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A new method for thioarsenate preservation in iron-rich waters by solid phase extraction

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ABSTRACT

In order to preserve iron-rich samples for arsenic speciation analysis, mineral acids or EDTA are typically added to prevent oxidation and precipitation of iron. However, when sulfide is present, and thioarsenates ($[HAs^{V}S^{-II}_{n}O_{4-n}]^{2-}$, n = 1–4) can form, these methods are unsuitable due to arsenic sulfide precipitation or artifact speciation changes. Here, a new method based on separating the anionic arsenic species from cationic iron in the presence of sulfide via solid phase extraction (SPE) has been investigated. Synthetic solutions containing arsenite, arsenate, monothioarsenate, and trithioarsenate were passed through the anion-exchange resin AG2-X8, after which the resin was washed, eluted, and speciation of each step analyzed by IC-ICP-MS. Retention on the resin of 96.8 ± 0.2%, 98.8 ± 0.2%, and 99.6 ± 0.3% was found for arsenate, monothioarsenate, and trithioarsenate, respectively. Cationic iron (90 μM Fe(II)) was not retained (0.4 ± 0.2%). Uncharged arsenite passed through the resin in the absence of sulfide, while 47.3% of arsenite were retained at tenfold sulfide excess via thiol groups binding to the organic resin structure. Elution with 3 × 15 mL of 0.5 M salicylate, including a soak time, resulted in quantitative recovery of all retained species. Stability of the retained species on the resin was tested with iron-rich, natural waters from a Czech mineral spring. Arsenate, monothioarsenate, dithioarsenate, and trithioarsenate were successfully separated from iron and recovered after 6 d. Thus, SPE presents a viable answer to the problem of preserving arsenic in the presence of both iron and sulfide.

1. Introduction

It is well documented that speciation is a key factor for understanding the fate of arsenic in the environment. Over the years, numerous studies have shown how the oxidation state of arsenic controls not just its mobility in natural systems (Ferguson and Gavis, 1972; Campbell and Nordstrom, 2014), but also its toxicity (Styblo et al., 2000; Dopp et al., 2008; Hinrichsen et al., 2014). In order to assess the potential impact of arsenic in the environment, it is therefore imperative to measure the correct arsenic speciation in natural samples. However, maintaining original speciation in a sample during collection and storage can be challenging, particularly in the presence of iron.

Iron has the potential to impair both the speciation and total arsenic concentration of a sample. In less than 1 d, 0.3 μM arsenite can be fully oxidized to arsenate in an unpreserved sample with 18 μM Fe(III) (Bednar et al., 2002). Furthermore, arsenite and arsenate readily co-precipitate with, or adsorb on, iron oxyhydroxides depending on pH (Dixit and Hering, 2003), which leads to loss of total dissolved arsenic. To overcome these problems, different preservation methods have been developed. Most of the published methods are based on the addition of mineral acids, such as HNO_3, HCl, H_2SO_4, or H_3PO_4 to the sample (Cherry et al., 1979; Cheam and Agemian, 1980; Aggett and Kriegman, 1987; Edwards et al., 1998; Hall et al., 1999; Daus et al., 2002). This approach is used to decrease the pH to <2 in order to keep iron in solution, which has been shown to preserve arsenic speciation in the presence of 300 μM Fe(II) for up to 6 weeks (Aggett and Kriegman, 1987). However, the addition of mineral acids has also been reported to change arsenic speciation and total concentrations. Rapid oxidation of arsenite has been found in samples preserved with HNO_3 or HCl (Hall et al., 1999; Bednar et al., 2002), as a result of photochemically-induced nitrate reduction or dichloro radical formation (Emett and Khoe, 2001), respectively. Other studies have evaluated the use of EDTA to chelate iron, and thus avoid oxidation and precipitation of iron oxyhydroxides (Gallagher et al., 2001; Bednar et al., 2002). Samples containing arsenite and arsenate

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were stable for up to 3 months when treated with EDTA and stored in opaque polyethylene bottles (Bednar et al., 2002).

Method development for arsenic preservation in iron-rich waters has focused on arsenite and arsenate so far. In sulfidic environments, however, thioarsenates ($[HAs^{V}S^{-II}_{n}O_{4-n}]^{2-}$, n = 1–4) can also play a significant role for arsenic speciation. Initially, thioarsenates were found in iron-free geothermal systems, representing up to 83% of total arsenic (Planer-Friedrich et al., 2007; Planer-Friedrich and Wilson, 2012; Ullrich et al., 2013). Despite the potential formation of iron sulfides, thioarsenates have also been shown to exist in iron-rich environments (Suess et al., 2011; Stucker et al., 2014). Furthermore, several laboratory studies on the mobility of thioarsenates reported their occurrence in the presence of nanohematite, goethite, ferrihydrite, mackinawite, and pyrite (Suess and Planer-Friedrich, 2012; Burton et al., 2013; Couture et al., 2013; Stucker et al., 2014). The reaction of free sulfide with arsenite to form thioarsenates is kinetically favored over the formation of iron sulfides. Therefore, thioarsenate formation will occur prior to precipitation of any iron sulfides such as mackinawite, greigite, or pyrite.

Preserving thioarsenates in a solution that contains iron and sulfide presents a delicate task. Acidification of such a sample would lead to precipitation of arsenic sulfides (Smieja and Wilkin, 2003). Preservation with EDTA, as recommended by Bednar et al. (2002), was found to accelerate oxidation of arsenite, while also causing artifact thioarsenate formation (Suess et al., 2015). Flash-freezing, which preserved thioarsenates in iron-free solutions for up to 67 d (Planer-Friedrich et al., 2007), leads to oxidation of Fe(II) and precipitation of iron oxyhydroxides upon thawing the sample prior to analysis. This promotes co-precipitation and adsorption of arsenic, which renders it unsuitable for the preservation of iron-rich samples. Overall, none of the established methods can preserve arsenic speciation in the presence of sulfide and iron.

This lack of a suitable preservation method for sulfidic, iron-rich waters can be addressed by applying solid phase extraction (SPE). It has been shown that arsenite and arsenate can be separated using SPE cartridges packed with aluminosilicate (Meng et al., 2001), or more commonly with anion-exchange resin according to Ficklin (1983). When a sample is passed through an anion-exchange resin, anionic arsenate will be adsorbed, while uncharged arsenite will pass without interaction (Kim, 2001; Yalcin and Le, 2001; Bednar et al., 2002; Watts et al., 2010; Bennett et al., 2011; Sugar et al., 2013). Most anion-exchange resins consist of a functional group, such as a quarternary ammonium group, attached to a styrene divinylbenzene copolymer lattice. In its original form the positively charged functional group binds a counter ion such as chloride or acetate. When a sample is applied to the resin, this counter ion is replaced with an anionic compound from the sample. The retained anionic compounds can be removed later from the resin by applying an eluting agent. In order to elute arsenate from an anion-exchange resin, 1 M HCl (Le et al., 2000), 6 M HCl (Jay et al., 2004), 0.16 M HNO_3 (Bednar et al., 2002), 1 M HNO_3 (Watts et al., 2010), or 2 M HNO_3 (Bennett et al., 2011) have been proposed.

The capability of SPE to retain anionic compounds on a resin can be employed for the preservation of thioarsenates in sulfidic, iron-rich waters. Under environmentally relevant conditions, thioarsenates occur as anionic species (Thilo et al., 1970) and can be expected to adsorb to the anion-exchange resin. At the same time, cationic iron should pass through the resin without interaction. Thus, arsenic speciation changes are prevented by separating thioarsenates on-site from iron. However, the main challenge consists of eluting the retained thioarsenates for analysis without changing speciation. Lord et al. (2012) used SPE to investigate arsenic speciation of geothermal waters shown to contain thioarsenates (Planer-Friedrich and Wilson, 2012; Ullrich et al., 2013). They speculated that thioarsenates were retained on the anion-exchange resin, but were unable to elute them for analysis. Elution with HCl or HNO_3, as previously presented for arsenate, will cause species conversion and arsenic sulfide precipitation. Druschel et al. (2003) studied SPE for the preservation of sulfate and thiosulfate in geothermal waters and showed that 0.5 M KCl can elute sulfate and thiosulfate without speciation changes, which might be transferable to thioarsenates.

The aim of this study was to explore the potential of SPE to preserve arsenic speciation in sulfidic, iron-rich waters. Based on the hypothesis that thioarsenates can be separated on-site from iron, this approach will prevent arsenic speciation changes and arsenic adsorption on iron oxyhydroxides. After ensuring full retention of the arsenic species on the anion-exchange resin, the development of a species-conserving elution was a major focus. Furthermore, the stability of the retained species on the resin was investigated over time. The method developed in this study is summarized in a detailed application protocol that demonstrates the preservation of arsenic in the presence of sulfide and iron using SPE.

2. Material & methods

2.1. Preparation of cartridges

Cartridges for SPE were prepared with 1 g of strongly basic anion-exchange resin (AG2-X8, Cl-form, BioRad). A polyethylene frit was inserted into a 6 mL polypropylene tube (Supelco, Sigma-Aldrich), and a slurry of resin and deionized water (MQ, 18 MΩ cm) was poured into the tube. Excess water was removed by applying vacuum at the tube outlet producing a compact resin bed. No top frit was inserted to promote mixing with the applied solutions. Prior to sample application the resin was conditioned with 12 mL of 0.1 M KOH (≥85%, Sigma-Aldrich) or 12 mL of MQ water, ensuring that the resin was fully equilibrated.

2.2. SPE procedure

During the first step of the SPE procedure, 250 mL of initial sample solution was passed through the resin at a flow rate of 1.7–2.0 mL min^{-1} (Fig. 1). A vacuum manifold was used to control constant flow during sample application. While applying the sample at the top of the cartridge, the passage was collected at the outlet of the tube. Hence, the passage contains the compounds not retained by the resin. The second step consisted of quickly washing the resin by applying 4 mL of MQ water to eliminate excess sample solution from between the resin beads. When a natural sample was applied, this step also removed any weakly bound matrix compounds.

The third step of the SPE procedure constitutes the elution, during which the retained compounds were removed from the resin. Elution of the target sulfur and arsenic species was investigated using 0.5 M and 3 M KCl (≥99.8%, VWR), 0.1 M NaOH (50% w/w, Sigma-Aldrich), 0.5 M sodium citrate ($C_6H_5Na_3O_7$, ≥99%, Sigma-Aldrich), and 0.5 M sodium salicylate ($C_7H_5NaO_3$, ≥99.5%, Sigma-Aldrich). Since sodium salicylate yielded the best results it was chosen for all further experiments. For the elution, 15 mL of 0.5 M salicylate were applied to the resin in three increments of 5 mL each, including 20 min soak time before eluting each increment. These three increments were collected as one sample. Eluting with 15 mL salicylate in this way was repeated three times generating eluates A, B, and C.

Synthetic sample solutions containing 31.2 μM ammonium sulfate ($[NH_4]_2SO_4$, ≥99.99%, Sigma-Aldrich), 46.8 μM sodium thiosulfate ($Na_2S_2O_3$, ≥99.99%, Sigma-Aldrich), 2.7 μM sodium