Analytica Chimica Acta 787 (2013) 102–110

Contents lists available at SciVerse ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

A modified sequential extraction method for arsenic fractionation in sediments

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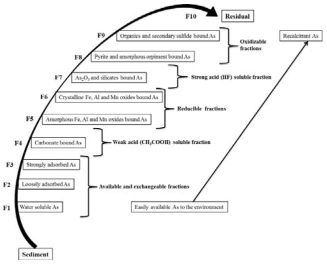
HIGHLIGHTS

- A sequential extraction method was developed to characterize As in sediment.
- The method can predict ~97% distribution of total As in 9 meaningful fractions.
- Extractants used are compatible with ICP-MS eliminating interference for As.
- This scheme can also be employed for fractionation of Cu, Co, Cr and Sr.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 February 2013
Received in revised form 22 May 2013
Accepted 28 May 2013
Available online 4 June 2013

Keywords:
Sequential extraction
Arsenic fractionation
Inductively coupled plasma mass spectroscopy
Polyatomic ion interference

ABSTRACT

A modified sequential extraction method was developed to characterize arsenic (As) associated with different solid constituents in surficial deposits (sediments), which are unconsolidated glacial deposits overlying bedrock. Current sequential extraction methods produce a significant amount of unresolved As in the residual fraction, but our proposed scheme can fractionate >90% of the As present in sediments. Sediment samples containing different As concentrations (3–35 $\mu g\,g^{-1}$) were used to assess the developed method. The pooled amount of As recovered from all the fractions using the developed method was similar (83–122%) to the total As extracted by acid digestion. The concentrations of As in different fractions using the developed scheme were comparable (89–106%) to the As fractions obtained by other existing methods. The developed method was also evaluated for the sequential extraction of other metals such as copper (Cu), cobalt (Co), chromium (Cr) and strontium (Sr) in the sediment samples. The pooled concentrations of these four individual metals from all the fractions were similar (96–104%) to their total concentrations extracted by acid digestion. During method development, we used extractants that did not contain chloride to eliminate formation of polyatomic ions of argon chloride ($^{40}Ar^{35}Cl$) that interfered with ^{75}As when analyzed using inductively coupled plasma mass spectrometer (ICP-MS). The results suggest that the developed method can reliably be employed for complete As and other metals' fractionation in sediments using ICP-MS.

1. Introduction

Arsenic (As) is a toxic trace element and its crustal abundance is ~0.0001% [1]. However through geogenic processing of crustal materials, As can concentrate in soils up to 57–110 $\mu g\,g^{-1}$ causing high concentrations of As in pore or surface water through desorption or dissolution [2,3]. High As concentration (>10 $\mu g\,L^{-1}$) in groundwater is of increasing concern due to its implications in human and ecological health [4,5]. Arsenic mobility is principally controlled by adsorption–desorption and solid phase precipitation–dissolution reactions. Important geochemical factors affecting these reactions in soils and sediments are porewater chemistry, pH, redox conditions, soil solid composition and As-bearing minerals [6]. To predict the fate of As in soils

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http://dx.doi.org/10.1016/j.aca.2013.05.050

or sediments and its transport to ground or surface water, it is important to understand nature of As association with different solid constituents.

Distribution and chemical association of As with various solid constituents, rather than its total concentration, affect As mobility in sediment and its transport to water bodies. Sorption of As on solid particles is one of the most important processes that immobilizes As [6]. Arsenic can adsorb on the surfaces of a variety of materials, especially oxides of iron (Fe), aluminum (Al) and manganese (Mn) [7]. Coprecipitation of As with Fe oxyhydroxides has also been defined as the major mechanism that strongly retains As in sediments [8] but As-bearing Fe oxyhydroxides may act as a source of As during reductive dissolution of both amorphous and crystalline oxyhydroxides [6]. Arsenic associated with hydrous Mn oxides (easily reducible oxides) is relatively more labile than Fe oxyhydroxides [9]. Arsenic adsorption on the edges of clay minerals and on the surface of calcite has also been observed [8]. Other more stable forms of As are naturally occurring As-bearing sulfide ores and silicate minerals; but weathering of these sulfides and silicate minerals can release As into the environment and/or may cause formation of other thermodynamically metastable new secondary minerals [6].

Arsenic distribution in different solid constituents can be studied by sequential extraction procedure (SEP). Several SEP schemes have been developed by previous researchers to fractionate As in sediments [9–12]. These schemes vary in terms of number of fractions, extraction solutions and conditions and the sequence of extraction steps but the common feature is that the fractions are operationally defined. Different methods target different As phases in sediments and yield ~40–50% of the total As in their final residual fractions. These unresolved residual fractions might contain As bound in silicates, pyrite and orpiment such as in Tessier, Hall and Wenzel methods [9,10,12] or As associated with organic and recalcitrant sulfides in Keon method [11]. Characterization of these residual fractions is important for comprehensive understanding of As fate in soils and sediments. Secondly, the common extractants used in the existing SEPs create interference during As determination if those extractants are analyzed by inductively coupled plasma mass spectrometry (ICP-MS). Chloride (Cl^-)-containing extractants produce polyatomic ions (argon chloride; $^{40}Ar^{35}Cl$) when Cl^- reacts with argon (Ar) in ICP plasma. These polyatomic ions can interfere with ^{75}As due to same mass to charge ratio (m/z) [13,14] even if the ICP-MS is equipped with a collision cell [15]. Therefore, we developed a sequential extraction scheme by modifying the existing methods to (1) quantify As in maximum possible meaningful fractions and (2) choose only those extractants that can be analyzed by ICP-MS without any polyatomic interference for As quantification. To check the applicability of the developed method, we compared it with the three existing sequential extraction methods described by Tessier et al. [9], Keon et al. [11] and Wenzel et al. [12] using sediment samples. We also used the new scheme to test the specificity of the extractants to target pure minerals such as calcite ($CaCO_3$), dolomite [$CaMg(CO_3)_2$], arsenopyrite (FeAsS) and orpiment (As_2S_3), which are dominant minerals in the sediments. In addition, the developed method was also evaluated for the fractionation of other metals such as copper (Cu), cobalt (Co), chromium (Cr) and strontium (Sr).

2. Experimental

2.1. Description of sediment samples used in sequential extraction protocol development

Sediment (surficial desposits) core samples used in the protocol development were obtained from Alberta Geological Survey (AGS) collected at 100–300 m depths from the Cold Lake region in Alberta, Canada, which is one of the As affected areas in northern Alberta. The air dried sediment samples were ground with agate mortar and pestle and passed through 2 mm sieve. The pH of the samples was determined by preparing a sediment slurry (sediment:0.05 M $CaCl_2$; 1:5) [16] and measuring pH using Accumet® AR20 pH meter. Total organic carbon content of the sediments was determined by the loss on ignition (LOI) method [17]. The information about the texture of the sediments was obtained from the report published by the Energy Resource Conservation Board-Alberta Geological Survey (ERCB-AGS) [18]. To determine the reduced inorganic sulfur, chromium reduction method [19] was employed that was based on the conversion of reduced inorganic sulfur to H_2S by a hot acidic $CrCl_2$ solution. The evolved H_2S was trapped in a zinc acetate solution as ZnS. This ZnS was quantified by iodometric titration. The reduced inorganic sulfur compounds determined by this method were: (1) pyrite and other metal sulfides, (2) elemental sulfur, and (3) acid volatile sulfides. The sediments were also subjected to total metal analysis particularly for Fe, calcium (Ca) and As. The samples were digested with nitric acid (trace metal grade HNO_3) in the microwave digestion unit [20] and analyzed using ICP-MS.

The total As concentrations in the core sediments ranged from 3 to 200 $\mu g\, g^{-1}$. Five samples with low As concentration (3.49–6.07 $\mu g\, g^{-1}$) and three samples with high As concentration (19.99–35.4 $\mu g\, g^{-1}$) were selected for the development of sequential extraction method. Physicochemical properties of the sediment samples used in this study are provided in Table 1.

2.2. Chemicals and minerals

To prepare the extraction solutions for As fractionation, trace metal grade hydrofluoric acid (HF), nitric acid (HNO_3), sodium acetate (CH_3COONa; abbreviated as NaOAc), sodium phosphate (NaH_2PO_4), ammonium oxalate [$(NH_4)_2C_2O_4 \cdot H_2O$], oxalic acid ($H_2C_2O_4$), titanium (Ti), sodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), sodium bicarbonate ($NaHCO_3$), acetic acid ($CH_3COOH$; abbreviated as HOAc) and EDTA ($C_{10}H_{14}N_2Na_2O_2 \cdot 2H_2O$) were purchased from Sigma–Aldrich. The extraction solutions were prepared using nanopure water (Barnstead nanopure, Thermo Scientific). The pH of the extractants, if required, was adjusted with either sodium hydroxide (NaOH) or appropriate acid (CH_3COOH, $H_2C_2O_4$, or HNO_3) to bring the pH to the desired values listed in Table 2. The reagent blanks from all the extraction solutions were also analyzed along with the experimental samples. To test the specificity of the extractants, pure minerals of calcite and dolomite were purchased from the Ward's scientific, and orpiment and arsenopyrite were collected from the Mineralogy Petrology Museum from the Department of Earth and Atmospheric Sciences, University of Alberta, Canada.

2.3. Development and use of sequential extraction protocol

A modified sequential extraction scheme was developed by combining the fractions reported in the existing methods [9,11,21]. We substituted Cl^--containing extractants by those solvents that eliminated formation of polyatomic ions ($^{40}Ar^{35}Cl$) and yielded same extraction efficiency in targeting As in different solid phase constituents. Table 2 summarizes the fractions, target solid phases, extractants, possible mechanisms to liberate the As and the source references for the extractants used in this proposed modified sequential extraction method.

In the sequential extraction, the sediment samples were treated with different extraction solutions in a sequence to collect the individual fraction from each extractant for As analysis. For the extraction of soluble fraction of As (F1), 0.4 g sediment was added to a 50-mL Nalgene (3118-0050, Fisher Scientific) centrifuge tube along with 40 mL of nanopure water. The sediment-extractant