	0.13	0.088
Cu	ICP-AES	31	130
Mn	ICP-AES	13	39
Ni	ICP-AES	0.73	1.7
Pb	ICP-AES	0.19	1.1
Zn	ICP-AES	80	35
Fe(II)	Colorimetric	246	707
Fe(III)	Colorimetric by difference	205	54

Table 4. Comparison of As(III) recovery in samples separated and not separated by cation exchange.

Sample ID	As(III) added mg/L	%As(III) Recovered	
		Separated	Not Separated
Reynolds Adit - 2	0.008	102	53
Reynolds Adit - 3	0.008	103	47
Chandler Monitoring Well - 3	0.008	102	44

Table 5. Comparison of As(III) concentration determined in samples separated and not separated by cation exchange.

Sample ID	As(III), mg/L	
	Separated	Not Separated
Reynolds Adit - 2	0.064	0.034
Reynolds Adit - 3	0.058	0.032
Chandler Monitoring Well - 3	0.036	0.027

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