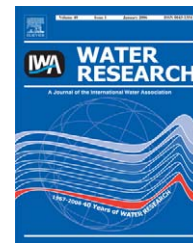


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# Enhanced recovery of arsenite sorbed onto synthetic oxides by L-ascorbic acid addition to phosphate solution: calibrating a sequential leaching method for the speciation analysis of arsenic in natural samples

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### Abbreviations:

DTPA:

diethylenetriaminepentaacetate

As(III): arsenite

As(V): arsenate

EXAFS: extended X-ray absorption fine structure

FTIR: fourier transform infrared spectroscopy

XAS: X-ray absorption spectroscopy.

## ABSTRACT

Stripping voltammetry capable of detecting 0.3 µg/L arsenate and arsenite was applied for speciation analysis of arsenic sorbed onto synthetic ferrihydrite, goethite at As/Fe ratio of ~1.5 mg/g with or without birnessite after sequential extraction using 1M phosphate (24 and 16h) and 1.2M HCl (1h). Precautions to avoid oxygen were undertaken by extracting under anaerobic conditions and by adding 0.1M L-ascorbic acid to 1M NaH<sub>2</sub>PO<sub>4</sub> (pH 5). Addition of L-ascorbic acid did not reduce As(V) to As(III). The recovery rate for As(III) using L-ascorbic acid for extraction (pH 5) but not for adsorption was 81% and 74% of total sorbed As, and was 99% and 97% of extracted As for ferrihydrite and goethite, respectively. Birnessite oxidized most As(III) during the adsorption procedure. L-ascorbic acid used both in adsorption and extraction procedures improved the recovery of As(III) to 79–94% for ferrihydrite–birnessite and 57–94% for goethite–birnessite systems with Fe/Mn ratios of 7, 70, 140 and 280 g/g.

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## 1. Introduction

The mobility of arsenic in the environment is influenced by the adsorption–desorption properties of various iron oxyhydroxides, including ferrihydrite and goethite (De Vitre et al., 1991; Manning and Goldberg, 1996). To assess how much As has the potential to mobilize from natural sediment or soil samples, a range of selective leaching methods, such as weak acid (e.g., 0.1 or 1.0M HCl), organic complexing agents (e.g., oxalate, citrate, DTPA), weak base (0.1M NaOH), and ligand (1.0M phosphate) are often applied (Loeppert et al., 2003). Among them, phosphate has been widely used to extract the adsorbed phase of As (Jackson and Miller, 2000; Keon et al., 2001; Alam et al., 2001). This is because As(V) and phosphate have similar ionic radius and acid dissociation constants of the protonated species (O'Reilly et al., 2001). Furthermore, spectroscopic studies using EXAFS and FTIR have provided evidence that As(III) is adsorbed to iron hydroxides by an inner-sphere mechanism analogous to As(V) and phosphate (Sun and Doner, 1996; Fendorf et al., 1997; Manning et al., 1998). Thus, phosphate displace adsorbed As(III) and As(V) by competing for the same adsorption sites.

The mobility of arsenic in the environment is also influenced by oxidation–reduction reactions involving Fe and As (Smedley and Kinniburgh, 2002). Microbial reduction of arsenate to arsenite has been shown to enhance As mobility in sediments of the Aberjona watershed (Ahmann et al., 1997). Yet the oxidation states of As in sediments or soil samples containing  $<10^2$  mg/kg As have rarely been evaluated because of high detection limit of XAS (O'Day et al., 2004). The wide-spread presence of elevated As in groundwater in many parts of the world are associated with naturally occurring As in sediments at concentration  $<10^1$  mg/kg (Smedley and Kinniburgh 2002). Understanding of As mobilization mechanism will be improved if speciation of mobilizable As in sediment can be determined.

Voltammetry, a sensitive technique that quantifies  $\sim 1\mu\text{g/L}$  As (He et al., 2004), has previously been applied to evaluate As speciation followed by sequential leaching (Cui and Liu 1988). However, oxidation of As(III) to As(V) during extractions performed aerobically has not been avoided in previous studies (Jackson and Miller, 2000; Manning et al., 2003). Jackson and Miller (2000) found that 9–100% of As was recovered as As(V) in  $\text{PO}_4$  and  $\text{OH}^-$  extracts of As(III)-loaded Fe oxides. This is not surprising because in addition to oxygen, Mn-oxides and Fe-oxides present in natural samples can both oxidize As(III) rapidly. The oxidation rate of As(III) by oxygen is accelerated microbially to a half-time of 0.3h (Wilkie and Hering, 1998). Manganese oxides oxidize As(III) with a half-time of 10–20 min (Oscarson et al., 1981; Scott and Morgan, 1995). De Vitre et al. (1991) reported that 50–75% of As(III) was oxidized to As(V) by Fe-oxides in 2 days.

In this paper, we document the effectiveness of two important modifications to the previously used As leaching scheme (Keon et al., 2001) to speciate sorbed As by voltammetric determination (He et al., 2004). First, L-ascorbic acid, a powerful anti-oxidant that scavenges reactive oxygen species and regenerates other antioxidants (Feldman, 1979; Griffiths and Lunec, 2001), is added to 1M phosphate solution to

liberate sorbed As. Second, 1M phosphate and 0.1M ascorbic acid (pH 5), and 1.2M HCl solutions are purged by nitrogen gas and solutions are added to the sample under a nitrogen environment. The extraction efficiency of As(III) and As(V) were evaluated using synthetic Fe-oxides with or without Mn-oxides that represent a range of Fe/Mn ratios encountered in the environment.

## 2. Experimental

As(III) was first adsorbed onto synthetic oxides in all experiments but in one, for which As(V) was used. The ratio of As/Fe is  $\sim 1.5$  mg/g in all experiments (Table 1). The system investigated includes ferrihydrite, goethite, mixed ferrihydrite–birnessite and mixed goethite–birnessite. The Fe/Mn ratios in the mixed system are 7, 70, 140, 280g/g (Table 1). Ferrihydrite, goethite and birnessite were synthesized following the protocols by Cornell and Schwertmann (2003), and by McKenzie (1971), respectively. The sorption of As(III) was conducted either with or without L-ascorbic acid.

The As-loaded oxides were then sequentially extracted in a 1M phosphate/0.1M ascorbic acid solution (pH 4 or 5) for 24 and 16 h, then in a 1.2M HCl solution for 1 h. The extractions of As(III) were conducted either with or without L-ascorbic acid (Table 1). Procedure for adsorption and extraction are detailed below to note the steps taken to avoid contact with oxygen during extraction. All reagents used are ACS reagent grade unless noted.

### 2.1. Adsorption procedure

The 1000 mg As/L stock solutions of As(III) and As(V) were prepared with  $\text{NaAsO}_2$  and  $\text{NaHAsO}_4 \cdot 7\text{H}_2\text{O}$  respectively. Ferrihydrite or goethite ( $\sim 100$  mg each) with or without Mn-oxide (18, 1.8, 0.9, 0.45 mg) was transferred to 10 mL amber glass serum bottles (Wheaton, Borosilicate). Then 10 mL solutions containing 10 mg/L As, with or without 0.1M L-ascorbic acid, was adjusted to pH = 5 and added to the serum bottles. The serum bottles with rubber septum (Wheaton, Chlorobutyl) and aluminum caps (Wheaton) were then crimp-sealed. The bottles were shaken for 36 h, then centrifuged at 5000 rpm for 20 min. Aliquots of the supernatant were saved for determination of As(III) and As(V).

### 2.2. Extraction procedure

First, 10 ml of 1M sodium phosphate ( $\text{NaH}_2\text{PO}_4$ ) solution with or without 0.1M L-ascorbic acid was adjusted to pH 5 using NaOH pellets and purged with nitrogen. (In several experiments, phosphate solution adjusted to pH 4 was used for the 24 h extraction for comparison). The solution was then added to serum bottles containing As-loaded solids, again crimp-sealed with septum and aluminum cap inside a nitrogen glove bag. Samples were shaken for 24 h and then centrifuged at 5000 rpm for 20 min. Aliquots of the supernatant were saved for determination of As(III) and As(V).

Second, the same extraction was performed, but for 16 h.

Lastly, the same extraction procedure was performed but using 10 ml of 1.2M HCl diluted with  $\text{N}_2$ -purged water for 1 h.

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