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Arsenic speciation in water samples containing high levels of copper: removal of copper interference affecting arsine generation by continuous flow solid phase chelation

Abstract A simple continuous flow method is proposed to eliminate copper interference in arsenic speciation by hydride generation, based on the selective retention of this interfering ion in an iminodiacetate chelating resin previous to the hydride generation process. The arsines generated were cold trapped and measured by ICP/OES. The proposed method allows about 98% of the copper present in the samples to be removed. Minor co-retention of As(V) was observed as a result of electrostatic interaction between the arsenate anion and the nitrogen of the iminodiacetate group of the chelating resin Muromac A-1, the charge distribution of which is modified when copper is chelated. The species As(III), MMA and DMA were not retained in the microcolumn, probably because these species are mainly in the molecular form at the working pH value (4.5). In synthetic samples containing 50 μg l^{-1} of each arsenic species together with 100 mg l^{-1} copper, the recoveries obtained were: As(V) 97.6%, As(III) 100%, MMA 99.8%, and DMA 99.9%. The method was applied to arsenic speciation in river water samples containing high levels of copper.

Keywords Copper removal · Arsenic speciation · Muromac A-1 chelating resin · Hydride generation · ICP/OES

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Introduction

Arsenic usually exists in environmental systems in different chemical forms such as As(V), As(III), monomethylarsonate (MMA) and dimethylarsinate (DMA), which exhibit different concentrations, mobilities, availabilities and toxicities [1–6].

Arsenic speciation in environmental samples has been extensively studied. The analytical methods most commonly used are based mainly on liquid chromatographic separation and spectroscopic detection [7–12].

The hydride generation (HG) reaction has also been widely used to determine arsenic species at trace levels, mainly due to the high sensitivity and selectivity achieved. By varying either the concentrations of the reaction media or the reaction time, inorganic arsenic speciation can be achieved [1, 13–16]. In some other cases, methylated species can also be determined [17–19]. Another speciation approach based on this HG reaction involves cold trapping of the arsines and their sequential volatilization towards a spectroscopic detector [20–23].

All arsenic speciation methods based on the HG reaction are subject to interferences from transition elements, which have been studied [1, 14–17, 20, 21] and minimized by using either masking agents [14, 16, 17] or the simpler and less time-consuming approach of using ion-exchange resins in both batch [1, 20] and continuous flow systems [21]. However, the use of ion-exchange resins has been neither systematically studied [1, 20, 21] nor used for copper removal in continuous flow systems [21]. Copper interference is particularly significant in environmental samples polluted by mining activities, in which the concentration ratio Cu/As can reach values near 100 [24].

In this context, the aim of this study was to assess a simple alternative method of eliminating copper interference during the determination of As(III), As(V), MMA and DMA. The method is based on the selective continuous retention of this interferent on iminodiacetate chelating resin previous to the hydride generation process.

Experimental

Instruments and apparatus

The manifold used for speciation (Fig. 1) has been described elsewhere [24]. It basically consists of a hydride generation (HG) system connected to a cold trap unit (a U-tube half-packed with Chromosorb W AW-DWCS 60/80 mesh OV-3 (15%) (Supelco, Bellfonte, PA, USA)) and an inductively-coupled plasma-optical emission spectrometer (ICP/OES, Perkin-Elmer, Optima 3300 XL).

A Tygon microcolumn (20 cm long, 3 mm i.d.) packed with resin was coupled before the HG system in order to remove copper interference. A peristaltic pump (Gilson Minipuls 3, Anachem, Luton, UK) was used to push sample and eluting agent solution alternatively through the microcolumn.

Reagents

Deionized water (NANOpure ultrapure water system, Barnstead, Dubuque, IA, USA) was used throughout. All chemicals used were of analytical reagent grade. As(III) stock standard solution (1,000 mg l^{-1}) was prepared from As_2O_3 (Aldrich, Milwaukee, WI, USA) in 0.1 mol l^{-1} NaOH solution (Merck, Darmstadt, Germany). As(V) stock standard solution (1,000 mg l^{-1}) was prepared from As_2O_5 (WAKO Pure Chemical Industries, Osaka, Japan) in 0.1 mol l^{-1} NaOH solution. Stock standard solutions of MMA and DMA (1,000 mg l^{-1}) were prepared from pure reagents (Tri Chemical Laboratory Inc., Yamanashi, Japan). A 1,000 mg l^{-1} copper standard solution was prepared using Tritrisol (Merck, Darmstadt, Germany). All standard solutions were kept at 4 °C. A 0.4 mol l^{-1} hydrochloric acid solution was prepared from 37% HCl (Merck, Darmstadt, Germany) in deionized water. A 0.38 mol l^{-1} citric acid/citrate buffer (pH 6.0) was prepared from monohydrated citric acid (Merck, Darmstadt, Germany) and the desired pH was reached by adding 5 mol l^{-1} NaOH. A 1 mol l^{-1} nitric acid solution was prepared from 65% HNO_3 (Merck, Darmstadt, Germany) in deionized water. A 0.1 mol l^{-1} ammonium acetate solution (Merck, Darmstadt, Germany) was prepared in deionized water. A 5% (w/v) $NaBH_4$ solution was prepared just before use by dissolving 5.00 g $NaBH_4$ in 100 ml of 0.25% NaOH. Dowex W50 X2-100 and Sephadex C-25 resins were obtained from Sigma (St. Louis, MD, USA). Chelex-100 (50–100 mesh) resin was obtained from Bio-Rad Lab. (Hercules, CA, USA). Muromac A-1 (20–50 mesh) resin was obtained from Muromachi Technos (Tokyo, Japan).

Procedure

The samples were adjusted to pH 4.5 with ammonium acetate and passed through the 20 cm long microcolumn (3 mm i.d., 0.84 g resin) packed with Muromac A-1 chelating resin at a flow rate of 5 ml min^{-1}, keeping the V_2 selecting valve at the waste position. If the copper concentration is above 20 mg l^{-1}, it is recommended that the first 200 ml of sample through the microcolumn be discarded. Then, by switching the V_2 valve, the next 5 ml of copper-free sample was carried to the reaction cell containing 15 ml of 0.4 mol ml^{-1} HCl (pH 1.0) or 15 ml of 0.38 mol l^{-1} citric acid/citrate buffer (pH 6.0), depending on the arsenic species to be determined. In both instances, the content of the reaction cell was purged with helium at 9 ml min^{-1} and then 1 ml of $NaBH_4$ was injected and the He-flow was directed to the U tube (CT system), which was immersed in a Dewar flask containing liquid nitrogen. After 3 min of cold-trapped preconcentration at −190 °C, the arsines were released from the U tube by removal of the tube from the liquid nitrogen and application of heat. Thus, the arsines were volatilized and separated one-by-one according to their boiling points. The helium flow containing the arsines merged with an argon flow (0.6 ml min^{-1}), which carried them to the ICP/OES used as the detection system. Only As(III) was selectively determined at pH 6.0; the determinations of As(III) + As(V), MMA and DMA were carried out at pH 1.0.

Finally, by switching the V_1 selecting valve, the resin was regenerated by passing 1 mol l^{-1} HNO_3 through it for 2 min at a flow rate of 5 ml min^{-1}.

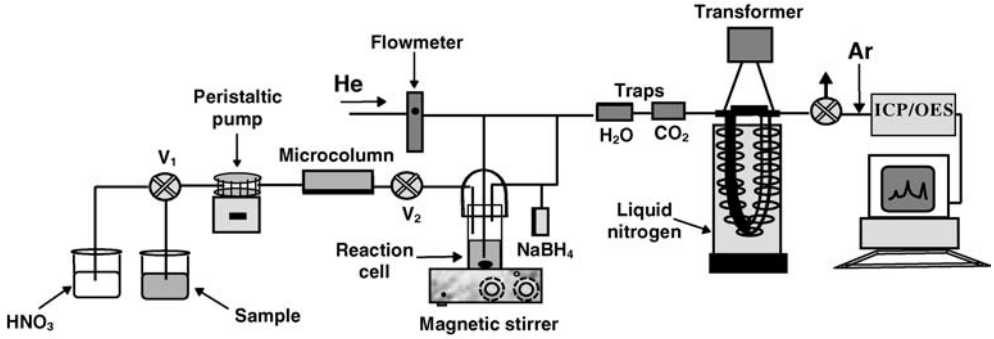

Fig. 1 Manifold for implementation of the method

Results and discussion

Optimizing parameters related to the removal of copper interference

We investigated and optimized parameters related to the removal of copper interference using solutions containing 50 μg l^{-1} of As(III), As(V), MMA, DMA and different copper concentrations ranging from 1 mg l^{-1} to 100 mg l^{-1}. Parameters associated with the arsenic speciation method (HG-CT-ICP/OES) have already been previously optimized [24].

Nature of the solid phase used for copper removal

The solid phase was selected by assessing resins with high copper retaining capacity such as Chelex-100, Muromac A-1, Dowex W50 X2-100 and Sephadex C-25. All of these resins, except Muromac A-1, exhibited high swelling levels, preventing free sample circulation throughout the microcolumn. As previously observed [25], Muromac A-1 did not exhibit swelling problems. Therefore, this resin was selected for the elimination of copper interference. Other interferents such as Fe, Zn, Mn, and Ni could also be eliminated by this method since they are easily retained in iminodiacetate resins [1, 26, 27].

Influence of microcolumn length (mass of resin)

By increasing the microcolumn length, the copper retention increased due to the increased number of coordination sites available for chelation. When the copper concentration in the sample was increased, the retention of this interferent decreased due to faster saturation of the resin (Fig. 2A).

When the microcolumn length was increased, As(V) co-retention also increased, the presence of a high copper concentration being imperative for significant As(V) co-retention (Fig. 2B). This phenomenon can be accounted for by modified charge distributions at the active sites in the resin resulting from the previous copper chelation, which facilitates electrostatic interaction between the nitrogen of the iminodiacetate bounded to copper and the arsenate present in the sample. The species As(III), MMA and DMA were not retained in the microcolumn, probably because these species are mostly in the molecular form at the working pH value (4.5). Due to these results, a microcolumn 20 cm long containing 0.84 g resin was selected for further studies.

Effect of flow rate of the sample circulating through the resin

Flow rate was studied from 1.3 ml min^{-1} to 5.0 ml min^{-1}. When the flow rate was increased, the copper retention remained almost constant due to both fast copper chelation and an adequate level of copper in the solution. Conversely, a clear attenuation of As(V) co-retention was observed when the flow rate increased, probably because the interaction between arsenate and the iminodiacetate group of the resin is slower than copper chelation. Therefore, a flow rate of 5 ml min^{-1} was selected.

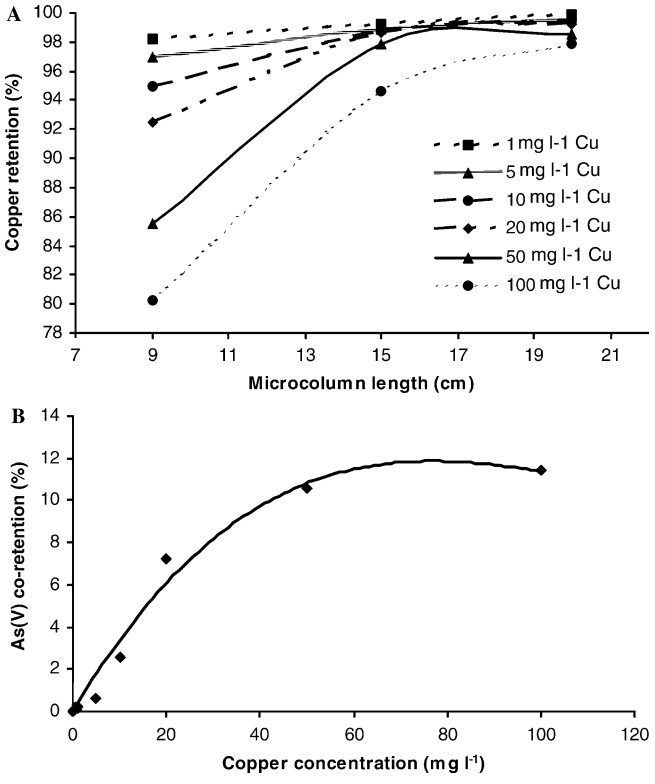

Fig. 2A–B **A** Effects of microcolumn length and copper concentration on copper retention. **B** Effect of copper concentration on As(V) co-retention at a fixed microcolumn length (20 cm). Working conditions: [As(V)]: 50 μg l^{-1}, resin: Muromac A-1, flow rate: 5 ml min^{-1}, pH 4.5, sample volume: 5 ml

Effect of pH

The effect of pH was only studied over the pH range 4.5–6.0, as recommended by the manufacturer. Copper retention remained constant within this interval. However, when pH decreased, As(V) co-retention also decreased, since the arsenate tends to become protonated. Accordingly, a pH of 4.5 was selected.

Effect of the sample volume circulating through the microcolumn

This variable was studied from 10 ml to 200 ml. When the sample volume increased, the copper retention diminished slightly. In addition, As(V) co-retention also diminished, tending to zero when over 200 ml of sample had passed through the microcolumn. This phenomenon

can be attributed to the fact that the arsenic interaction only occurs at the surface, and the surface becomes saturated with arsenic after passing 200 ml of a 50 $\mu g\ l^{-1}$ solution through the column. According to these results, in order to avoid arsenate co-retention, it is recommended that the first 200 ml of sample passing through the microcolumn be discarded before taking the aliquot for analysis.

Under the selected conditions, the recoveries of As(V), As(III), MMA and DMA were assessed in the presence of different copper concentrations. Table 1 shows the recovery percentages obtained, including those determined when the first 200 ml of sample circulating through the microcolumn were discarded.

Application: arsenic speciation in real samples

The method was applied to arsenic speciation in real samples containing high levels of copper. The samples were collected in the Cachapoal basin (VI Region, Chile). These aquatic systems have been polluted by copper smelter processes for many years. The samples processed without copper separation produce a finely-dispersed dark precipitate (metallic copper) after addition of sodium tetrahydroborate. This fact causes severe analytical drawbacks, such as co-precipitation of the arsenic species, adsorption of the volatile hydrides formed [28], and clogging of the glass frit of the reaction cell. These effects inhibit arsine transport from the reaction cell to the cold trap system to some degree and depress the arsenic signal in the subsequent determination due to memory interference [29].

Table 2 shows the results obtained for arsenic speciation with and without separation of copper, in addition to the total copper and arsenic determined directly by ICP-OES. As can be seen, when the speciation was carried out in the presence of copper, the concentrations of arsenic species were lower than those determined after this interferent was separated. This is particularly significant in the case of As(V) and methylated species.

Table 1 Recoveries of the arsenic species As(III), As(V), MMA and DMA at different copper concentrations

Copper ($mg\ l^{-1}$)	Recovery (%)			
	As(V)	As(III)	MMA	DMA
1	99.8	100	99.8	100
10	97.4	99.9	99.7	99.9
20	92.8	100	99.5	99.9
20[a]	98.7	100	99.8	100
50	89.4	99.9	99.3	99.8
50[a]	98.1	100	99.7	100
100	88.6	99.9	99.0	99.6
100[a]	97.6	100	99.8	99.9

Working conditions: [As species]: 50 $\mu g\ l^{-1}$, microcolumn length: 20 cm, resin: Muromac A-1, flow rate: 5 ml min^{-1}, pH 4.5, sample volume: 5 ml

[a]The first 200 ml of sample circulating through the microcolumn were discarded

Conclusions

This study describes a simple alternative method for removing copper interference during arsenic speciation, which is based on the selective retention of this interfering ion in an iminodiacetate chelating resin previous to the hydride generation process, -cold trapping and ICP/OES determination. The proposed method allows the removal of about 98% of the copper present in the samples. If the copper concentration in the sample is high (over 20 $mg\ l^{-1}$), it is recommended that the first 200 ml of sample passed through the microcolumn be discarded before taking an aliquot for analysis, in order to avoid the co-retention of As(V). The resin may be reused after elution with 1 $mol\ l^{-1}$ nitric acid. The method was applied to arsenic speciation in river water. Results indicate that the signals for As(V), MMA and DMA are significantly higher when copper is removed from the sample.

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Table 2 Total concentrations of Cu and As, and the concentrations found for As(III), As(V), MMA and DMA with and without the removal of copper

Sample	Cu total ($mg\ l^{-1}$)	As total (μl^{-1})	With elimination of copper interference				Without elimination of copper interference			
			As(V) ($\mu g\ l^{-1}$)	As(III) ($\mu g\ l^{-1}$)	MMA ($\mu g\ l^{-1}$)	DMA ($\mu g\ l^{-1}$)	As(V) ($\mu g\ l^{-1}$)	As(III) ($\mu g\ l^{-1}$)	MMA ($\mu g\ l^{-1}$)	DMA ($\mu g\ l^{-1}$)
Coya river[a]	23.0 ± 0.2	289 ± 3	201 ± 8	53.3 ± 0.8	ND	ND	150 ± 8	51 ± 2	ND	ND
Cachapoal river[a]	6.0 ± 0.1	112 ± 1	81 ± 3	17.2 ± 0.3	ND	ND	71 ± 4	17 ± 1	ND	ND
Coya river[b]	59.2 ± 0.3	358 ± 4	176 ± 7	145 ± 2	4.6 ± 0.1	2.4 ± 0.1	140 ± 8	135 ± 4	ND	ND
Cachapoal river[b]	4.7 ± 0.1	80.8 ± 0.9	59 ± 2	12.5 ± 0.2	ND	ND	49 ± 3	12 ± 1	ND	ND

ND not detected

[a]River water sampled in autumn

[b]River water sampled in spring

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