Field-based Speciation of Inorganic Sb Using Ion-exchange Resin Cartridge and ICP-MS Detection

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ABSTRACT: A field-based speciation method of inorganic Sb in environmental water samples is proposed using ion-exchange resin separation and determination by inductively coupled plasma mass spectrometry (ICP-MS). The problem of chemical species alteration, which occurs after the water is sampled and stored, then separated using a laboratory-based method, was solved successfully. The water samples pass directly through an ion-exchange column cartridge on-site, and then the separated solutions are analyzed by ICP-MS in the laboratory. Two promising ion-exchange cartridge columns were evaluated for the effective separation of Sb(V) and Sb(III): i) a strong cation-exchange (SCX) column, on which all Sb(III) is retained, while only Sb(V) passes to the effluent, and ii) a strong anion-exchange (SAX) column, on which both Sb(V) and Sb(III) are retained, but only Sb(V) is eluted when 12% HNO_3 is used. The two Sb species can be separated efficiently using the SCX and SAX columns in the pH range of 4–10 and 6–7, respectively. The limits of detection (LODs) for Sb(V) were 0.03 and $0.05 \mu\text{g L}^{-1}$ with the SCX and SAX methods, respectively. The repeatability, expressed as the relative standard deviation, was determined as 1.2–5.3% for the SCX column and 4.6–9.3% for the SAX column for two groundwater samples. The recoveries for Sb(V) with spiked samples ranged from 91% to 103% for the SCX method and 85% to 120% for the SAX method. The coexisting ion interference experiments showed that the SCX method has a stronger matrix tolerance than the SAX method. Ten natural water samples (two river water, five spring water, and three well water samples), collected from the Xikuangshan area (Hunan, China), were analyzed using the proposed SCX method. The results show that the dominant species in all samples was Sb(V) ($64\text{--}12016 \mu\text{g L}^{-1}$), followed by Sb(III) ($<\text{LOD}\text{--}1792 \mu\text{g L}^{-1}$). Compared to the conventional laboratory-based methods, the proposed SCX method has the advantages of being solvent-free, simple, fast, easy to operate, low cost, and can be applied to Sb speciation analysis both in the field as well as in the laboratory.

INTRODUCTION

Antimony (Sb) exists naturally in water and in the Earth's crust at levels of $1 \mu\text{g L}^{-1}$ and 0.3 mg kg^{-1} , respectively. However, elevated concentrations of Sb in environmental, biological, and geochemical systems originating from natural, geological, and anthropogenic sources are of particular global concern.^{1–3} Studies on the mechanisms of mobilization of Sb from host mineral phases and its transformation through different environmental compartments have recently become very popular.^{4,5} The global distribution of Sb-contaminated aquifer sediments is still not fully understood; as a result, the

groundwater in Sb-contaminated regions such as Xikuangshan (XKS) may contain Sb at levels that exceed the Chinese safety threshold of $5 \mu\text{g L}^{-1}$ for drinking water.⁶ However, the toxicity levels of different Sb species and their environmental transport-behaviors change depending on the chemical form of Sb.^{7,8} Antimonite (Sb(III)) is ten times more toxic than antimonate (Sb(V)), and inorganic Sb species are more toxic than organic Sb species.^{9,10}

Speciation analysis of Sb in aqueous systems is commonly conducted using high-performance liquid chromatography (HPLC) or ion chromatography (IC), coupled online with highly

sensitive atomic spectrometry, such as atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), or inductively coupled plasma mass spectrometry (ICP-MS).^{11–16} These coupled techniques have become the most popular tools for Sb speciation for various types of samples (*e.g.* natural water, food, soil extracts, and biological samples), mainly because of their capacity for the simultaneous analysis of inorganic (*e.g.* Sb(III), Sb(V)) and organic Sb species.^{17–22}

Organic Sb species (*e.g.* $(\text{CH}_3)\text{SbO}(\text{OH})_2$, $(\text{CH}_3)_2\text{Sb}(\text{O})\text{OH}$, $(\text{CH}_3)_3\text{Sb}$, $(\text{CH}_3)_3\text{SbCl}_2$, HSb_2S_4^- , and $\text{Sb}_2\text{S}_4^{2-}$) have been found in geothermal waters and seawater. However, to date, these organic Sb species have not been studied in surface water or groundwater.^{23,24} A simpler non-chromatographic method, based on the selective hydride generation (HG) or photochemical vapor generation (PVG) coupled with atomic fluorescence spectrometry (AFS), AAS, or ICP-MS, can be used to measure the amount of inorganic Sb species in natural water (*e.g.* groundwater, spring water or river water).^{25,26} With this method, Sb(III) and Sb(V) can be discriminated through their pH-dependent reduction to stibine with borohydride.²⁷ The Sb(III) and total Sb concentrations are determined by yielding the Sb(V) concentration as the difference.

Although the above coupled techniques and the non-chromatographic method can be used to achieve the speciation analysis of inorganic Sb at trace levels in most laboratories, obtaining accurate analysis results remains a challenge because of the instability of the Sb redox species during sample storage, transportation, and analysis. Sayago *et al.*²⁸ observed that distinct losses of the Sb(III) species (18.2–30.2%) occurred while studying the stability of well water samples over 48 h, while the concentration of Sb(V) increased. Even though the samples were stored frozen, Sb(III) may have oxidized to Sb(V) during transport.²⁹

In our previous study,³⁰ a portable and solvent-free method was developed, based on using the parallel cartridge ion-exchange columns for on-site separation of Cr(VI) and Cr(III) in natural water. The field-separated solutions were preserved and analyzed later using AAS, ICP-OES, or ICP-MS in the laboratory.³⁰ This strategy introduced the possibility of developing field sampling and separation techniques for other inorganic metal species, thus eliminating the need for the sampling and preservation steps required prior to final analysis of the samples in the laboratory.

Consequently, a method based on the field separation of Sb(III) and Sb(V) using ion-exchange cartridge columns was developed in this study, and the separated solutions were analyzed by ICP-MS in the laboratory. The feasibility of using a strong cation-exchange (SCX) cartridge and a strong anion-exchange (SAX) cartridge for the speciation of inorganic

Sb was evaluated, respectively. Optimization of the technique, assessment of its analytical performance, and its application to the determination of Sb(V) and Sb(III) species in surface water and groundwater samples are also described.

EXPERIMENTAL

Field separation assembly and analysis procedures. The field separation assembly consisted of an Onsite CUG-1C SCX cartridge (500 mg, 55 μm particle size, Wuhan NS Ltd., China), a disposable syringe (10 mL), a syringe filter (cellulose acetate, 0.45 μm), an adapter cap, and a centrifuge tube (Fig. S1). The on-site separation procedures (Fig. 1a) were as follows: Two mL of a water sample are slowly forced through the filter and split into the SCX column; Sb(V) passes to the effluent and is collected, while all Sb(III) is retained in the column. The collected Sb(V) solutions are diluted to 4 mL with 6% nitric acid. Another method based on an Onsite CUG-1A SAX column (500 mg, 55 μm particle size, Wuhan NS Ltd., P.R. China) was also used to evaluate the separation performance for inorganic Sb. Fig. 1b shows the separation apparatus used in the SAX method. Two mL of water sample are slowly forced through the filter and split into the SAX column. Both Sb(V) and Sb(III) are retained on the column, and only Sb(V) is eluted with 12% HNO_3 . Finally, the collected solution (containing the Sb(V) species) is diluted to 4 mL with high-purity water. All collected solutions (each 4 mL) were preserved and later analyzed by ICP-MS in the laboratory. Before use, the SCX and SAX cartridges were activated with 10 % sulfuric acid (2 h) and high-purity water (0.5 h), respectively, to ensure good separation.

Instrumentation, reagents, and standards. A PerkinElmer NexION 350D ICP-MS (Waltham, MA, USA) was used for measurement of the separated Sb(V) and total Sb in the laboratory. An IRIS ICP-OES system (Thermo Fisher, USA) and an ICS-900 IC system (Thermo Fisher, USA) were used to measure the concentrations of the coexisting ions (*i.e.* K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Mn^{2+} , Zn^{2+} , Al^{3+} , Cl^- , NO_3^- , SO_4^{2-} , F^- , and Fe^{3+}) in the water samples.^{31,32} A HACH portable water quality analyzer was used to measure the pH and the electrical conductivity (EC) in the field. A portable pH meter (PH-100, ± 0.01 , LiChen Technology, Shanghai, P.R. China) was used to determine the pH value levels of the water solutions in the laboratory. High-purity water (18.2 $\text{M}\Omega\text{-cm}$) was obtained from a water purification system (Millipore Corporation, France). Analytical-grade nitric acid, hydrochloric acid, sulfuric acid, acetic acid, methanol, and ammonia were purchased from Alfa Aesar Ltd. (Tianjin, P.R. China). Standard solutions of Sb(V) and Sb(III), single-element stock solutions (containing K, Na, Ca, Mg, Fe, Mn, Zn, and Al), and anion solutions (containing Cl^- , NO_3^- , SO_4^{2-} , and F^-) were purchased from the National Institute of Metrology of China (NIMC, P.R. China).

Fig. 1 Separation of Sb(V) and Sb(III) with an Onsite CUG-1C SCX cartridge (a) and an Onsite CUG-1A SAX cartridge (b).

Water sample collection. Three sets of water samples (Table S1) were collected from the XKS area (the largest Sb mine in the world) on April 10, 2019. Three groundwater samples were taken from the wells used by local villagers. Five spring water samples were collected directly from the mine. Two surface water samples were collected from local rivers—the Batangshan streams. The pH and EC were measured with a HACH portable water quality analyzer. Water (or a diluted sample) from each sampling point underwent direct Sb speciation separation using the SCX or SAX procedures (Fig. 1). For the measurement of total Sb and other ions, the filtered samples (0.45 μm filters) were acidified with HNO_3 (pH 1–2) and collected into 500 mL high-density polyethylene (HDPE) bottles.

RESULTS AND DISCUSSION

Feasibility of separating Sb(V) and Sb(III) using ion-exchange cartridges. Most surface water and groundwater is either neutral, weakly acidic, or alkaline, with a pH of 4–10. At this pH range, the main forms of Sb(V) and Sb(III) are

anionic species (e.g. H_2SbO_4^- and/or $\text{Sb}(\text{OH})_6^-$) and neutral species (e.g. H_3SbO_3 and/or $\text{Sb}(\text{OH})_3$), respectively (Fig. S2).² The anionic Sb(V) species have strong affinity for anion-exchange resin columns, and poor or no retention on cation-exchange resin columns. However, the affinity of the neutral Sb(III) species for the cation-exchange resin and the anion-exchange resin is dependent on the pH of the solution.

In this study, two commercially available strong ion-exchange resin (SCX and SAX) columns were employed to investigate the feasibility of the speciation separation of these inorganic Sb species. Our initial experiments were based on the analysis of the recovery of individual Sb species ($10.0 \mu\text{g L}^{-1}$ for each species) in the first collected effluent (without elution) and the second collected effluent (with elution using 2 mL 12% HNO_3) after they were injected into the SCX or SAX cartridge, respectively. The collected effluents were analyzed using ICP-MS. Table 1 reveals that the Sb(V) species can effectively pass through the SCX cartridge into the effluent (91%), and the Sb(III) species are almost completely retained (only 5%) in the effluent. Lower recovery (1–2%) was observed in the second

Table 1. Recoveries of Sb(V) and Sb(III) with the Ion-exchange Cartridges (% , n=3)

Cartridge	Recovery in the 1 st collected effluent (without elution)		Recovery in the 2 nd collected effluent (with elution using 2 mL 12 % HNO ₃)	
	Sb(III)	Sb(V)	Sb(III)	Sb(V)
SCX	5±2	91±2	2±1	1±1
SAX	2±1	4±1	11±1	88±2

Fig. 2 Effect of sample solution pH on the recoveries of Sb(V) and Sb(III) using the SCX and SAX methods. The concentration of each species was 5 µg L⁻¹. The tests were performed three times (n=3).

collected effluent when 12% nitric acid (2 mL) was used as the elution reagent (Table 1). This may be because of the conversion of Sb(III) and Sb(V) to their cationic species (e.g. Sb(OH)₂⁺, SbO₂⁺) at low pH (Fig. S2), thus favoring retention on the SCX cartridge. The retention properties of the inorganic Sb species on the SAX cartridge are different from those on the SCX cartridge. As shown in Table 1, both types of Sb species are effectively adsorbed (2–4% recovery) on the SAX cartridge, and the Sb(V) species can be quantitatively eluted (88% recovery) using 12% HNO₃, while a large amount of the Sb(III) species remains retained on the column. This relatively low elution rate of the Sb(III) species (11%) may be attributed to its stronger binding capacity. The above results show that the speciation separation of Sb(III) and Sb(V) can be achieved regardless of which cartridge column (SAX or SCX) is used.

The retention capacity of an ion-exchange cartridge is also dependent on the activity of the ion-exchange functional groups

(i.e. sulfonic groups on SCX resin, tertiary amino group on SAX resin) and the pH of the sample solution; thus, some parameters (i.e. activation type and concentration, activation time, and pH of the sample solution) need to be optimized to improve the separation efficiency. Different reagents (i.e. high-purity water, sulfuric acid and acetic acid for SCX cartridge activity; high-purity water, methanol and ammonia for SAX cartridge activity) were examined towards obtaining high Sb(V) species recovery and low Sb(III) species recovery. As shown in Table 2, the optimal activation conditions were 10% sulfuric acid with an activation time of 2 h for the SCX cartridge and high-purity water with an activation time of 0.5 h for the SAX cartridge. The effect of sample solution pH on the separation of Sb(V) and Sb(III) using the SCX cartridge is shown in Fig. 2. When the sample solution pH increased from 4 to 10, the recoveries ranged from 85% to 98% for the Sb(V) species and from 3% to 5% for the Sb(III) species. A low pH (<4) leads to poor Sb(V) recovery and a high pH (>11) leads to high Sb(III) recovery, owing to the strong correlation between the Sb ionic state and solution pH (Fig. S2).² However, the optimal sample solution pH range for the SAX cartridge separation (Sb(V) recovery > 85% and Sb(III) recovery < 10%) was 6–7 (Fig. 2). An additional step to adjust the sample solution acidity with a buffer should be conducted for the separation of the Sb species using the SAX method. Selection of appropriate eluents is also crucial for the effective separation of the target from the Sb(III) species. It was found that the use of 12% nitric acid leads to the complete elution of the Sb(V) species (95% recovery), while only 6% of the Sb(III) species is released from the SAX cartridge. It can, therefore, be seen that the results with nitric acid are better than those obtained with hydrochloric acid and acetic acid (Fig. S3).

The coexisting interfering ions in water samples should be considered, because they can compete with the target ions in the absorption on the surface of the ion-exchange resin. In this work, the tolerability of the SCX method for frequently coexisting ions at different concentrations was studied by spiking the solutions containing 10 µg L⁻¹ Sb(V). Table 3 shows that the Sb(III) ions, at concentrations at least 200 times higher than of the target Sb(V) ions, can be removed (97.3% recovery) using the SCX method. Nearly all of the investigated ions have a

Table 2. Sb(V) Recoveries with Different Activation Reagents and Activation Times (% , n=3)

Cartridge	Activation time (h)	Activation reagent				
		High-purity water	50 % sulfuric acid	50 % acetic acid	50 % methanol	50 % ammonia
SCX	0.5	86±3	91±3	86±2	/	/
	1	85±2	94±4	89±3	/	/
	2	88±2	98±2	89±2	/	/
	6	87±1	98±3	88±4	/	/
	0.5	91±2	/	/	89±3	89±3
SAX	1	88±2	/	/	86±2	84±5
	2	89±3	/	/	88±3	87±3
	6	90±2	/	/	88±4	85±4

Table 3. Effect of Coexisting on the Separation of Sb (V) Using the SCX and SAX Methods (n=3)

Foreign species	Concentration ratio	Sb(V) ^a recovery (%)	
		SCX method	SAX method
Sb(III) ^b	200	97.3 ± 1.2	93.5 ± 1.4
K ⁺ , Na ⁺ , Ca ²⁺ , Mg ²⁺ ^c	40,000	94.3 ± 0.2	93 ± 2
Fe ³⁺ ^d	100	85.2 ± 0.8	91.5 ± 0.6
Al ³⁺ , Zn ²⁺ , Mn ²⁺ ^e	3000	102 ± 1	88.7 ± 2.1
F ⁻ , Cl ⁻ , SO ₄ ²⁻ , NO ₃ ⁻ ^f	80,000	96.7 ± 1.8	77 ± 3
F ⁻ , Cl ⁻ , SO ₄ ²⁻ , NO ₃ ⁻ , Sb(III) ^g	80,200	96.0 ± 1.9	78 ± 4

^a The concentration of Sb(V) was 10 µg L⁻¹; ^b the concentration of Sb(III) was 200 µg L⁻¹; ^c the concentration of each ion was 100 mg L⁻¹; ^d the concentration of each ion was 1.0 mg L⁻¹; ^e the concentration of each ion was 10 mg L⁻¹; ^f the concentration of each ion was 200 mg L⁻¹; ^g the concentration of each anion was 200 mg L⁻¹ and the concentration of Sb(III) was 200 µg L⁻¹.

Table 4. Sb(V) Recoveries for Groundwater Samples (n=3)

Sample	Method	Measured, µg L ⁻¹	Spiked, µg L ⁻¹	Found, µg L ⁻¹	Recovery, %
Spring water, GW-1	SCX	264	100	361	97
			300	536	91
	SAX	253	100	338	85
Well water, GW-8	SCX	64	300	525	91
			20	83	95
	SAX	61	60	126	103
			20	85	120
			60	116	92

Table 5. Concentrations of Total Sb and Sb Species in 10 Water Samples (µg L⁻¹)

Sample No.	Sample type	Total Sb	Sb(V)	Sb(III)
GW-1	Spring water	287	264	23
GW-2		13,808	12016	1792
GW-3		3700	3710	<LOD
GW-4		2587	2637	<LOD
GW-5	Well water	1441	1426	15
GW-6		774	771	3
GW-7		1598	1728	<LOD
GW-8		80.6	64.0	16.6
RW-1	River water	1241	1055	186
RW-2		2241	2036	247
Mean value		2776	2571	228

negligible effect on the recovery of Sb(V) in the SCX method. Except for Fe³⁺ (85.2% recovery), the recoveries ranged from 94.3% to 102% when the ratios of the concentration of foreign species to that of the target ion were 3000–80,000 (Table 3). The tolerance limits for Fe³⁺ are relatively low (1 mg L⁻¹), and its concentration in our collected water samples does not exceed 0.25 mg L⁻¹ (Table S1). The degree of interference of the coexisting metal ions in the Sb(V) species separation with the SAX method agreed with those of the SCX method (Table 3).

However, two underestimation results for Sb(V), (77% and 78% recovery), were observed when anions were present in high concentrations (800 mg L⁻¹). This phenomenon is due to the competitive adsorption on the SAX column between the coexisting anions and the target Sb(V) species.

Figures of merit and validation. All of the above field-separated Sb(V) solutions and original water samples were preserved and analyzed in the laboratory using ICP-MS. Calibration curves with a good linear correlation coefficient ($R^2 = 0.9998$) were constructed using a series of Sb standard solutions (0.1–1000 µg L⁻¹). The limit of detection (LOD), which was defined as three times the standard deviation of a procedural blank divided by the sensitivity (*i.e.* the slope of the calibration curve), for Sb(V) was 0.03 and 0.05 µg L⁻¹ for the SCX and SAX methods, respectively. The LODs of the proposed speciation methods for Sb(V) are comparable with those of the HPLC-ICP-MS (0.04 µg L⁻¹)³³ and HPLC-HG-AFS (0.09 µg L⁻¹) methods.³⁴ The concentration of the Sb(III) species was calculated from the difference between the amounts of total Sb and Sb(V) species. Some organic Sb species (*i.e.* (CH₃)SbO(OH)₂, (CH₃)₂Sb(O)OH, (CH₃)₃Sb, (CH₃)₃SbCl₂, HSb₂S₄⁻, and Sb₂S₄²⁻) and colloid-Sb species can exist in geothermal waters or seawater. However, the concentrations of organic Sb species in surface water and groundwater are negligible.^{23,24}

Validation of the analytical methods for Sb speciation is difficult owing to the lack of certified reference materials (CRMs) for this element. Therefore, two spiked groundwater samples were prepared to evaluate the proposed method of this study. As shown in Table 4, the recoveries of the Sb(V) species were in the 91–103 % and 85–120 % range for the SCX and SAX methods, respectively. The relative standard deviation (RSD) for Sb(V), calculated from the relative deviation of three consecutive measurements of spring water (GW-1) and well water (GW-8), was 1.2–5.3% and 4.6–9.3% for the SCX and SAX methods, respectively. The reproducibility of the different ion-exchange cartridges was also examined by injecting a well water sample (GW-6) into ten different SCX cartridges and ten different SAX cartridges. The measured Sb(V) amounts were not significantly different for these 20 cartridges (mean value: 771 µg L⁻¹, RSD: 5.3%). A simple dilution with high-purity water before the ion-exchange separation procedures (SCX or SAX) is recommended when the water samples have high total Sb concentrations (>1000 µg L⁻¹) or high ionic strength (or total dissolved solids, TDS > 1000 mg L⁻¹). Compared to the SAX method, the SCX method is easier to operate and more tolerant to high concentrations of coexisting anions, and it does not require an elution reagent; thus, it is more suitable for field separation of inorganic Sb species.

Application to surface water and groundwater. The proposed

SCX method was used for field separation of inorganic Sb species in eight groundwater (5 spring water and 5 well water) and two surface water (river water) samples, collected from the XKS area. As shown in Table 5, the total Sb concentrations of the ten selected water samples ranged from 80.6 to 13808 $\mu\text{g L}^{-1}$ with a mean of 2776 $\mu\text{g L}^{-1}$, and reached up to 555 times the Sb concentration limit for drinking water as stipulated by the Chinese Government (5 $\mu\text{g L}^{-1}$).⁶ The dominant species in the selected samples were the Sb(V) species (64–12016 $\mu\text{g L}^{-1}$, approximately 92%), followed by the Sb(III) species (<LOD–1792 $\mu\text{g L}^{-1}$, approximately 8%). Our results for the Sb species are in agreement with the reported values of (Sb(V): 330–11400 $\mu\text{g L}^{-1}$; Sb(III): <LOD trace level) from the same area and obtained using HPLC-ICP-MS (Table 5).³⁵

CONCLUSIONS

Field-based speciation of the inorganic Sb species using an ion-exchange resin column cartridge, followed by analysis of the eluted fractions by ICP-MS, can provide good quantitative recovery and repeatability. The problem of chemical species alteration after collecting the water samples and their storage, then final separation and analysis in a conventional laboratory, was solved successfully by using the proposed method. Compared to other laboratory-based methods, the proposed SCX method offers the advantages of being solvent-free, simple, fast, easy to operate, low cost, and can be applied to Sb speciation analysis on-site in the field and in the laboratory.

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Notes

The authors declare no competing financial interest.

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