



# Speciation of inorganic arsenic in drinking water by wavelength-dispersive X-ray fluorescence spectrometry after *in situ* preconcentration with miniature solid-phase extraction disks



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## ABSTRACT

A rapid and simple method using wavelength-dispersive X-ray fluorescence (WDXRF) spectrometry after *in situ* solid-phase extraction (SPE) was developed for the speciation and evaluation of the concentration of inorganic arsenic (As) in drinking water. The method involves the simultaneous collection of As(III) and As(V) using 13 mm  $\phi$  SPE miniature disks. The removal of  $Pb^{2+}$  from the sample water was first conducted to avoid the overlapping  $PbL\alpha$  and  $AsK\alpha$  spectra on the XRF spectrum. To this end, a 50 mL aqueous sample (pH 5–9) was passed through an iminodiacetate chelating disk. The filtrate was adjusted to pH 2–3 with HCl, and then ammonium pyrrolidine dithiocarbamate solution was added. The solution was passed through a hydrophilic polytetrafluoroethylene filter placed on a Zr and Ca loaded cation-exchange disk at a flow rate of  $12.5 \text{ mL min}^{-1}$  to separate As(III)-pyrrolidine dithiocarbamate complex and As(V). Each SPE disk was affixed to an acrylic plate using adhesive cellophane tape, and then examined by WDXRF spectrometry. The detection limits of As(III) and As(V) were  $0.8$  and  $0.6 \mu\text{g L}^{-1}$ , respectively. The proposed method was successfully applied to screening for As speciation and concentration evaluation in spring water and well water.

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## 1. Introduction

Arsenic (As) is one of the most toxic elements found in water derived from various environmental sources, and the World Health Organization (WHO) has prescribed an As limit of  $10 \mu\text{g L}^{-1}$  for drinking water. Water derived from natural sources mainly contains the inorganic species arsenite (As(III)) and/or arsenate (As(V)), and the distribution of As(III)/As(V) fluctuates widely according to environmental conditions. The toxicity levels of As depends on its chemical form due to differences in the mechanisms of action, where, for example As(III) is more toxic than As(V) [1]. Therefore, it is important to differentiate between As(III) and As(V) when evaluating the toxicity of water samples.

Sensitive analytical methods using chromatographic or extraction separation incorporating various instrumental detection techniques such as high-performance liquid chromatography inductively coupled

plasma mass spectrometry [2–4], solid-phase extraction (SPE) hydride generation atomic absorption spectrometry (HGAAS) [5,6], and liquid-liquid extraction graphite furnace atomic absorption spectrometry (GFAAS) [7,8], have been used for the *in lab* speciation of As in water. However, these methods must incorporate a rapid assay to obtain the correct quantitative values because As(III) and As(V) tend to be unstable in natural water depending on the water chemistry [9]. There is a possibility that As(III) and As(V) are adsorbed on suspended matter, and coprecipitated with Fe and Mn hydroxides. Moreover, oxidation-reduction substances in water may cause a change in the chemical form of As(III) and As(V). Some pretreatment techniques to improve the stability of inorganic As species have been reported [9,10]. However, all these methods require severe thermal management, addition of preservatives, and rapid removal of suspended matter. Naturally, these complications can be avoided by the *in situ* analysis or the separation of As(III) and As(V) in water.

Stripping voltammetry (SV) [11] and colorimetry [12–15] have been developed for the *in situ* speciation of inorganic As in water. These methods are applied so easily and inexpensively that they are available not only to analysts but also to the general public. However,

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SV requires a power supply and As standard solutions for the *in situ* calibration. Colorimetry can be performed the speciation of As on a scale of  $\mu\text{g L}^{-1}$  using densitometer [12] or absorptiometer [13–15] instead of visual inspection. However, this method requires the operation of oxidizing and/or reducing with heating.

SPE is suitable for *in situ* separation and collection of As species in environmental water because it does not require a power supply and numerous acid-base solutions and/or organic solvents in the sample flow step. An *in situ* preconcentration method using a column-type SPE followed by HGAAS has been developed for the determining As(III) and As(V) in water [16]. This method is simple and useful for sensitive analysis, although the method cannot be applied to the screening of a large number of water samples because the elution step is tedious. In contrast, as a pretreatment before assay, membrane disk SPE agents retain their shape during the pretreatment, and are useful for wet analysis [17–19] as well as direct analysis such as X-ray fluorescence (XRF) spectrometry. Several methods combining disk SPE with XRF spectrometry have been reported for the screening of trace elements in water [20–23]. However, the separation analysis of As(III) and As(V) using this method has not yet been reported.

In this article, we describe a method for determining As(III) and As(V) in drinking water using *in situ* membrane disk SPE followed by wavelength-dispersive XRF (WDXRF) spectrometry. This method involves the preconcentration of As(III) and As(V) on a hydrophilic polytetrafluoroethylene (PTFE) filter and a Zr and Ca loaded cation-exchange extraction disk (ZrCa-CED). The remainder of this study addresses (1) the optimum sample pH and flow rate, (2) the preservation of the SPE disk, (3) calibration curves, (4) the removal of  $\text{Pb}^{2+}$  from the sample water, and (5) the effect of coexisting ions. The proposed method was successfully used to determine the levels of As(III) and As(V) in drinking water on a scale of  $\mu\text{g L}^{-1}$ .

## 2. Experimental

### 2.1. Apparatus

A RIX3100 WDXRF spectrometer (Rigaku) with an end-window 4-kW Rh X-ray tube operating at 50 kV and 80 mA under vacuum conditions was employed for the analysis. The irradiation diameter of the primary X-ray beam was 20 mm. The instrumental conditions are listed in Table 1. A ZEE nit 600 s graphite furnace atomic absorption spectrometer (Analytik Jena) was used for determining As and Pb in the filtrates. The measurements of As were conducted under equivalent conditions, as previously reported [18]. The measurement conditions for Pb were as follows: analytical line, 283.3 nm; drying step, 90 °C–110 °C for 72 s; pyrolysis step, 900 °C for 13 s; and atomizing step, 2400 °C for 4 s. A Demi-Ace Model DX-15 demineralizer (Kurita Water Industries) was used to prepare deionized water. An F-52 pH meter (Horiba) was used for the pH control of the test solution. A U-52 multi water tester (Horiba) was used to monitor the

pH, temperature, and dissolved oxygen of the sample water. An FS-320 electric oven (Advantec) was used for drying the SPE disks.

### 2.2. Reagents

A 1000  $\text{mg L}^{-1}$  As(III) stock solution (pH 5) was prepared by dissolving arsenic(III) oxide (chemical grade, 99%; Junsei Chemical) in a 0.1  $\text{mol L}^{-1}$  sodium hydroxide solution, and then adding 1  $\text{mol L}^{-1}$  hydrochloric acid and deionized water. A 1000  $\text{mg L}^{-1}$  As(V) stock solution was prepared by dissolving disodium hydrogen arsenate heptahydrate (guaranteed grade, 99%; Junsei Chemical) in deionized water. A 1000  $\text{mg L}^{-1}$  Pb stock solution was prepared by dissolving lead nitrate (guaranteed grade; Kanto Chemical) in deionized water. A 0.05  $\text{mol L}^{-1}$  Zr solution and a 0.01  $\text{mol L}^{-1}$  Ca solution, utilized for modifying the cation-exchange disks, were prepared by dissolving zirconyl nitrate dihydrate (guaranteed grade; Junsei Chemical) and calcium nitrate tetrahydrate (guaranteed grade; Wako Chemical), respectively, in 0.1  $\text{mol L}^{-1}$  nitric acid. A 0.06  $\text{mol L}^{-1}$  ammonium pyrrolidine dithiocarbamate (APDC, analytical-reagent grade; Wako Chemical) solution was prepared in deionized water. All other reagents used were of extra pure grade.

Iminodiacetate chelating disks and cation-exchange disks (Empore™ Chelating and Cation-SR, respectively; 8.0 nm pore size, 47 mm diameter, and 0.5 mm thickness; 3 M) and hydrophilic PTFE membrane filters (0.5  $\mu\text{m}$  pore size, 47 mm diameter, and 35  $\mu\text{m}$  thickness; Advantec) were used. These disks were cut to 13 mm diameter and then washed with 1  $\text{mol L}^{-1}$  nitric acid before use. The sample and conditioning solutions were passed through the SPE miniature disks by pressurization using a plastic syringe with a filter holder.

### 2.3. Conditioning of the solid-phase extraction disks

Chelating disks were swollen with methanol and conditioned successively with 2.5 mL of deionized water, 5 mL of a 0.1  $\text{mol L}^{-1}$  ammonium acetate solution, and 2.5 mL of deionized water. Cation-exchange disks were swollen with methanol, and then ZrCa-CEDs were prepared by successively passing 2.5 mL of deionized water, 2.5 mL of a 0.05  $\text{mol L}^{-1}$  Zr solution, 2.5 mL of deionized water, 2.5 mL of a 0.01  $\text{mol L}^{-1}$  Ca solution, and 2.5 mL of deionized water through the cation-exchange disk.

### 2.4. *In situ* preconcentration procedure

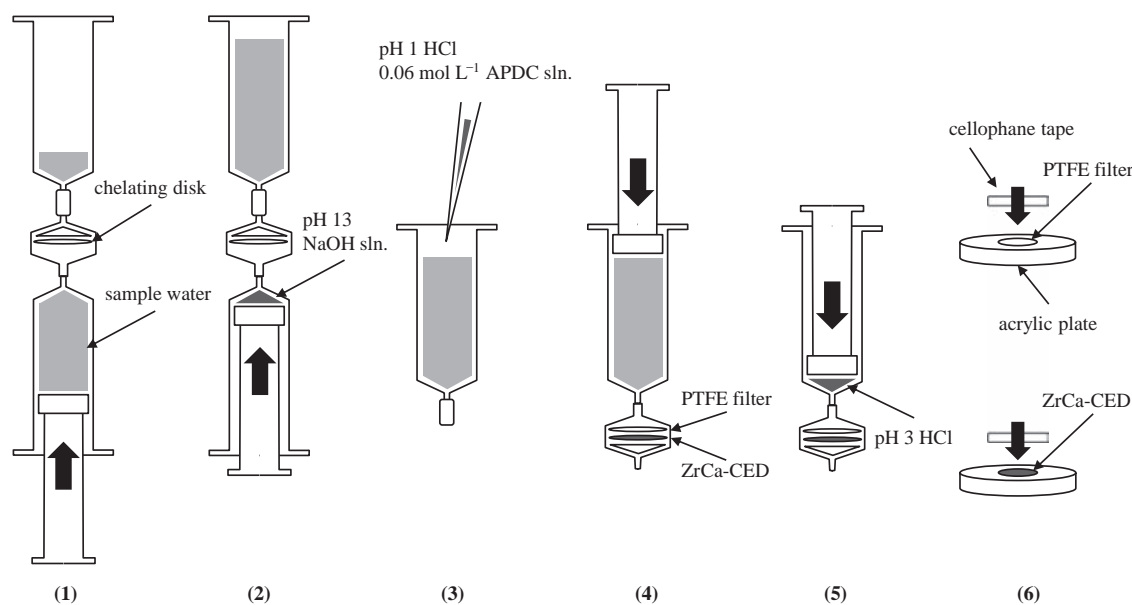
The *in situ* SPE procedure for the preconcentration and separation of As(III) and As(V) is illustrated in Fig. 1. A 50 mL water sample of pH 5–9 adjusted as needed with hydrochloric acid or sodium hydroxide solution was passed through a chelating disk at a flow rate of 20  $\text{mL min}^{-1}$  for removing  $\text{Pb}^{2+}$  and suspended matter. As(III) and As(V), which were partially adsorbed on the disk, were eluted with 0.5 mL of a pH 13 sodium hydroxide solution, and the eluent was added to the filtrate. The filtrate was adjusted to pH 2–3 with a pH 1 hydrochloric acid solution. One milliliter of 0.06  $\text{mol L}^{-1}$  APDC solution was added and stirred for 2 min to form the As(III)–PDC complex. This solution was passed through a PTFE filter placed on a ZrCa-CED at a flow rate of 12.5  $\text{mL min}^{-1}$  to separate As(III) and As(V). As(III) was collected by the upper PTFE filter, and As(V) by the lower ZrCa-CED. The disks were washed with 0.5 mL of a pH 3 hydrochloric acid solution, and then separated. Each SPE disk was affixed to an acrylic plate (47 mm diameter and 10 mm thickness) with adhesive cellophane tape (15 mm width and 50  $\mu\text{m}$  thickness).

### 2.5. Determination procedure

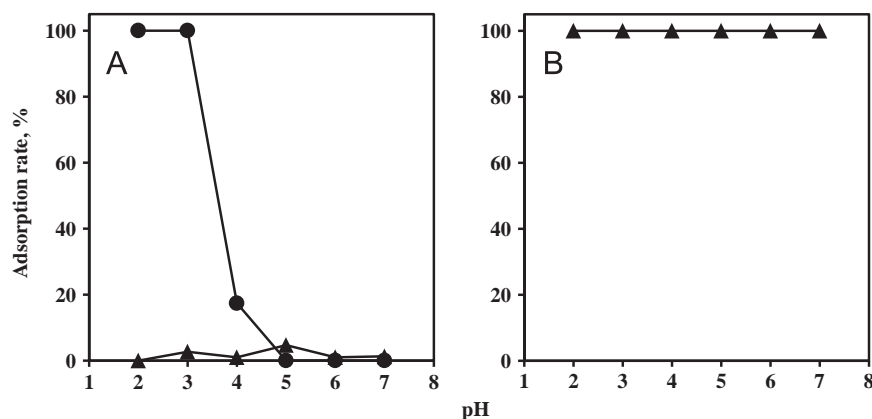
SPE disks on acrylic plates were dried at 100 °C for 15 min in an electric oven. The specimen was fitted to a sample holder (50 mm

**Table 1**  
Instrumental conditions of WDXRF spectrometer for As determination.

Apparatus	Rigaku RIX3100
Analytical line	K $\alpha$
Slit	Coarse
Crystal	LiF(200)
Detector	Scintillation counter
Beam filter	Cu
Peak angle, $2\theta/^\circ$	33.98
Counting time/s	100
Background angle, $2\theta/^\circ$	33.35, 34.85
Counting time/s	100



**Fig. 1.** Proposed process of *in situ* solid-phase extraction for separation and preconcentration of As(III) and As(V) in water. (1) Removal of  $\text{Pb}^{2+}$  and suspended matter, (2) elution of analytes, (3) pH adjustment and complex formation, (4) separate collection of As(III) and As(V) on PTFE filter and ZrCa-CED, respectively, (5) elution of interfering substances, and (6) fixation of the disks on acrylic plates and covering by cellophane tape.



**Fig. 2.** Adsorption rates of As(III)-PDC (●) and As(V) (▲) at different pH values using (A) a PTFE filter and (B) a ZrCa-CED, respectively.

diameter), and then analyzed using a WDXRF spectrometer. The concentrations of As(III) and As(V) were calculated using the calibration curves previously constructed using a set of standard SPE disks.

### 3. Results and discussion

#### 3.1. Effect of pH

Sample pH is an important factor in adsorption studies; therefore, the pH dependence of adsorption rates of As(III) and As(V) collected on a PTFE filter and a ZrCa-CED was investigated. Twenty-five milliliter of water samples containing 0.3 mmol APDC and 5  $\mu\text{g}$  of As(III) or As(V) were adjusted to pH 2–7 with hydrochloric acid or sodium hydroxide solution. The adsorption rate of As on the SPE miniature disk was calculated from the difference between the As concentrations in the initial solution and the filtrate, which was measured by graphite furnace atomic absorption spectrometry. The pH dependencies of the adsorption rates for As(III) and As(V) are shown in Fig. 2. As(III) was adsorbed quantitatively at pH 2–3, but As(V) was not adsorbed by the PTFE

filter, indicating that PTFE filters can be used to separate As(III) from As(V) at pH 2–3. The pH dependence of the adsorption rate of As(III) collected on a PTFE filter is the result of the As(III)-PDC complexation. A non-polar interaction mechanism is considered to be responsible for the adsorption of As(III)-PDC by a PTFE filter [24]. The ZrCa-CED adsorbed As(V) completely at pH 2–7. The adsorption is a complex-forming reaction between As(V) and the Zr of the ZrCa-CED. In addition, Ca in the ZrCa-CED inhibits the elution of As(V) [18]. Therefore, a sample solution of pH 2–3 was adopted for the separation of As(III) and As(V) in water.

#### 3.2. Effect of the sample flow rate

It is expected that the likelihood of As(III) and As(V) passing through the solid phase without adsorption would increase with sample solution flow rate. Therefore, the influence of the flow rate on the adsorption rates of the 5  $\mu\text{g}$  analytes was investigated. As shown in Fig. 3, All of As(III)-PDC was adsorbed at flow rates of 5–20  $\text{mL min}^{-1}$ , but the adsorption rate of As(V) was insufficient for a flow rate above 12.5  $\text{mL min}^{-1}$ . Therefore, a sample flow rate of 12.5  $\text{mL min}^{-1}$  or less is required to collect the analytes using the two SPE miniature disks.

### 3.3. Preservation

The preservation of the SPE miniature disks was investigated after the sample was kept for a month in ambient atmosphere. The fluorescent X-ray intensities of 2  $\mu\text{g}$  of As(III) collected on a PTFE filter and 2  $\mu\text{g}$  of As(V) collected on a ZrCa-CED were measured after storage for 0, 1, 2, 4, 8, 16, and 32 days. Although the X-ray intensities of each measurement were found to vary slightly, the relative standard deviations (0.67%–0.68%) of X-ray intensities were below the variation coefficient (1.4%) of X-ray counting. Consequently, we concluded that the SPE miniature disks demonstrated sufficient preservative ability over a one month period. The proposed method is able to obtain accurate measurements of the concentration of As(III) and As(V) in water, even though considerable time may elapse between the preconcentration step and analysis by XRF spectrometry.

### 3.4. Calibration curves

Calibration curves of As(III) and As(V) for WDXRF were constructed from a set of standard SPE miniature disks. Fig. 4 shows XRF spectra of 0, 0.5, 1, 2, 5  $\mu\text{g}$  of As preconcentrated on PTFE filter and ZrCa-CED. HfL $\gamma$ 1 fluorescent line ( $2\theta_{\text{LiF}(200)}=34.04^\circ$ ) was found on the XRF spectra of blank ZrCa-CED, because zirconyl nitrate dihydrate for modifying the cation-exchange disks contained Hf as an impurity. However, the amounts of Hf in every ZrCa-CEDs are same, so the AsK $\alpha$  intensity of As(V) collected on a ZrCa-CED can be measured without correction. The calibration curves of As(III) and As(V) showed good linearity in the range of 0.5–5  $\mu\text{g}$ . Linear equations for the calibration curves were

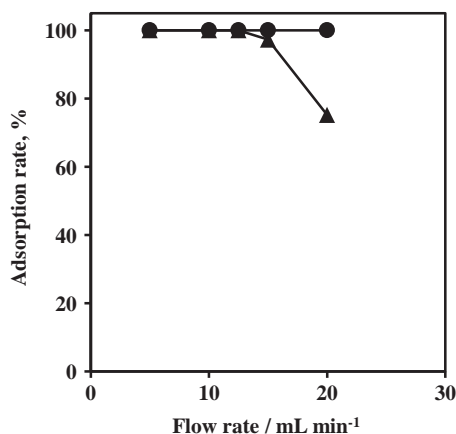


Fig. 3. Adsorption rates of As(III)-PDC (●) and As(V) (▲) at different solution flow rates using a PTFE filter and a ZrCa-CED, respectively.

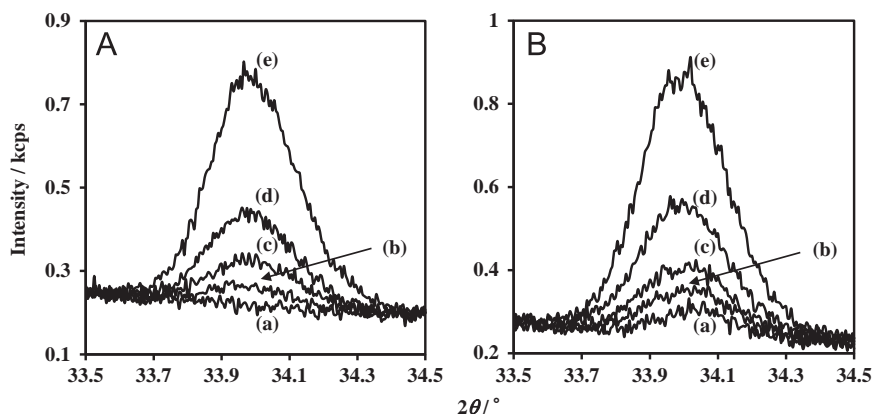


Fig. 4. XRF spectra of AsK $\alpha$  of (A) As(III)-PDC collected on a PTFE filter, and (B) As(V) collected on a ZrCa-CED. (a): blank, (b): 0.5  $\mu\text{g}$  of As, (c): 1  $\mu\text{g}$  of As, (d): 2  $\mu\text{g}$  of As, (e): 5  $\mu\text{g}$  of As.

determined by fitting to be  $I=0.118 M-0.0175$  ( $r=0.9997$ ) for As(III), and  $I=0.117 M+0.0468$  ( $r=0.9998$ ) for As(V), where  $I$  is the fluorescent X-ray intensity (kcps),  $M$  is the absolute amount ( $\mu\text{g}$ ), and  $r$  is the correlation coefficient of the liner fit. The detection limits, defined as three times the standard deviation, as evaluated by its relationship to the slope of the calibration curve, were 0.04  $\mu\text{g}$  for As(III) and 0.03  $\mu\text{g}$  for As(V). Therefore, for a 50 mL water sample, the detection limits were 0.8  $\mu\text{g L}^{-1}$  for As(III) and 0.6  $\mu\text{g L}^{-1}$  for As(V). These values are lower than the maximum value of As (10  $\mu\text{g L}^{-1}$ ) established by the WHO for drinking water. The detection limit of proposed method was found to be comparable with other values using SPE followed by AAS methods: SPE-flow injection HGAAS, 0.5  $\mu\text{g L}^{-1}$  [6]; *in situ* SPE/HGAAS, 0.3  $\mu\text{g L}^{-1}$  [16]; SPE/GFAAS, 0.1  $\mu\text{g L}^{-1}$  [26].

### 3.5. Removal of Pb from sample water

Mutual interference between the AsK $\alpha$  and PbL $\alpha$  fluorescent lines occurs because of their close proximity to each other (*i.e.*,  $2\theta_{\text{LiF}(200)}=33.98^\circ$  for AsK $\alpha$  and  $2\theta_{\text{LiF}(200)}=33.92^\circ$  for PbL $\alpha$ ). As such, if As(III) and As(V) coexist with Pb $^{2+}$  in sample water, this overlap may cause serious analytical error because both APDC [24] and the cation-exchange disk used in the present study react with Pb $^{2+}$ . This problem could be solved by measuring the AsK $\beta$  line intensity for determining As. However, the intensity of AsK $\beta$  line is minuscule relative to that of the AsK $\alpha$  line, which would prohibit the determination of  $\mu\text{g L}^{-1}$  levels of As in water. It is also possible to evaluate the PbL $\alpha$  line intensity relative to the AsK $\alpha$  line intensity using PbL $\beta$  line intensity, and to apply this as a correction of the AsK $\alpha$  line intensity [23,25]. However, water samples typically contain selenite as well, which reacts with both APDC [26,27] and Zr [28], and the SeK $\beta$  line overlaps with the PbL $\beta$  line. Consequently, the intensity of the PbL $\beta$  line must be similarly corrected with respect to the intensity of the SeK $\alpha$  line. Therefore, XRF measurements of three angles and the multilevel correction illustrated in Fig. 5 would be necessary to obtain a quantitative value of As by this method. For a much easier determination of As using XRF spectrometry, it was decided to first remove Pb $^{2+}$  from the water samples using a chelating disk. As shown in Fig. 6, the AsK $\alpha$  intensity (b) of the SPE disk spiked with equivalent amount of As and Pb without pretreatment using a chelating disk was about 1.4 times that of the normal AsK $\alpha$  line intensity (a) with no Pb. However, when Pb $^{2+}$  in the sample water was removed using a chelating disk before the collection of As, the AsK $\alpha$  line intensity (c) of the SPE disk was equivalent to that of the normal AsK $\alpha$  line intensity (a). In most cases, As(III) and As(V) were not adsorbed by the chelating disk because these As species are anions and/or neutral forms in the sample solution. However, As(III) and As

(V) were found to be partially adsorbed on the chelating disk when  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  coexisted in the sample water, indicating that the As species reacts with Al [29] and Fe [30] collected by the chelating disk. This problem was resolved by the elution of As using 0.5 mL of a pH 13 sodium hydroxide solution. By so doing, As(III) and As(V) were completely eluted and then recovered by the mixture of the eluate and filtrate.

The pH dependences of the adsorption rates for 5  $\mu\text{g}$  of As(III), As(V), and  $\text{Pb}^{2+}$  collected on a chelating disk concluding the elution using the sodium hydroxide solution was investigated. As shown in Fig. 7,  $\text{Pb}^{2+}$  was not eluted at all using the 0.5 mL of a pH 13 sodium hydroxide solution, and was removed completely for a sample flow rate of 20  $\text{mL min}^{-1}$  by the chelating disk without the loss of As at pH 5–9. This pH range nearly covers the entire pH range of drinking water. Moreover, the pore size of the SPE disk is very small, so the chelating disk was useful for the simultaneous removal of  $\text{Pb}^{2+}$  and suspended matter in the water samples.

### 3.6. Effect of coexisting ions

Coexisting ions in a water sample may decrease the recoveries of As(III) and As(V) in the preconditioning step. A spike test was conducted for 0.5  $\mu\text{g}$  of As(III) and As(V) in 50 mL of artificial freshwater containing 5  $\text{mg L}^{-1}$   $\text{Na}^+$ , 3  $\text{mg L}^{-1}$   $\text{K}^+$ , 5  $\text{mg L}^{-1}$   $\text{Mg}^{2+}$ , 50  $\text{mg L}^{-1}$   $\text{Ca}^{2+}$ , 10  $\text{mg L}^{-1}$   $\text{Cl}^-$ , and 20  $\text{mg L}^{-1}$   $\text{SO}_4^{2-}$ . The recoveries of As(III) and As

(V) were 97% and 98%, respectively, in this solution. As such, the concentrations of typical major ions found in freshwater did not interfere with the recoveries of the analytes. The effects of minor ions found in fresh water on the recoveries of As(III) and As(V) were also tested. When 0.5  $\mu\text{g}$  of As(III) and As(V) were added to 50 mL of test water coexisting with 100  $\mu\text{g L}^{-1}$   $\text{Al}^{3+}$ , 10  $\mu\text{g L}^{-1}$   $\text{V}^{5+}$  ( $\text{H}_2\text{VO}_4^-$ ), 10  $\mu\text{g L}^{-1}$   $\text{Cr}^{3+}$  ( $\text{H}_2\text{CrO}_2^+$ ), 10  $\mu\text{g L}^{-1}$   $\text{Mn}^{2+}$ , 100  $\mu\text{g L}^{-1}$   $\text{Fe}^{3+}$ , 10  $\mu\text{g L}^{-1}$   $\text{Ni}^{2+}$ , 10  $\mu\text{g L}^{-1}$   $\text{Cu}^{2+}$ , 100  $\mu\text{g L}^{-1}$   $\text{Zn}^{2+}$ , 300  $\mu\text{g L}^{-1}$   $\text{Sr}^{2+}$ , and 10  $\mu\text{g L}^{-1}$   $\text{Pb}^{2+}$ , the recoveries of As(III) and As(V) were 108% and 107%, respectively.  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  retard the complexation of As(III)–PDC [31], and  $\text{Fe}^{3+}$  affects the adsorption of As(V) on Zr loaded resin [32], as reported previously. However, minimal interferences were observed in the present study because the interfering cations in the sample were removed by the chelating disk. Next, the effect of organic arsenics (10  $\mu\text{g L}^{-1}$  diphenylarsenic acid and phenylarsonic acid) on the recoveries of arsenic compounds was investigated. As(III) was recovered quantitatively (94%–108%), but the recovery of As(V) were 120%–127%. Organic arsenics and Pb in the water sample will be removed simultaneously by a chelating disk based on activated carbon.

### 3.7. Spike tests and applications

To evaluate the quantitative performance of the proposed method, spike tests were performed for As(III) and As(V) in mineral drinking water sampled at Kanagawa, Japan. The results of the spike tests are

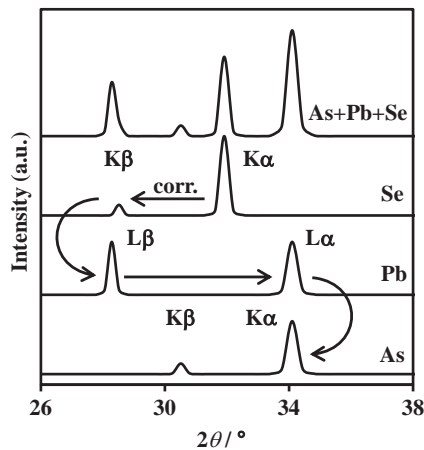


Fig. 5. Mutual interferences of As, Pb and Se XRF spectra, and the multilevel correction required to obtain a quantitative value for the AsK $\alpha$  line intensity.

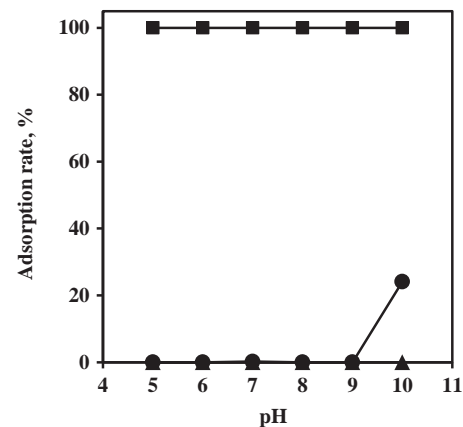


Fig. 7. Adsorption rates of As(III) (●), As(V) (▲), and  $\text{Pb}^{2+}$  (■) at different pH values using a chelating disk.

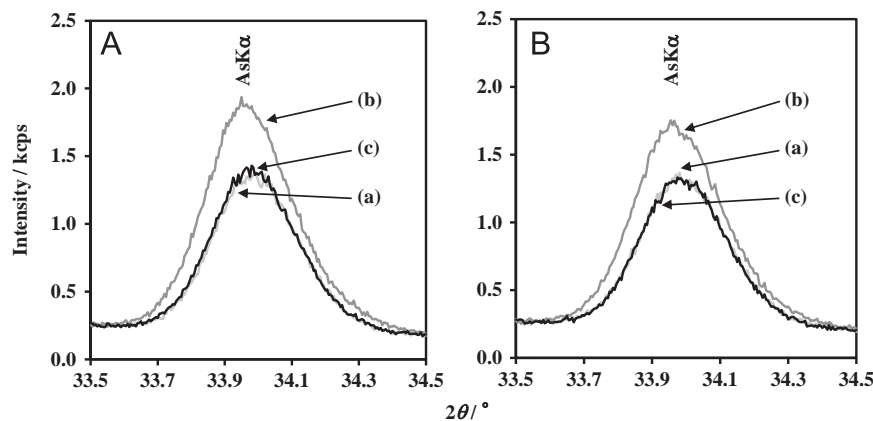


Fig. 6. XRF spectra of (A) As(III)–PDC collected on a PTFE filter, and (B) As(V) collected on a ZrCa-CED under the following conditions.

- (a): 10  $\mu\text{g}$  of As spiked without pretreatment using a chelating disk.
- (b): 10  $\mu\text{g}$  of As and 10  $\mu\text{g}$  of  $\text{Pb}^{2+}$  spiked without pretreatment using a chelating disk.
- (c): 10  $\mu\text{g}$  of As and 10  $\mu\text{g}$  of  $\text{Pb}^{2+}$  spiked with pretreatment using a chelating disk.

**Table 2**  
Spike tests for As(III) and As(V) added to mineral drinking water.

Sample	Added/ $\mu\text{g L}^{-1}$		Found/ $\mu\text{g L}^{-1}$		Recovery, %	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
Mineral drinking water	0	0	N.D. <sup>a</sup>	N.D. <sup>a</sup>	–	–
	10.0	0	10.0 (5.3) <sup>b</sup>	N.D. <sup>a</sup>	100	–
	0	10.0	N.D. <sup>a</sup>	9.8 (3.8) <sup>b</sup>	–	98
	10.0	10.0	10.4 (3.9) <sup>b</sup>	10.4 (6.3) <sup>b</sup>	104	104

<sup>a</sup> Not detected.

<sup>b</sup> Relative standard deviation, % ( $n=4$ ).

**Table 3**  
Analytical results of As(III) and As(V) in drinking water sampled at northern Chiba.

Sample	Concentration/ $\mu\text{g L}^{-1}$		pH	Temp./ $^{\circ}\text{C}$	DO <sup>a</sup> / $\text{mg L}^{-1}$
	As(III)	As(V)			
Spring water 1	1.2	N.D. <sup>b</sup>	6.22	18.0	4.35
Spring water 2	N.D. <sup>b</sup>	N.D. <sup>b</sup>	6.63	17.4	5.05
Spring water 3	N.D. <sup>b</sup>	N.D. <sup>b</sup>	7.26	18.9	5.96
Spring water 4	N.D. <sup>b</sup>	N.D. <sup>b</sup>	7.57	19.6	4.35
Well water 1	1.5	N.D. <sup>b</sup>	8.53	20.4	0.06
Spring water 5	N.D. <sup>b</sup>	N.D. <sup>b</sup>	9.23	16.5	0.01
Well water 2	0.9	N.D. <sup>b</sup>	8.90	15.8	0.01
Spring water 6	N.D. <sup>b</sup>	N.D. <sup>b</sup>	8.66	15.7	0.02
Spring water 7	1.1	N.D. <sup>b</sup>	8.09	15.9	5.47
Spring water 8	N.D. <sup>b</sup>	N.D. <sup>b</sup>	8.32	17.1	4.04
Spring water 9	0.9	N.D. <sup>b</sup>	7.82	15.5	5.01
Spring water 10	N.D. <sup>b</sup>	N.D. <sup>b</sup>	7.52	15.1	4.63
Well water 3	1.0	7.5	8.49	14.3	1.39
Spring water 11	1.4	N.D. <sup>b</sup>	8.02	15.8	4.13

<sup>a</sup> Dissolved oxygen.

<sup>b</sup> Not detected.

listed in Table 2. Good recoveries of 98%–104% were obtained, indicating that the proposed method was useful for determining  $\mu\text{g L}^{-1}$  levels of As in drinking water.

The proposed screening method was applied to determine As(III) and As(V) in spring water and well water samples collected at the area of 613 km<sup>2</sup> in a northern Chiba, Japan. Fourteen SPE samples were collected at 19 sites (the water samples were not collected at 5 sites due to the drought), and immediately treated using the proposed *in situ* preconcentration method. The time required for travel, sampling, and pretreatment was 15 h, and the analyses required 2.5 h. The analytical results are presented in Table 3. The highest concentration of As(III) found was 1.5  $\mu\text{g L}^{-1}$  for the sample denoted as well water 1, and that of As(V) was 7.5  $\mu\text{g L}^{-1}$  for well water 3. The total As concentrations (As(III)+As(V)) of all sites fell below the drinking water standard set by the WHO (10  $\mu\text{g L}^{-1}$ ). The dominant species was As(III) for 6 of the sites considered, whereas As(V) was dominant for one site. The concentrations of arsenic species in ground water are controlled by many factors including the source of the arsenic and water quality. In regards to pH, temperature and/or dissolved oxygen, no relationships were observed at any of the sites considered.

## 4. Conclusions

A rapid and simple method combining *in situ* disk SPE with WDXRF spectrometry was proposed for determining inorganic As in drinking water. A hydrophilic PTFE filter, APDC, and ZrCa-CED were used for separating As(III) and As(V). As(III) and As(V) could be determined directly without an elution step. To avoid the overlapping PbL $\alpha$  and AsK $\alpha$  fluorescence line in WDXRF spectrometry, Pb was removed using a chelating disk before the separation of As(III) and As(V). Spike tests comprised of 10  $\mu\text{g L}^{-1}$  of As(III) and As(V) in mineral drinking water demonstrated that quantitative recoveries were achieved (98%–104%). The proposed method was successfully applied to screening for the speciation and evaluation of the concentration of As in actual drinking water samples.

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