J Radioanal Nucl Chem (2014) 299:867–877
DOI 10.1007/s10967-013-2694-5

Simultaneous determination of inorganic As(III), As(V), Sb(III), Sb(V), and Se(IV) species in natural waters by APDC/MIBK-NAA

Y. Shi · A. Chatt

Received: 12 August 2013 / Published online: 13 September 2013

Abstract A solvent extraction preconcentration as well as separation method involving ammonium pyrrolinedithiocarbamate (APDC) and 4-methyl-2-pentanone (MIBK) in conjunction with neutron activation analysis (NAA) was developed for the simultaneous measurement of low levels of inorganic arsenic, antimony and selenium species in natural waters. Several critical factors affecting the APDC/MIBK-NAA method were studied in detail including the selection of chelating agent, solvent, aqueous pH for the extraction of six species as well as a few organoarsenic species as representatives for organic species, the stability of the complexes in organic phase, phase volume ratios for extraction and back-extraction steps, and the reduction of the species from higher to lower oxidation state. The detection limits for arsenic, antimony and selenium were found to be as low as 0.026, 0.010 and 0.12 μg L^{-1}, respectively. Trace amounts of As(III), As(V), Sb(III), Sb(V), and Se(IV) in different types of natural water sample and two water certified reference materials were measured using the APDC/MIBK-NAA method.

Keywords Speciation analysis · Solvent extraction · Neutron activation · Arsenic, antimony, selenium species · Natural waters

Y. Shi · A. Chatt (✉)
Department of Chemistry, Trace Analysis Research Centre, Dalhousie University, 6274 Coburg Road, Room 212, PO BOX 15000, Halifax, NS B3H 4R2, Canada
e-mail: A.Chatt@Dal.Ca

Present Address:
Y. Shi
Analytical Chemistry Branch, Chalk River Laboratories, Atomic Energy of Canada Limited, Chalk River, ON K0J 1J0, Canada

Introduction

The speciation of trace elements in general and that of arsenic in particular in natural waters has increasingly become important. A large number of papers and review articles have been published on this subject and will not be dealt with here unless especially relevant. Speciation analysis methods using chemical and biochemical separation techniques in conjunction with neutron activation have been developed in our laboratory for more than 40 years. In the late 1990s toxic element species in natural waters was of particular interest to us. Initially, speciation methods for arsenic and its co-contaminants in water were developed but soon our attention was focused on various arsenic species. A HPLC-NAA method with very low detection limits was reported for the first time in literature for the simultaneous determination of arsenic species, namely As(III), As(V), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), arsenobetaine (AsB), and organically bound arsenic (OBAs) in water samples [1]. Recently, a solid phase extraction-NAA (SPE-NAA) method for the above arsenic species has also been published [2]. Many regulatory authorities require the levels of only As(III); a simple solvent extraction method for As(III) and As(V) has been reported for this purpose [3]. As noted above, our original interest included speciation analysis of arsenic and its co-contaminants such as antimony and selenium because of their co-existence in many water supplies and biological materials, possible intra- as well as inter-species effects, and their biologically related transformations. There is a resurging interest in the speciation studies of these three elements. Inorganic As(III), As(V), Sb(III), Sb(V), Se(IV) and Se(VI) appear to be the predominant species of these elements in natural waters. An APDC/MIBK-NAA method was developed at that time for the

determination of the above species in water [4–6] and is reported here in detail.

Since arsenic, antimony and selenium species are often present in water at very low levels, analytical methods of high sensitivity involving chemical separations are generally required. The simultaneous analysis of the inorganic species of these three elements using solvent extraction is not very common. Most of the publications employing solvent extraction focused on individual species where it was used as a sample pretreatment method prior to analysis by hyphenated techniques such as HPLC-HG-AAS, HPLC-HG-AFS, HPLC-HG-AES, and HPLC-ICP-MS. Subramanian and Meranger [7], on the other hand, used APDC/MIBK-ET-AAS for the simultaneous speciation analysis of As(III), As(V), Sb(III), Sb(V), Se(IV), and Se(VI). They first extracted As(III), Sb(III) and Se(IV) at pH 3.5–5.0. Then they measured total arsenic and antimony after reduction of As(V) to As(III) and of Sb(V) to Sb(III) by $Na_2S_2O_3$ prior to extraction. Total selenium was determined after reduction of Se(VI) to Se(IV) with HCl before the extraction. Hence, the levels of As(V), Sb(V), and Se(VI) were calculated by difference. Narukawa et al. [8] used water as the solvent for the simultaneous extraction of arsenic, antimony and selenium species in fly ash and reported As(V), Sb(III) and Se(IV) as the predominant species.

NAA is a very sensitive technique for the determination of arsenic, antimony and selenium. One of the first papers using solvent extraction and NAA to study arsenic and antimony species in seawater was published in 1975 by Gohda [9]. He employed diethyldithiocarbamate (DDTC) in $CHCl_3$ to extract As(III) and Sb(III) from freshly collected seawater samples, back-extracted into dilute HNO_3, cocrystallized with thionalide, and analyzed by NAA. Then he determined As(V) and Sb(V) by NAA after cocrystallization with thionalide from the original seawater sample. This DDTC/$CHCl_3$ method effectively removed the major interfering elements, such as bromine, chlorine and sodium, and thereby dramatically improved the detection limits of the elements of interest by NAA. Mok and Wai [10, 11] used APDC/$CHCl_3$ at pH 3–6 to simultaneously extract As(III) and Sb(III). As(V) and Sb(V) were first reduced with $K_2S_2O_3$ and KI at pH 1 then extracted. The arsenic- and antimony-APDC complexes in the organic phase were then back-extracted into HNO_3 and analyzed by NAA. Another APDC/$CHCl_3$–NAA method was reported by Yusof et al. [12] for As(III) and As(V) in seawater and marine organisms.

Compared to solvent extraction, coprecipitation yields a solid sample which can be easily irradiated and handled in NAA. The chelating agents used in solvent extraction can also be used to separate total arsenic, As(III) and As(V) by coprecipitation. For example, Van Elteren and Das [13] first coprecipitated As(III) with DBDC and then As(V) with the same reagent after reduction with $K_2S_2O_3$ and KI, collected the precipitates on 0.45 μm membrane filters, and determined the arsenic content by NAA. Yusof et al. [14] used DBDC and phenolphthalein to coprecipitate Se(IV) from marine sediment and then determined it by NAA. Sun and Yang [15] reported a method for the speciation of As(III), As(V), Sb(III), Sb(V), Se(IV), and Se(VI) by coprecipitation with $Pb(PDC)_2$ followed by NAA. Since the development of the APDC/MIBK-NAA method for the above species in 2000 [4] and reported below, many papers have been published on the analysis of some of these species by a variety of techniques but none dealt with the simultaneous determination of all the above species in natural waters by solvent extraction and NAA to the best of authors' knowledge.

Experimental

Standards and reagents

Five different arsenic compounds were used as speciation standards. They were sodium arsenite (NaH_2AsO_3, ACS certified grade, Fisher), potassium arsenate (KH_2AsO_4, Sigma), cacodylic acid ($C_2H_6AsO_2H$, >99 %, Fluka), sodium monomethylarsonate ($CH_3AsO_3Na_2$, synthesized by the authors), and arsenobetaine (1,031 ± 6 mg kg^{-1} in solution, CRM 626 prepared by the SM&T progamme of EU). Potassium antimonyl tartrate ($KSbC_4H_4O_4$, 99.95 %, Aldrich), potassium hexahydroxyantimonate ($KSb(OH)_6$ 99.99 %, Aldrich), sodium selenite (Na_2SeO_3 99.999 %, Aldrich) and sodium selenate (Na_2SeO_4 99.999 %, Aldrich) were used as the speciation standards for antimony and selenium, respectively. Stock solutions of 1,000 μg mL^{-1} arsenic in forms of As(III), As(V), MMA and DMA were prepared by dissolving the corresponding compounds in distilled deionized water (DDW). Stock solutions of 1,000 μg mL^{-1} antimony and selenium in forms of Sb(III), Sb(V), Se(IV) and Se(VI) were also prepared by dissolving their corresponding compounds in DDW. The arsenobetaine (AsB) standard solution was used as the stock solution without further treatment.

Two chelating agents, namely ammonium pyrrolinedithiocarbamate (APDC) and sodium dibenzyldithiocarbamate (DBDC), were purchased from Sigma and Aldrich, respectively. A 5 % (w/v) of APDC aqueous solution was first prepared then purified by extraction with 5 mL of 4-methyl-2-pentanone (MIBK). This purification step also served as a step to co-equilibrate the aqueous APDC solution with MIBK. This solution was found to be stable for more than 1 month when it stored in a dark and cool place. A 2 % DBDC solution in 75 % methyl alcohol was first prepared, then also purified and co-equilibrated with MIBK.

Solvents, namely MIBK (99.5+ %, HPLC grade) and methyl alcohol (99.9+ %, PRA grade) were purchased from Aldrich. Chloroform, *o*-xylene and 2,6-dimethyl-4-heptanone (DIBK) were purchased from Caledon. Cyclohexane (certified ACS) and toluene (AR) were purchased from Fisher and BDH, respectively.

L-Cysteine (>99.5 %) and potassium thiosulphate (hydrate) were purchased from Fluka and Sigma, respectively. 5 % (w/v) solutions of these two chemicals were freshly prepared before use and purified by extraction with 1 mL of 5 % APDC and 5 mL of MIBK. Disodium ethylenediaminetetraacetate (EDTA, AR) was purchased from Fisher. A 6 % (w/v) solution was prepared and purified by APDC/MIBK extraction method as described above.

Quartz sub-boiling distilled nitric acid (67–70 %) and acetic acid (glacial, >99 %) were purchased from Seastar. Ammonia solution (20–22 %) was also purchased from Seastar. The DDW was prepared by passing quartz-distilled water through a Fisher mixed-bed deionizing water purification column. A pH 5.5 acetic acid-acetate buffer solution was prepared from 0.05 M acetic acid and 1 M ammonia solution and further purified by APDC/MIBK extraction.

Collection of water samples

Prior to the collection and storage of the water samples to be analyzed, all containers and apparatus used were thoroughly precleaned. The cleaning procedure comprised washing the container with laboratory grade detergent, soaking in 4 M reagent grade HNO_3 for 24 h, washing with tap water, rinsing with DDW, and drying. The natural water samples for speciation analysis were collected from different sources. A commercially available natural spring water sample (Evian) was purchased from the local grocery store. The seawater sample was collected from one of the seawater taps located in the Department of Oceanography of Dalhousie University. The lake surface water sample was collected from the Morris Lake located in Dartmouth, Nova Scotia in 1999 September. The rain water sample was collected in the Studley campus of Dalhousie University in 1999 July.

The natural water samples were suction filtered soon after collection using a Nuclepore membrane of 0.2 μm pore size to remove any particulate matter that might have been present. The speciation analysis on the soluble fraction of the water was performed soon after the filtration. If the analysis was delayed for some reason, the water samples were stored in a refrigerator at 4 °C until the time of analysis. If the sample needed to be stored for a longer period and for the determination of the total elemental content then it was acidified to pH 3 with 20 % HNO_3 solution and stored in a refrigerator at 4 °C.

Two certified reference materials (CRM) of natural origin for trace metals prepared by the National Research Council of Canada (NRCC), namely Riverine water SLRS-4 and Seawater NASS-1, were used for the validation of the methods developed. The acidification and filtration steps were not applied to these CRMs.

General procedure for separation of As(III), Sb(III) from As(V) and Sb(V)

The water sample and MIBK were saturated with each other before the solvent extraction step. Two aliquots of water sample (100 mL of each) were used for the determinations of trivalent arsenic and antimony species alone and the sum of their tri- and pentavalent species, respectively. (i) The first 100 mL of the water sample was adjusted to pH 5 to 6, and the following solutions were added to this sample in sequence: 15 mL of 0.05 M acetic acid-ammonium acetate buffer of pH 5.5, 8 mL of 6 % EDTA solution, and 2 mL of 5 % APDC. The As(III) and Sb(III) species was extracted from this solution by vigorously shaking it with 10 mL of MIBK for 10 min on a wrist action shaker. After the phase separation, 8 mL of the MIBK was back-extracted with 2 mL of 4 M HNO_3 solution. Then this HNO_3 solution was transferred into a medium-size irradiation vial, dried under an IR lamp, and heat-sealed for neutron irradiation. (ii) The second 100 mL aliquot of the water sample was adjusted to about pH 4, and 5 mL of 5 % L-cysteine solution were added to it, and the mixture was allowed to react for 30 min. After this reduction step, the pH of the solution was checked and adjusted to 5–6 if needed, and the extraction of As(III+V) and Sb(III+V) were carried out using the same procedure as that described for As(III) and Sb(III) alone.

General procedure for separation of Se(IV) species

To a 200 mL water sample, 20 mL of pH 5.5 buffer, 10 mL of 6 % EDTA solution, 3 mL of 5 % APDC solution, and 2 mL of MIBK were added. The separation was carried out by vigorously shaking for 10 min on a whist action shaker. After the phase separation, 1 mL of the MIBK was pipetted into a small irradiation vial and sealed for NAA.

Irradiation and counting

All samples and standards were irradiated in one of the five inner pneumatic sites of the Dalhousie University SLOWPOKE-2 Reactor (DUSR) at a neutron flux was 5×10^{11} cm^{-2} s^{-1}. The composition, stability, homogeneity, and reproducibility of the DUSR neutron flux have previously been described [16–18].

For the determination of arsenic and antimony, the samples were irradiated for 2 h, and counted for 10–24 h after a minimum decay of 2 days. The 559.1 and 564.1 keV γ-rays of ^{76}As and ^{122}Sb were used for assaying arsenic and antimony, respectively, on an EG&G ORTEC 92X Spectrum Master spectroscopy system with a GammaVision-32 γ-ray analysis and an MCA emulator. The detector used was an HPGe coaxial detector with a resolution of 1.89 keV, a peak-to-Compton ratio of 56:1, and an efficiency of 32.3 % at the 1,332 keV photopeak of ^{60}Co.

For the determination of selenium, the irradiation-decay-counting times were set as 30-10-30 s. If a cyclic INAA was involved, several cycles of irradiation-decay-counting were performed on the same sample and the spectra were added up. The 162 keV γ-ray of ^{77m}Se was used for assaying selenium on a 60 cm^3 APTEC Ge(Li) semiconductor detector with a resolution of 1.9 keV, a peak-to-Compton ratio of 35:1, and an efficiency of 9.5 % measured at the 1,332 keV photopeak of ^{60}Co.

Results and discussions

Selection of a solvent

Six solvents, namely chloroform, cyclohexane, DIBK, MIBK, toluene, and *o*-xylene, were evaluated for their suitability of extracting As(III), Sb(III), and Se(IV) species. The recoveries of each species together with some of the properties of these solvents are listed in Table 1. Quantitative recoveries (>95 %) of all three species were obtained with four solvents, namely chloroform, DIBK, MIBK, and toluene. Although *o*-xylene was found to extract Sb(III) and Se(IV) quantitatively, the recovery for As(III) was only 77 %. Cyclohexane gave very poor recoveries, as expected, due to the non-polar nature of the solvent. Similar very low extraction yield for Sb(III) was reported by Kamada and Yamamoto [19] using another non-polar solvent, namely CCl_4. The extraction yields were found to decrease with decreasing values of both dielectric constant and dipole moment as shown in Table 1. Other parameters used for selecting a solvent include density, boiling point, and its solubility in water. Obviously, solvents with higher boiling points, lower solubility in water, and greater difference in density compared to water are preferred. Chloroform has the highest difference in density with water and should be a very good solvent; however, the chlorine in $CHCl_3$ becomes highly active on irradiation with neutrons and makes the use of short-lived nuclides, such as ^{77m}Se (half-life = 17.4 s) very difficult if not impossible. The unpleasant smell of DIBK makes it an undesirable solvent for extraction. Both toluene and MIBK would be good solvents for the present study. MIBK was finally selected by the overall consideration of its higher boiling point, lower solubility in water, acceptable density difference with water, not a very unpleasant odor, and no interfering elements for NAA.

Selection of a chelating agent and pH

Both APDC and DBDC chelating agents were evaluated in conjunction with MIBK for the extractions of As(III), As(V), Sb(III), Sb(V), Se(IV) and Se(VI) as a function of pH (ranging from 1 to 10), and the results are presented in Figs. 1 and 2, respectively.

As shown in Fig. 1, As(III) can be quantitatively extracted by APDC/MIBK in the pH range of 3–9 while As(V) is not extracted at all at pH 5–10. The lower recovery of As(III) at pH less than 3 might have been caused by the instability of As(III)-PDC$^-$ complex in MIBK during the phase separation as explained later. Up to 25 % As(V) can be extracted at pH 2–5. Therefore, these two arsenic species can be separated from each other by APDC/MIBK at pH 5–9.

The quantitative recovery of Sb(III) in the pH range of 1–10 indicates that Sb(III) is more readily extracted than As(III) and Se(IV) by APDC/MIBK. It was found that about 80 % of Sb(V) could be extracted into MIBK at pH 1–3, and none above pH 5. Therefore, Sb(III) can be quantitatively separated from Sb(V) at pH 5–10. Other researchers have also reported similar results using APDC/$CHCl_3$ [10], APDC/$CHCl_3$–CCl_4 mixed solvent system [20], and APDC/MIBK [21]. The pH range for the quantitative extraction of Se(IV) from Se(VI) was found to be from 1 to 7 using the APDC/MIBK system.

The different effects of pH on the extraction of As(V), Sb(V) and Se(VI) can be explained in terms of their acid dissociation constants. Se(VI) in the form of H_2SeO_4 has a pK_{a2} 1.7, and As(V) in the form of H_3AsO_4 has pK_{a1} 2.2, pK_{a2} 6.9 and pK_{a3} 11.5; however, Sb(V) in the $HSb(OH)_6$ form has pK_a 4.4. So Sb(V) is weakest among these three acids and shows a higher partition between the organic and aqueous phases.

In general, the extraction behavior of As(III), Sb(III) and Se(IV) by DBDC/MIBK at pH 1–10 is similar to that by APDC/MIBK. However, APDC was selected as the chelating agent in this work because of its high purity, ease of availability, and high solubility in water.

Effect of pH on the extraction of MMA, DMA and AsB

Experiments were carried out in order to ensure that MMA, DMA and AsB do not interfere with the extraction of As(III) in the selected pH range. The extraction of the above three organic arsenic species by organic solvents has

Table 1 Recoveries of As(III), Sb(III) and Se(IV) by different solvents [30, 31]

Solvent	Recovery, %			Density (20 °C) g mL^{-1}	b.p., °C	Solubility (20 °C), wt%	Dielectric constant (20 °C)	Dipole moment (20 °C), debye unit
	As(III)	Sb(III)	Se(IV)					
MIBK	103 ± 5	100 ± 6	100 ± 4	0.801	115.7	1.7 (25 °C)	13.11	
Chloroform	104 ± 5	101 ± 6	99 ± 4	1.484	61.7	0.80	4.81	1.1 (25 °C)
DIBK	101 ± 5	100 ± 6	100 ± 2	0.806	165	0.05		
Toluene	101 ± 4	100 ± 6	100 ± 2	0.866	110.6	0.05	2.38	0.45
o-Xylene	77 ± 4	97 ± 6	102 ± 2	0.880	144		2.57	0.64
Cyclohexne	4 ± 1	8 ± 2	5.1 ± 0.5	0.779	80.7	0.01	2.02 (25 °C)	0

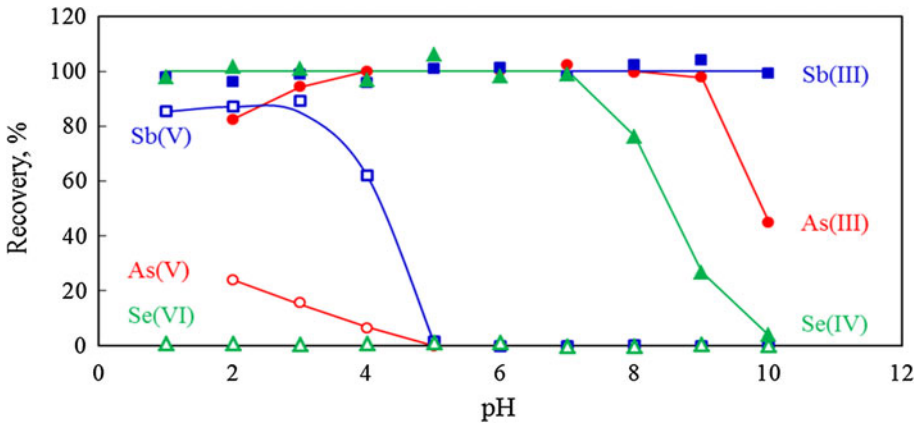

Fig. 1 Recovery of various species by APDC/MIBK at different pH

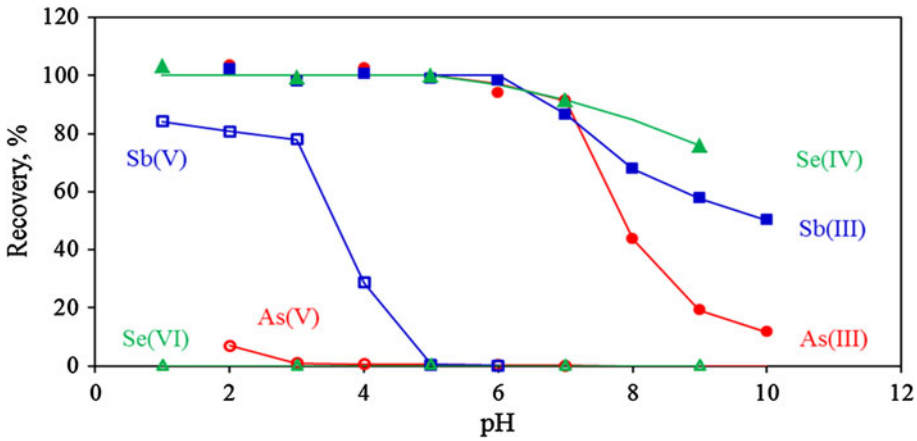

Fig. 2 Recovery of various species by DBDC/MIBK at different pH

not yet been extensively studied. Hasegawa and coworkers [22] reported that MMA and DMA could not be extracted with DDTC/$CHCl_3$ at a pH range of 2–10. The results obtained in this work using APDC/MIBK are presented in Fig. 3. These graphs clearly indicate that AsB remained completely unextracted in the aqueous phase in the pH range of 2–10. No MMA was extracted above pH 3 while no DMA was extracted above pH 4. These results suggest that MMA, DMA and AsB would not interfere with the determination of As(III) and As(V) above pH 4 by the APDC/MIBK system.

Back-extraction of As(III), Sb(III) and Se(IV)

The use of a back-extraction step in a separation procedure has certain advantages [10–12]. It can remove an organic solvent, as needed for some elemental determination techniques, as well as preconcentrate the analyte further. In the present work, aqueous solutions of 0.1 to 6 M HNO_3 were used to back-extract As(III), Sb(III) and Se(IV) from MIBK. The results are presented in Table 2. It is evident that 4 M HNO_3 could be used to quantitatively back-extract As(III) and Sb(III). However, only 36 % of Se(IV)

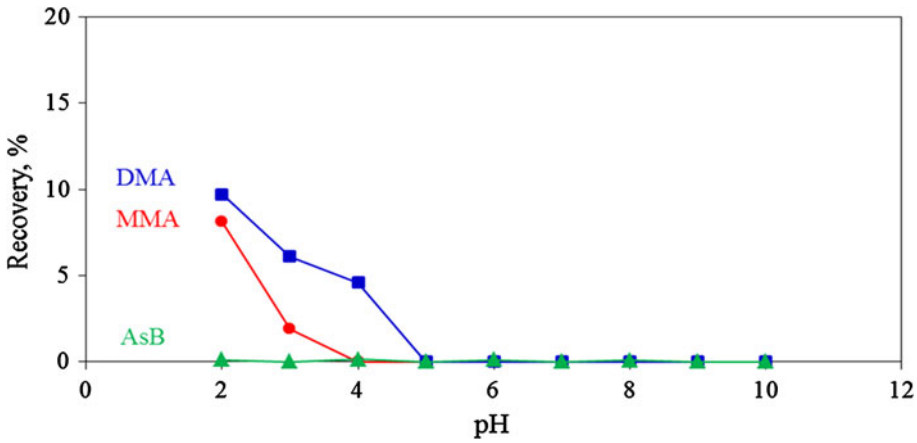

Fig. 3 Effect of pH on the extraction of MMA, DMA and AsB by APDC/MIBK

Table 2 Variation of back-extraction recovery (%) with HNO_3 concentration (M) for As(III), Sb(III) and Se(IV)

HNO_3, M	As(III)	Sb(III)	Se(IV)
0.1	93 ± 4	82 ± 4	7 ± 2
1	99 ± 4	90 ± 3	8 ± 2
4	99 ± 2	98 ± 3	36 ± 2
6	99 ± 1	100 ± 4	66 ± 3

could be extracted at this acidity, which increased to 66 % with 6 M HNO_3.

In order to achieve detection limits of the order of ppb by NAA using relatively low neutron flux at the DUSR facility, the samples needed to be irradiated for at least a few hours. Liquid samples, whether in MIBK or HNO_3, could not be directly irradiated for such a long time because of the possible rupture of the polyethylene irradiation vials due to pressure build-up in them. Attempts were made to evaporate MIBK to dryness by heating under an IR lamp for about 3.5 h. The results obtained show that there is a significant loss of As(III), viz. an average of 27 ± 3 % for 9 replicates (35, 26, 28, 25, 26, 20, 33, 26 and 25), during evaporation. It is possible that the As(III) extracted in MIBK as $As(PDC)_3$ is volatile enough to cause this extent of loss. Back-extraction into an aqueous phase not only eliminated this loss but also reduced the time required to evaporate the sample to dryness so that it can be directly irradiated.

Effect of phase volume ratios

The aqueous-to-organic phase volume ratios in both extraction and back-extraction steps are related to the enrichment factor of the species. A higher aqueous-to-organic phase volume ratio (V_a/V_o) in the extraction step and a lower value in the back-extraction step are obviously preferred. The recoveries of various species obtained at different organic-to-aqueous volume ratios at both extraction and back-extraction (by 4 M HNO_3) steps are presented in Figs. 4 and 5, respectively.

From the results presented in Fig. 4, it is evident that nearly 100 % recoveries of As(III) and Sb(III) were obtained if the ratio in extraction step is kept between 1 and 10. Mok and Wai [10] found that a ratio of 20 or less is desirable for the quantitative extraction of As(III) and Sb(III) using an APDC/$CHCl_3$ system. For the back-extraction step, It was observed that a ratio of 0.2–1 gave the best yield for As(III) and Sb(III) as shown in Fig. 5.

For the quantitative recovery of Se(IV) in the extraction step, the V_a/V_o can be as high as 100, as indicated in Fig. 4. Since selenium was concentrated in the MIBK phase and since it could be determined free from interference through the short-lived nuclide ^{77m}Se by directly irradiating the organic liquid, it was not necessary to go through the back-extraction step for this element. Moreover, the back-extraction of Se(IV) in 4 M HNO_3 was not quantitative as it gave a yield of only 36 % at a V_a/V_o ratio of 1.

Stability of PDC complexes of As(III), Sb(III) and Se(IV)

The stability of As(III), Sb(III) and Se(IV) complexes with APDC in MIBK with time was investigated. Experiments were carried out at two pH values (2 and 5.6) for 326 h from the time of extraction. At pH 5.6, the concentrations of As(III), Sb(III) and Se(IV) in MIBK were found to be extremely stable for more than 300 h after the extraction as shown in Fig. 6. However, at pH 2, the concentrations of the three species decreased with increasing time. This was particularly true for As(III) which decreased significantly within a short time, viz. to about 50 % of the original value within 5 h. The decomposition of APDC itself at low pH and of the relatively less stable arsenic PDC^- complex could be the main reasons for this observation. Therefore, if the pH of the aqueous phase is kept within 5 and 7, sufficient time (such as overnight) can be allowed for the

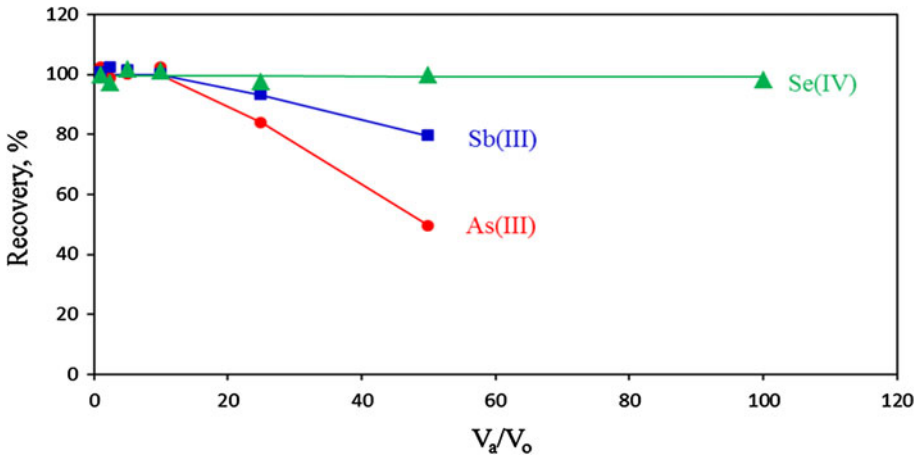

Fig. 4 Recovery of As(III), Sb(III) and Se(IV) at different extraction phase volume ratio

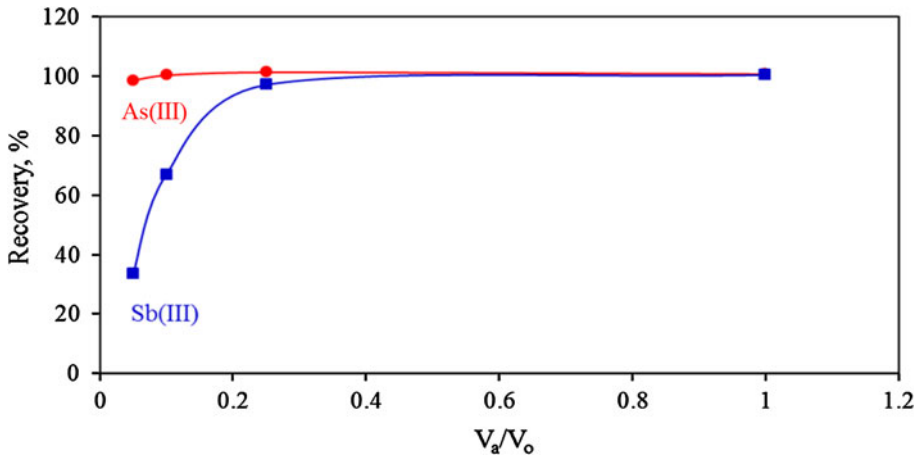

Fig. 5 Recovery of As(III) and Sb(III) at different back-extraction phase volume ratio

phase separation without any loss of As(III), Sb(III) and Se(IV).

Kamada and Yomamoto [19] also reported that Sb(III) complex with APDC was stable in MIBK for at least 6 h at pH 5–8. Chung [20] found that As(III) and Sb(III) APDC complexes could be stable in the MIBK and $CHCl_3$–CCl_4 mixed solvent for 24 h at pH 5 and that of Se(IV) for 6 h at the same pH.

Reduction of As(V), Sb(V) and Se(VI)

Experiments were carried out using three different reducing agents, namely $K_2S_2O_3$ (25 %), KI (25 %), and L-cysteine (5 %), to evaluate their ability to reduce of As(V), Sb(V), and Se(VI) to As(III), Sb(III), and Se(IV), respectively. About 1 mL of each of the reducing reagent solutions was used, and the reactions were allowed for a period of 30 min. The expected reduced species, namely As(III), Sb(III) and Se(IV), were extracted by APDC/MIBK at pH 5.5 by the procedure described above.

The degree of reduction for As(V), Sb(V) and Se(VI) by $K_2S_2O_3$ and KI at pH 1 and 4 are shown in Table 3, and that by L-cysteine at pH from 1 to 7 are presented in Table 4. The reductions of As(V) and Sb(V) by $K_2S_2O_3$ were found to be quantitative at pH 1 (Table 3). However, at pH 4, the yield of As(III) was about 33 % and that of Sb(III) was even lower, viz. less than 2 % (Table 3).

The use of KI for the reduction of As(V) and Sb(V) at pH 1 was found to be interesting. The reduction reaction took place at pH 1 as indicated by the color change due to the formation of iodine (i.e. I_2). However, the color disappeared after the pH of the mixture was adjusted to 5.5, as required for the solvent extraction method. It appears that the direction of the reaction is reversed at pH 5.5. Very low yields of As(III) and Sb(III) were obtained. Potassium iodide at pH 4, on the other hand, did not reduce As(V) and Sb(V) as there was no color change.

The reduction of As(V), Sb(V) and Se(VI) by L-cysteine was studied for a wider pH range of 1–7. As shown in Table 4, the reduction of As(V) and Sb(V) were found to be complete between pH 1 and 6. A 5 % L-cysteine solution was selected as the reducing reagent for this work. The pH chosen was 5.5 which also happened to be the pH for the solvent extraction procedure so that no pH adjustment

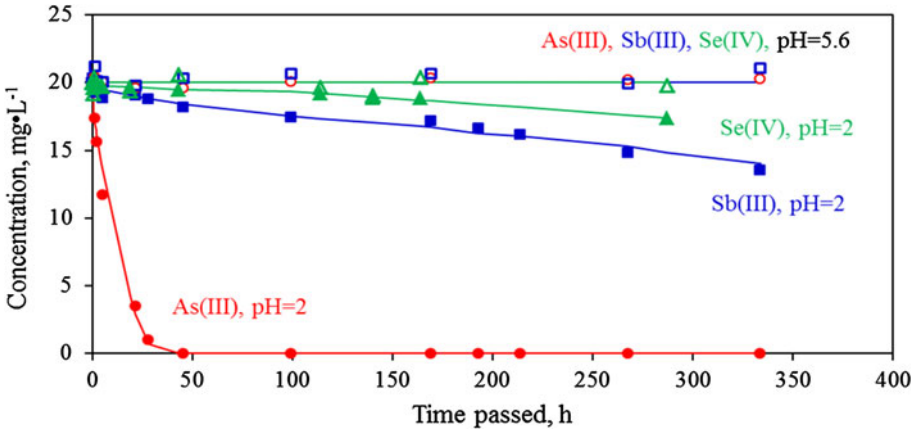

Fig. 6 Concentrations of As(III), Sb(III) and Se(IV) at different times after extraction into MIBK

was necessary between the reduction and the extraction steps. In addition, L-cysteine did not form any precipitate which made the phase separation step in the solvent extraction method easier than $K_2S_2O_3$ which tended to give a precipitate.

Unfortunately, the reduction of Se(VI) to Se(IV) by L-cysteine, $K_2S_2O_3$ and KI was found to be unsuccessful. The reason could be that these agents reduced Se(VI) to Se(0) which tended to remain as a precipitate under the experimental conditions and not extracted by APDC/MIBK.

Reduction and extraction of MMA, DMA and AsB and their potential interferences to determination of As(V)

It is evident from the discussion above that MMA, DMA and AsB did not interfere with the determination of As(III) and As(V) at pH 5.5 by the APDC/MIBK solvent extraction method developed here. In this method, As(V) is determined after its reduction to As(III). It is therefore necessary to investigate any interference that may arise from the reduction of MMA, DMA and AsB.

Experiments were carried out to evaluate the effects of reduction of MMA, DMA and AsB by L-cysteine at pH 5.5 as well as by $K_2S_2O_3$ at pH 4. The yields of extractable arsenic species are given in Table 5. It is evident that essentially no arsenic (<0.1 %) was extracted from AsB. However, about 45 % of arsenic in MMA and 53 % of arsenic in DMA were extracted by APDC/MIBK after their reduction by L-cysteine, respectively. Therefore, there exists a potential interference from MMA and DMA to the determination of As(V) by this method.

It was found that the reduction yields for MMA and DMA were 25 and 1 %, respectively, by $K_2S_2O_3$ at pH 4. It appears that MMA was more readily reduced than DMA by $K_2S_2O_3$. It is also evident from Table 5 that $K_2S_2O_3$ did not reduce AsB at all.

In the speciation analysis of real water samples, it should be noted here that MMA and DMA are found to be very minor species in most natural water samples, while As(V) is the predominate species. So the potential interference from MMA and DMA to the determination of As(V) in this work was considered negligible.

The reduction products from MMA and DMA by L-cysteine are not presently known. Hasegawa and coworkers [22] reported that MMA(III) and DMA(III) could be produced from MMA and DMA by hydrogen sulfide; the trivalent

Table 3 Reduction (%) of As(V), Sb(V) and Se(VI) by 25 % $K_2S_2O_3$ and by 25 % KI at pH 1 and 4

Species/pH	As(V)		Sb(V)		Se(VI)	
	1	4	1	4	1	4
$K_2S_2O_3$	100 ± 3	33 ± 2	98 ± 2	<2	<1	<1
KI	<2	<2	8 ± 1	<2	<1	<1

Table 4 Reduction (%) of As(V), Sb(V) and Se(VI) by 5 % L-cysteine at different pH

Species	pH						
	1	2	3	4	5	6	7
As(V)	100 ± 2	98 ± 2	98 ± 2	102 ± 2	101 ± 2	99 ± 2	63 ± 2
Sb(V)	100 ± 2	100 ± 2	101 ± 2	99 ± 2	102 ± 2	103 ± 3	98 ± 2
Se(VI)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Table 5 Yields of extractable reduction products (%) of MMA, DMA and AsB

Species	MMA		DMA		AsB	
Reducing agent	L-Cysteine	$K_2S_2O_3$	L-Cysteine	$K_2S_2O_3$	L-Cysteine	$K_2S_2O_3$
pH	5.5	4	5.5	4	5.5	4
Yield	45 ± 11	25 ± 5	53 ± 21	1.0 ± 0.5	<0.1	<0.1

Table 6 Levels of As(III), As(V), Sb(III), Sb(V) and Se(IV) species in selected natural water samples by APDC/MIBK-NAA (ng mL^{-1})

Species	Seawater	Tap water	Rain water	Spring water	Lake water
As(III)	0.31 ± 0.01	0.13 ± 0.04	0.10 ± 0.02	0.03 ± 0.005	<0.06
As(V)	1.26 ± 0.09	0.37 ± 0.10	0.16 ± 0.03	0.06 ± 0.006	0.09 ± 0.01
Sb(III)	0.060 ± 0.008	<0.10	<0.10	0.021 ± 0.003	<0.10
Sb(V)	0.065 ± 0.004	<0.10	0.12 ± 0.02	0.040 ± 0.006	<0.10
Se(IV)	<0.16	<0.30	<0.30	<0.30	<0.30

species were extracted by DDDC/$CHCl_3$, which is also a dithiocarbamate chelating extraction system. These APDC/MIBK extractable products observed in our work might also be MMA(III) and DMA(III).

Analysis of natural water samples

Five different types of natural water sample were analyzed using the solvent extraction method developed. The levels of the inorganic arsenic, antimony and selenium species are presented in Table 6. The As(V) was found to be the predominant species in all water samples. The total concentration of As(III) and As(V) in these samples were found to be <1 ng mL^{-1} except the seawater which had a value of 1.57 ng mL^{-1} which is within the normal range of 1–2 ng mL^{-1} for seawater [9, 10, 12, 23]. The level of As(III) in the lake water sample was below the detection limit of 0.06 ng mL^{-1}.

Very small amounts of Sb(III) and Sb(V) were found in the seawater and the spring water samples. Only Sb(V) could be quantitatively measured in the rain water samples. Both antimony species were found to be below the detection limits in the tap water sample. Concentrations of Se(IV) in all water samples were also below the detection limits.

Analysis of reference materials

Although a number of water CRMs with certified values for the total elemental concentrations are available, no CRM with information on arsenic, antimony and selenium species was found at the time this work was done. We analyzed two CRMs, namely NRCC Nearshore Seawater NASS-1 and Riverine Water SLRS-4, for As(III), As(V), Sb(III), Sb(V), and Se(IV) using the APDC/MIBK-NAA method. The results are given in Table 7. It appears that the inorganic arsenic species account for most of the total

Table 7 Levels of As(III), As(V), Sb(III), Sb(V) and Se(IV) species in selected NRCC certified reference materials by APDC/MIBK-NAA (ng mL^{-1})

Sample	SLRS-4	NASS-1
As(III)	0.22 ± 0.04	0.21 ± 0.03
As(V)	0.39 ± 0.08	1.33 ± 0.09
Sb(III)	0.010 ± 0.004	<0.10
Sb(V)	0.21 ± 0.04	0.31 ± 0.05
Se(IV)	0.16 ± 0.02	<0.16
Certified total arsenic	0.68 ± 0.06	1.65 ± 0.19
Certified total antimony	0.23 ± 0.04	

elemental concentrations in both samples, viz. about 93 % of NASS-1 and about 79 % of SLRS-4. The sum of Sb(III) and Sb(V) in SLRS-4 was found to be 0.22 ng mL^{-1}, which accounts for about 96 % of the total antimony content of 0.23 ng mL^{-1}. A higher level of Sb(V) was found in NASS-1 than in SLRS-4. The Se(IV) content in SLRS-4 was found to be 0.16 ± 0.02 ng mL^{-1} and that in NASS-2 was below the detection limit. Neither certified nor information values were provided for total selenium in these CRMs.

Sensitivities and detection limits

The detection limits were calculated according to Currie's definition [24] and sensitivities were defined as the number of counts obtained per nanogram of the analyte. The detection limits and sensitivities for arsenic and antimony in natural water samples by the APDC/MIBK-NAA method are presented in Table 8 with different NAA time schemes.

It is evident from Table 8 that using a longer counting time the detection limits were lowered and the sensitivities were enhanced as shown by the comparison among the

Table 8 Sensitivities and detection limits for arsenic and antimony in water samples by APDC/MIBK-NAA (ng mL^{-1})

Expt. no.	t_i-t_d-t_c, h	Sample type	Detection limit, ng mL^{-1}		Sensitivity, counts ng^{-1}	
			As	Sb	As	Sb
1	2-50-4	NASS-1	0.056	0.044	142	188
2	2-50-8	NASS-1	0.040	0.029	270	367
3	2-50-12	Tap water	0.027	0.020	385	540
4	2-95-12	SLRS-4	0.038	0.013	118	334
5	2-76-24	Seawater	0.026	0.010	336	768

Table 9 Evaluation of APDC/MIBK-CINAA method for Se(IV) in SLRS-4

t_i-t_d-t_c, s	Number of cycles	Sensitivity, counts ng^{-1}	L_D, ng mL^{-1}	SLRS-4, Se ng mL^{-1}
30-10-30	1	1.12	0.19	<0.19
30-10-30	2	2.22	0.17	<0.17
30-10-30	3	3.31	0.14	0.14
30-10-30	4	4.46	0.13	0.17
30-10-30	5	5.61	0.12	0.16

Expt. #1 to #3. Use of a longer decay time continued to improve the detection limit for antimony as shown by Expt. # 3 and 4, because of the longer half-life of ^{124}Sb (2.06d) than that of ^{76}As (1.09d). Detection limits of as low as 0.026 and 0.010 ng mL^{-1} for arsenic and antimony, respectively, were obtained by using a t_i-t_d-t_c of 2-76-24 h which enabled the determination of ultra low levels of arsenic and antimony species in natural waters.

The use of the short-lived ^{77m}Se nuclide by cyclic INAA (CINAA) to assay selenium gives a lower detection limit and a higher sensitivity [25–29]. These parameters in CINAA depend on the number of cycles in addition to other factors affecting conventional NAA. The sensitivities and detection limits for selenium in a Riverine Water CRM (SLRS-4) using the APDC/MIBK-NAA method are presented in Table 9. It can be seen that the sensitivity improved with increasing number of cycles when other factors are kept constant. The detection limits decreased with the increasing number of cycles. The improvement of the detection limits in SLRS-4 from 0.19 ng mL^{-1} using one cycle to 0.12 ng mL^{-1} using 5 cycles allowed the quantitative measurement of selenium at 0.16 ng mL^{-1} (Table 9). Although the detection limit generally decreased with increasing number of cycles, the rate of decrease slowed down considerably after a few cycles. Therefore, a proper selection of the number of cycles must be made for optimum results.

Conclusions

The APDC/MIBK solvent extraction method developed in this work was used to selectively extract As(III), Sb(III) and Se(IV) species in the pH range of 5–7. Within this pH range, the potential interference for As(III) from organic arsenic species, such as MMA and DMA, was eliminated. The determination of Se(IV) species was performed by direct irradiation of the organic solvent without any back extraction and using its short-lived nuclide, ^{77m}Se. The determinations of arsenic and antimony species were more conveniently done using a back-extraction step and irradiation of the dried solid sample. L-Cysteine was found to be an efficient reducing agent for As(V) and Sb(V) species; however, none of the three reducing agents used was able to reduce Se(VI) to Se(IV). The APDC/MIBK-NAA method was observed to give high enrichment factors for arsenic, antimony and selenium species, which allowed the determination of ultra low levels of As(III), As(V), Sb(III), Sb(V), and Se(IV) in several water samples and water CRMs.

Acknowledgments The authors would like to thankfully acknowledge the cooperation of the Dalhousie University SLOWPOKE-2 Reactor (DUSR) facility for irradiations, the Natural Sciences and Engineering Research Council (NSERC) of Canada for research operating/discovery, major facilities access, and research network grants to AC, and the Dalhousie University Faculty of Graduate Studies for a stipend to YS. This paper was presented at the 3rd International Nuclear Chemistry Conference (3rd—INCC) held in Città del Mare (Palermo), Sicily, Italy, during 2011 Sep 18–23.

References

1. Shi Y, Acharya R, Chatt A (2004) J Radioanal Nucl Chem 262:277–286
2. Menendez Sanchez W, Zwicker B, Chatt A (2009) J Radioanal Nucl Chem 282:133–138
3. Zwicker R, Zwicker BM, Laoharojanaphand S, Chatt A (2011) J Radioanal Nucl Chem 287:211–216
4. Shi Y (2000) PhD Thesis, Dalhousie University, Halifax

5. Shi Y, Chatt A (2000) 5th International conference on methods and applications in radioanalytical chemistry (MARC-V), Kona, 9–14 Apr 2000
6. Shi Y, Menendez Sanchez W, Chatt A (2008) Annual Session of Sri Lanka Association for the Advancement of Science (SLAAS), Colombo, 1–6 Dec 2008
7. Subramanian KS, Meranger JC (1981) Anal Chim Acta 124:131–142
8. Narukawa T, Takatsu A, Chiba K, Riley KW, French DH (2005) J Environ Monit 7:1342–1348
9. Gohda S (1975) Bull Chem Soc Jpn 48:1213–1216
10. Mok WM, Wai CM (1987) Anal Chem 59:233–236
11. Mok WM, Wai CM (1988) Talanta 35:183–186
12. Yusof AM, Ikhsan ZB, Wood AKH (1994) J Radioanal Nucl Chem Artic 179:277–283
13. Van Elteren JT, Das HA (1989) Anal Chim Acta 222:159–167
14. Yusof AM, Hanafiah Z, Wood AKH (1998) Sci Total Environ 214:247–252
15. Sun YC, Yang JY (1999) Anal Chim Acta 395:293–300
16. Ryan DE, Stuart DC, Chattopadhyay A (1978) Anal Chim Acta 100:87–93
17. Holzbecher J, Chatt A, Ryan DE (1985) Can J Spectrosc 30:67–72
18. Ryan DE, Holzbecher J, Chatt A (1987) Anal Chim Acta 200:89–100
19. Kamada T, Yamamoto Y (1977) Talanta 24:330–333
20. Chung CH, Iwamoto E, Yamamoto M, Yamamoto Y (1984) Spectrochim Acta 39B:459–466
21. Kamada T, Yamamoto Y (1977) Talanta 24:330–333
22. Hasegawa H, Sohrin Y, Matsul M, Hojo M, Kawashima M (1994) Anal Chem 66:3247–3252
23. Taskaev E, Penev I, Kinova L (1988) J Radioanal Nucl Chem 120:85–88
24. Currie LA (1968) Anal Chem 40:586–593
25. Chattopadhyay A, DeSilva KN (1979) Trans Am Nucl Soc 32:185–186
26. DeSilva KN (1981) PhD Thesis, Dalhousie University, Halifax
27. DeSilva KN, Chatt A (1982) J Trace Microprobe Tech 1:307–337
28. Shi Y, Sullivan EE, Holzbecher JJ, Chatt A (1999) Biol Trace Elem Res 71–72:377–386
29. Zhang W, Chatt A (2009) J Radioanal Nucl Chem 282:139–143
30. Dean JA (1995) Analytical chemistry handbook. McGraw-Hill Inc, New York
31. Lide DR (ed) (1989–99) CRC handbook of chemistry and physics, 79th edn. CRC Press, Boca Raton