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Simultaneous multi-element analysis of total As, Se and Sb on titanium dioxide by slurry sampling—graphite furnace atomic absorption spectrometry

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Abstract

A simple and rapid method for simultaneous determination of As, Se and Sb was studied by graphite furnace atomic absorption spectrometry (GFAAS). Titanium dioxide adsorbing As, Se and Sb was separated from sample solution (100 ml) with a membrane filtration (0.45 μm), and then prepared to be slurry (5.0 ml) by adding ultrapure water. The behavior and influence of titanium dioxide on determination of As, Se and Sb were investigated in this experiment. The optimal conditions of a furnace for these elements were chosen as follows: pyrolysis temperature was 150 °C, and atomization temperature was 2300 °C. The optimal conditions of adsorption for As, Se and Sb on titanium dioxide were listed: pH 2.0 in sample solution; 10 min of stirring time; and 20.0 mg titanium dioxide. The difference of the chemical valence of each element had no effect on the recovery of each element at the same optimal conditions. Limits of detection (3σ) for As, Se and Sb were found to be 0.21 $\mu g\,l^{-1}$, 0.15 $\mu g\,l^{-1}$ and 0.15 $\mu g\,l^{-1}$, respectively, with enrichment rate of 20, when 20 μl of slurry was injected into a Zr-coating tube. The proposed method was applied to tap water and river water.

Keywords: Multi-element determination; GFAAS; Titanium dioxide; Slurry sample introduction; As; Se; Sb

1. Introduction

Determination for contents of As, Se and Sb is important to hold health of a person and protect environment from contamination because of their toxicity, especially of inorganic ions [1]. But direct determination for these elements is very difficult due to their volatilization and low content in natural water. Since Holak [2] used Zinc metal and hydrochloric acid for determination of As by AAS, the pretreated technique has been widely applied and developed for simultaneous determination of volatile elements [1,3–5]. With introduction of the new detect apparatus, simultaneous determination of As, Se and Sb by ICP-MS/AES [6,7] were much reported, furthermore, the generation of volatile hydride coupled with ICP-MS/AES [8–10] has become one of the most sensitive analytical methods. Hydride generation, as a pretreated method, is suitable for determination of As, Se and Sb, but it cannot be directly utilized for graphite furnace atomic absorption spectrometry (GFAAS). Therefore, it is important to have a rapid and sensitive method for determination of these elements with a GFAAS applied widely in analytical field.

Direct determination cannot be performed for some trace and ultra trace elements because of limited sensitivity of instrument used in particular measurement. Thereby, the technique of enrichment to solid phase (sorbent) from liquid phase (sample solution) is used as a pretreated method. Inorganic metal oxides have been applied as solid sorbent, such as aluminum oxide [11], cobalt oxide [12] and titanium dioxide, etc. With its high surface area titanium dioxide is chosen in pretreatment procedures [13–18]. Generally, titanium dioxide as same as the other inorganic metal oxides was used to adsorb metal ions as a sorbent in a column. The elution is necessary to determine these ions. However, the elution is time-consuming and sometimes results in loss of analyte. Slurry sampling is an effective procedure to solve the above problem, and has been widely utilized as a sampling method [19–26]. Isozaki et al. [24] had established a method for determination of copper at ppb level by introducing resin-suspension into a graphite furnace in 1981. Nukatsuka et al. [25] have also reported a similar method for molybdenum with a cel-

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Table 1
Furnace program for determination of As, Se and Sb

Steps	Temperature (°C)	Time (s)		Argon gas (ml min^{-1})
		Ramp	Hold	
1. Dry	130	1	30	250
2. Pyrolysis	150	15	30	250
3. Atomization	2300	0	5	0
4. Clean up	2450	1	3	250

lulose nitrate resin-suspension by GFAAS. Recently, Minami et al. [26] have studied direct determination of aluminum, calcium, iron in silicon carbide and silicon nitride powders by slurry sampling-GFAAS. In addition, it has been also reported that the metallic ions adsorbed on nanometre titanium dioxide are directly detected by ICP-AES/MS and GFAAS [22,23]. There were only a few reports on simultaneous determination of As, Se and Sb by using slurry sampling-GFAAS with titanium dioxide.

In this work, titanium dioxide was used to concentrate the trace elements and then contents of As, Se and Sb adsorbed on titanium dioxide was directly detected by slurry sampling-GFAAS. Zirconium nitrate was employed for coating the graphite tube. The objective of this work was to establish optimal conditions of simultaneous determination of As, Se and Sb.

2. Experimental

2.1. Instrumentations

A Perkin-Elmer, model SIMAA 6000, simultaneous multi-element graphite atomic absorption spectrometer with a transversely heated graphite atomizer (THGA), longitudinal Zeeman-effect background correction and an AS-72 autosampler was used for this study. Standard THGA graphite tubes (part no. B0504033) and Perkin-Elmer ‘EDL system 2’ electrodeless discharge lamps (As, 193.7 nm, 380 mA; Se, 196.0 nm, 290 mA; Sb, 223.1 nm, 380 mA) were applied. The furnace program is shown in Table 1.

Ultrasonic (Bransonic 12, branson) was employed to make the homogeneity of slurry. A pH meter (HM-26S) manufactured by DKK-TOA Corporation was used for pH measurement. Electric Balance (300 × 0.0001 g, Sartorius model BP301S-EA BR-1010) and magnetic stirrer (Advantec SR 506) were used. In addition, all glasswares, pipette tips and storage bottles were soaked in dilute nitric acid for 24 h and finally rinsed for three times prior to using with ultrapure water.

2.2. Reagents and materials

All the reagents were of analytical grade. High purity water (Milli-Q Water System, Millipore, Japan) was employed. The standard mixed solution of As(III) (5.0 of pH with hydrochloric acid), Se(IV) and Sb(III) was prepared on a daily basis by diluting appropriate aliquots of 1000 mg l^{-1} stock metal solutions. The standard solutions of As(V), Se(VI) and Sb(V) were prepared by diluting as same as the above. The standard solutions of Sb(III) with 20% hydrochloric acid and Sb(V) were purchased from SPEX CERTIPREP LTD in Japan. The nitric acid (60%) for poisonous metal analysis, sulfuric acid and phosphoric acid (98.0%) were from KANTO CHEMICAL CO. ING. in Japan. Titanium(IV) dioxide (anatase form, 99%, −0.5 μm) was applied as a sorbent. Zirconium nitrate ($ZrO(NO_3)_2{\cdot}2H_2O$) was employed to treat the graphite tube. Water samples were filtrated with a 0.45 μm pore size nitrocellulose acetate membrane filter (Advantec, Tokyo), and kept at pH 2.0 with nitric acid. The other chemicals and reagents used in this work were purchased from WAKO in Japan.

2.3. Analytical procedure for determination of As, Se and Sb

Sample solution (100 ml) with less than 5.0 μg l^{-1} of As, Se and Sb was placed in a beaker; pH was adjusted to 2.0 with 2.0 M nitric acid. The sample solution added 20.0 mg of titanium dioxide was stirred by a magnetic stirrer about 10 min, and immerged in a sonication bath about 10 min. After the solution was filtrated by a 0.45 μm membrane filter, the remained solid phase was transferred to a 15 ml centrifugal tube, and then 5.0 ml ultrapure water was added to form 5.0 ml of the slurry sample. The enrichment ratio is about 20. Then, 20 μl of the slurry was injected into a graphite tube by an automatic sampler for each cycle.

2.4. Graphite tube coating with zirconium nitrate [17,22]

Zirconium nitrate was chosen to coat a graphite tube for determination of As, Se and Sb. After the conditioning of a new graphite tube, it was soaked in 4% zirconium nitrate for 20 min under a reduce pressure. All of the graphite tube was covered homogeneously by zirconium nitrate and dried in oven at 100 °C for 1.5 h. And then the tube was subjected to a temperature program in order to reduce the salt to its metal and produce a reactive surface layer. The graphite tube was gently dried at 110 °C for 60 s and subsequently at 250 °C for 60 s. A second drying step at 750 °C for 60 s was also used. Following this, a reduction step at 2200 °C was applied for 5 s. This procedure was repeated for three times. This coating only needs to be applied once during lifetime of the tube.

3. Results and discussion

3.1. Stability of titanium dioxide slurry

Stability for slurry is very important during determination of elements because instable slurry can only obtain poor reproducibility of the result. Stability of titanium dioxide slurry is affected by the pH value of the media [17]. In this work, the slurry standard solutions (Section 3.4) were very stable when $1 \leqq \text{pH} \leqq 7$ and no phase separation could be observed during determination of As, Se and Sb. But the slurry samples prepared according to the recommended analytical procedure were instable and the phase separation occurred at the same pH value as the slurry standard solution. The reason might be change of the surface character of titanium dioxide during preparation according to the recommended analytical procedure. In order to keep the stability, the slurry was agitated before the injection. In this case, R.S.D.% of the slurry was less than 5% ($n = 5$).

3.2. *Effect of zirconium nitrate on the tube*

By the use of the coating tube, reproducibility of results and life of the tube were obviously improved. Using the treatment of a graphite tube under reduced pressure, a solid layer of zirconium carbide (ZrC) is founded to form on a graphite surface [22]. Zirconium carbide with high melting point exceeding the 3000 °C is very stable under heating in an inert atmosphere. Therefore, life of the coating tube is longer than that of the standard graphite tube. In addition, titanium dioxide reacts easily with carbon to form titanium carbide when temperature exceeds 900 °C [17], which is main reason that the surface of graphite tube is easily destroyed when the slurry is used.

3.3. *Optimization of atomization condition*

In this work, the conditions of atomization for As, Se and Sb were investigated by the use of standard solutions and titanium dioxide slurry with a temperature program presented in Table 1. The pyrolysis temperature was varied from 150 °C to 1300 °C. The optimum pyrolysis temperature of 150 °C was further used to optimize the atomization temperature in the region 1200–2500 °C. The result obtained in Fig. 1 shows that atomization mechanism of As, Se and Sb in the titanium dioxide slurry was basically same as that in the standard solution. Therefore, the same furnace conditions can be applied for both sample solutions.

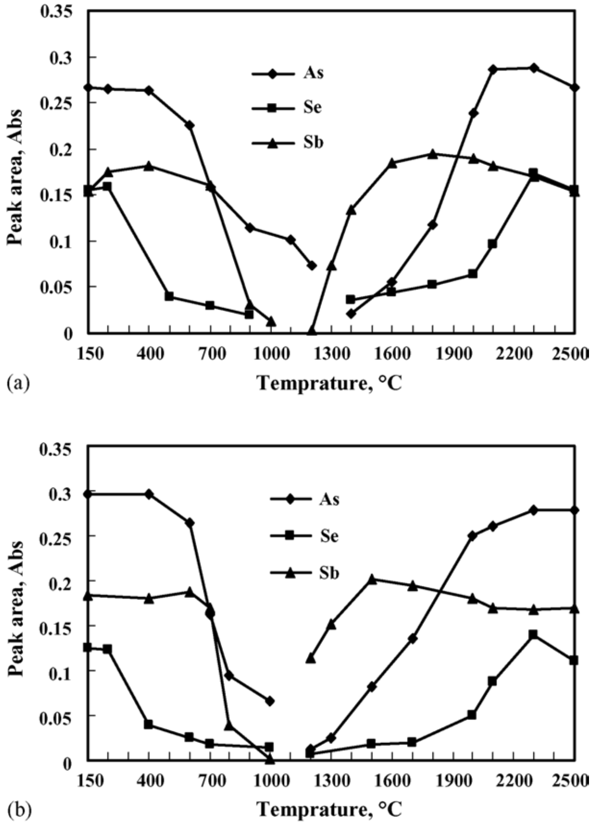

Fig. 1. Pyrolysis and atomization curves for As, Se and Sb in a Zr-coating tube: atomization temperature, 2500 °C; pyrolysis temperature, 150 °C; injected volume, 20 μl; (a) standard solution (100.0 $\mu g\,l^{-1}$); (b) titanium dioxide slurry (the slurry was prepared with 5.0 $\mu g\,l^{-1}$ solution according to the recommended analytical procedure).

3.4. *Effect of titanium dioxide on the sensitivity*

In order to investigate the effect of titanium dioxide, the two same 100.0 $\mu g\,l^{-1}$ solutions (As(III), Se(IV) and Sb(III)) were prepared: one was the standard solution; the other was the slurry standard solution (20.0 mg titanium dioxide per 5.0 ml standard solution). 20.0 μl of the above solutions was injected for each cycle. As seen in Fig. 2, increasing of absorbance for As, Se and Sb in the slurry standard solution was found in the tube. The profiles of atomization for these elements in Fig. 2 were similar for the both solutions, whereas the absorbance for As, Se and Sb in the slurry became larger than that in standard solution; moreover the increasing range of the absorbance for As was lower than that for Se and Sb. The increasing of the sensitivity of As, Se and Sb was also found by comparing the two-calibration curves. The sensitivity of these elements in the standard solution (As, $y = 0.002766x + 0.01054$, $R^2 = 0.9990$; Se, $y = 0.001261x - 0.00141$, $R^2 = 0.9993$; Sb, $y = 0.001517x + 0.005448$, $R^2 = 0.9989$) was lower than that in the slurry standard solution (As, $y = 0.002876x + 0.01252$, $R^2 = 0.9992$; Se, $y = 0.001549x - 0.002057$, $R^2 = 0.9987$; Sb, $y = 0.002005x + 0.00909$, $R^2 = 0.9995$).

The usage of titanium dioxide as a chemical modifier has been reported [17]. Except for as a chemical modifier, a possible increase in the sensitivity is due to the adsorption on titanium dioxide as a matrix. It is known that the chlorides of As(III), Se(IV) and Sb(III) are evaporated at low temperature, which is main reason for loss of these elements. There may be the following species of these elements in acidic solution: $AsO_3^{3-}/AsCl_3$, $SeO_3^{2-}/SeOCl_2$, $SbO_3^{3-}/SbCl_3$, etc., and there are the chemical equilibriums among the different species for the same element. As seen in Fig. 2, titanium dioxide is not related to atomization mechanism of these elements in the slurry standard solution, which can also be proved by comparing the pyrolysis curves of (a) and (b) in Fig. 1. Therefore, the increasing of the sensitivity may be due to transform of species of these elements. Because titanium dioxide can adsorb the acid radical in the acidic solution (discussion on adsorption seen in effect of the pH), the equilibriums for the species of these elements are destroyed and transformed to produce acid radical. The loss of chlorides of these elements is decreased because chlorine is mainly evaporated as hydrochloride, which makes sensitivity be improved. In addition, the different increasing of the sensitivity for each element is caused by the difference of the existed acid radical in acidic solution. The main species for As are acid radical in acid solution, thereby, the effect of titanium dioxide on sensitivity is not obvious, whereas the influence is visible for Se and Sb in acid solution.

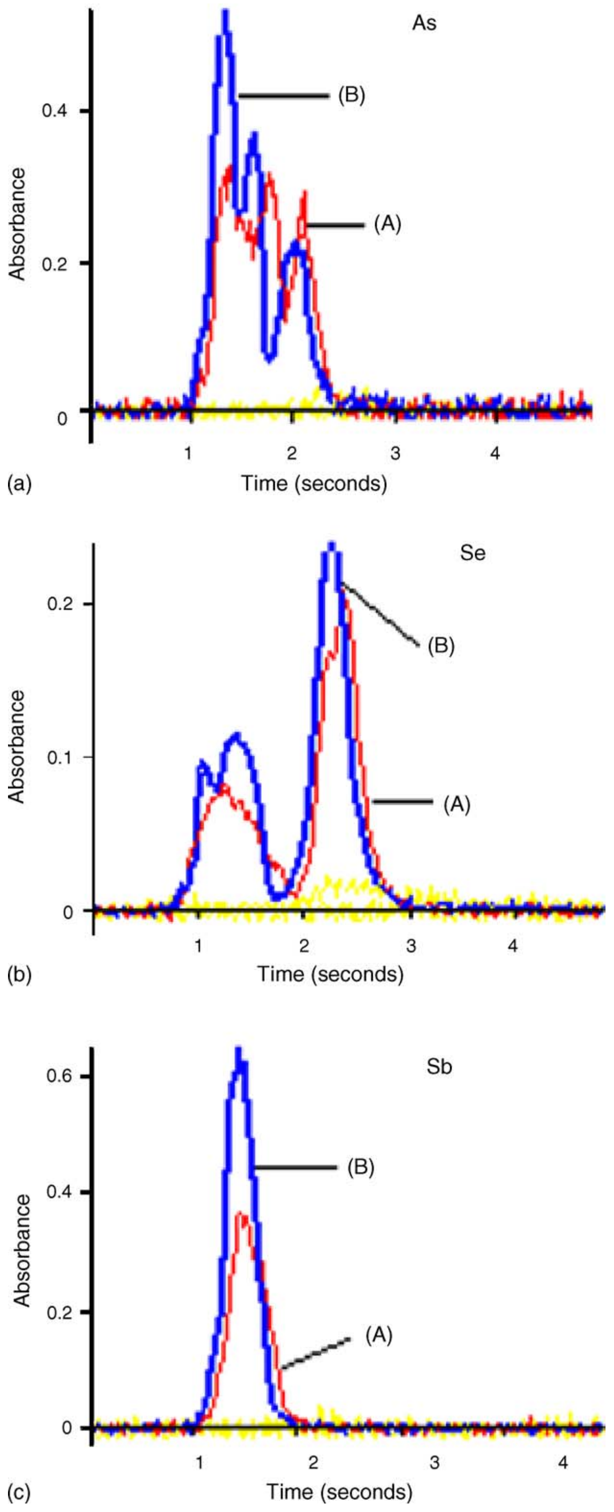

Fig. 2. Atomic profiles of a 100.0 μg l^{-1} solution of As, Se and Sb atomized at 2500 °C in a Zr-coating tube: injected volume, 20 μl; (A) standard solution; (B) slurry standard solution (20.0 mg titanium dioxide was added into 5.0 ml standard solution).

3.5. *Effect of the pH on adsorption*

The dependence of the recoveries of these elements in the sample solution on the pH is shown in Fig. 3. According to the recommended analytical procedure, 5.0 μg l^{-1} sample solutions were employed under different pH. The pH values of sample solution prior to adsorption were changed from 1.0 to 6.0. The high recoveries of these elements were found to be pH 2.0 for 10 min of stirring time.

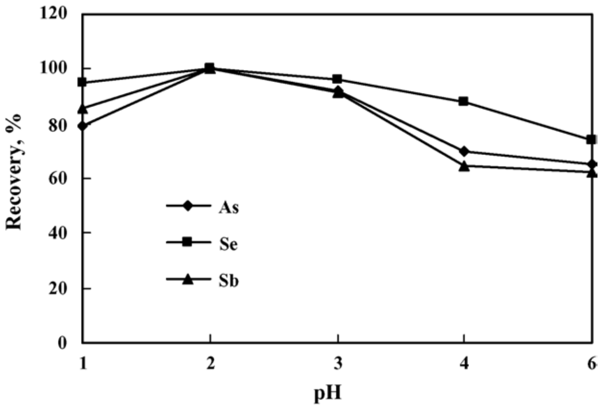

Fig. 3. Effect of pH on the recoveries of As, Se and Sb: stirring time, 10 min; titanium dioxide, 20.0 mg.

The pH plays an important role for the adsorption of ions on oxide metals [23]. According the theory, the adsorption of anion ion on amphoteric oxides, such as titanium dioxide, proceeds when the pH of the solution is lower than the isoelectric point (IEP) of the oxide (6.2 of pH). On the base of the theory, Vasileva et al. [18] further have pointed out that the spontaneous adsorption of H^+ on titania results in a positive charge on the anatase surface and thus the latter becomes active to the adsorption of anions. The adsorption for these anions of As, Se and Sb on anatase correlates with the above theory. As an explanation for adsorption for these elements, possible mechanism is suggested in a following equilibrium:

$$M_yO_z{}^{-(2z-ym)} + H^+ \rightleftharpoons HM_yO_z{}^{-(2z-ym-1)} \tag{1}$$

$$HM_yO_z{}^{-(2z-ym-1)} + (x-1)H^+ \rightleftharpoons H_xM_yO_z \tag{2}$$

where M represents those determined elements in this work, m is charge for M and x, y and z are number of atoms. Evidently, they are more strongly adsorbed than the other anion present, $NO_3{}^-$ and Cl^-. It suggests that charge of anatase surface and the existed form of these elements are affected by the concentration of H^+. With the increasing of H^+, the positive charge of anatase surface is increased; the parts of these elements are transformed to $HM_yO_z{}^{-(2z-ym-1)}$ and $H_xM_yO_z$. Obviously, the forms of anions are not strongly adsorbed on anatase as the most monovalent ions. In the contrast, decreasing of H^+, the positive charge of anatase surface becomes small, affinity for these anions becomes weak, and the recovery reduces. The mechanism is confirmed by the pH dependence seen in Fig. 3 and also suitable for the high valence for these elements shown in Fig. 4. Moreover, the above mechanism is also possible for explanation for the adsorption of complex anions of metal on the anatase in acidic solution.

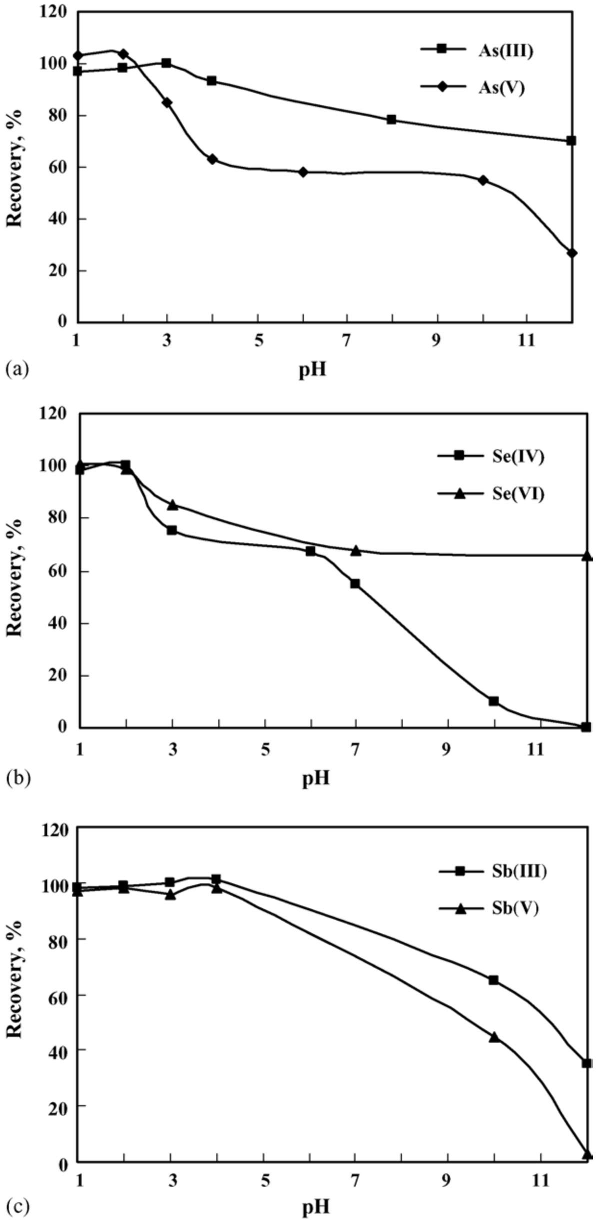

Fig. 4. Effect of pH on the recoveries of As, Se and Sb at the different valence: (a) As(III) and As(V); (b) Se(IV) and Se(VI); (c) Sb(III) and Sb(V); stirring time, 10 min; titanium dioxide, 20.0 mg.

3.6. *Effect of amount of titanium dioxide*

A 5.0 μg l^{-1} sample solution (As, Se and Sb) was applied to investigate the influence of amount of titanium dioxide on the recoveries for As, Se and Sb at pH 2.0 for 10 min of stirring time, as described in the analytical procedure. The range of amount of titanium dioxide was from 5.0 mg to 30.0 mg. While, amount of titanium dioxide was up to 20.0 mg, the recoveries of As, Se and Sb were over 95%, after that, the recoveries were basically kept at equality, but with increasing of amount of titanium dioxide, titanium dioxide did considerable damage to the graphite tube. Therefore, 20.0 mg of titanium dioxide was chosen as a sorbent in the subsequent experiments.

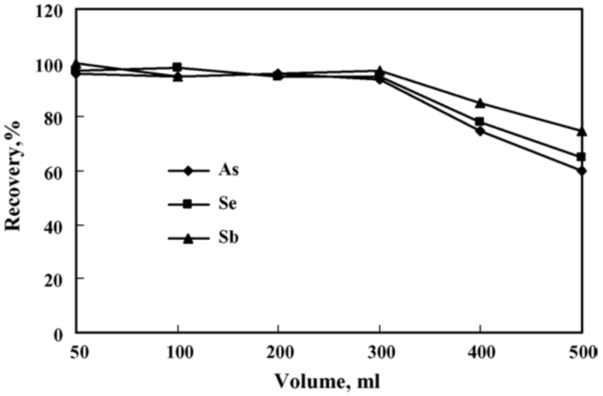

Fig. 5. Effect of the sample volume on the recoveries of As, Se and Sb. The amount of As, Se and Sb is 200 ng, respectively; pH: 2.0; stirring time: 10 min; titanium dioxide: 20.0 mg.

3.7. *Effect of stirring time*

To understand the effect of stirring time on the recoveries, 2.0 μg l^{-1} sample solutions (As, Se and Sb) were investigated under the above optimal adsorption conditions according to the recommended analytical procedure. Stirring time of 0–30 min was performed. The recoveries for As, Se and Sb exceeded 80% under the static condition for 10 min; when stirring time was up to 5 min, the recoveries for these elements were over 90%. In order to keep a constant adsorption for As, Se and Sb, 10 min of stirring time was chosen for the subsequent experiment.

3.8. *Effect of valence of As, Se and Sb*

In the above investigation, the mixed solution of As(III), Se(IV) and Sb(III) was used to study. In fact, the inorganic speciation of high valence of these elements also exists in natural water, such as As(V), Se(VI) and Sb(V). In order to understand the effect of different speciation of As, Se and Sb on adsorption, 2.0 μg l^{-1} sample solutions of these elements (the low and

Table 2
Interference of coexisting ions on the determination of As, Se and Sb ($C = 2.0$ μg l^{-1})

Ion	Concentration (mg l^{-1})	Recovery (%)		
		As	Se	Sb
Na^{+}	20000	101	102	103
K^{+}	10	96	92	100
Ca^{2+}	100	101	89	92
Mg^{2+}	100	100	93	100
Cu^{2+}	0.1	102	98	97
Co^{2+}	0.1	100	96	90
Ni^{2+}	0.1	99	91	93
Fe^{3+}	10	104	98	97
Al^{3+}	1	93	95	93
SO$_4$$^{2-}$	10	83	96	92
	1	91	99	94
PO$_4$$^{3-}$	100	75	55	91
	10	94	103	91

Table 3
Analytical results of As, Se and Sb in water samples

Sample	Added ($\mu g\,l^{-1}$)			Founded ($\mu g\,l^{-1}$)			Recovery (%)		
	As	Se	Sb	As	Se	Sb	As	Se	Sb
Tap water[a]	–	–	–	N.D.*	N.D.	N.D.	–	–	–
	4.0	4.0	4.0	3.9	3.8	4.2	97	95	106
River water[b]	–	–	–	0.8	N.D.	0.3	–	–	–
	4.0	4.0	4.0	3.7	4.0	4.6	72	100	107

* N.D.: not detected.
[a] Chiyoda-ku, Tokyo (21 December 2004).
[b] Edogawa-river, Tokyo (20 January 2005).

high valence ions) containing 20 mg titanium dioxide were used to investigate the influence at the different pH for 10 min of stirring time, as descried in the analytical procedure. Obtained results (Fig. 4) suggest optimal adsorption conditions are appropriate for both valences of each element investigated in this work.

3.9. Effect of sample volume

In order to explore the possibility of enriching low concentration of elements from large volumes, the maximum applicable sample volumes must be determined. For this purpose, 50, 100, 200, 300, 400, and 500 ml of sample solutions (containing 200 ng of As, Se and Sb, respectively) were used under the optimal adsorption conditions. As shown in Fig. 5, the recoveries of As, Se and Sb are quantitative (>95%) up to 300 ml of sample volume. It makes rate of enrichment be increased from 20 to 60, enlarges the detecting range for these trace elements.

3.10. Interference of coexisting ions in water sample

The effect of the coexisting ions on determination of As, Se and Sb was investigated under the optimal conditions. The coexisting ions and their concentrations in this study are listed in Table 2. Sample solution of 2.0 $\mu g\,l^{-1}$ (As, Se and Sb) containing the foreign ions was pretreated according to the analytical procedure. The obtained results in Table 2 suggest that the presence of major cations has no obvious influence on the determination under the selected condition. With increasing of concentration of the anions ($SO_4^{2-} > 1.0\,mg\,l^{-1}$, $PO_4^{3-} > 10.0\,mg\,l^{-1}$), the recoveries has been obvious affected on determination of As and Se. The influence of anions on the determination of As, Se and Sb could be explained with competitive sorption. This effect was not observed with NO_3^- and Cl^- as far as these anions are also presented in a standard solution.

3.11. Limitation of detection and precision

According to the definition of IUPAC, limitations of detection (3σ) for As, Se and Sb with an enrichment factor of 20 are 0.21, 0.15, and 0.15 $\mu g\,l^{-1}$, respectively; relative standard deviations (R.S.D.%.) for these elements are 1.4%, 1.0% and 1.0%, respectively ($n = 6$, $C = 5.0\,\mu g\,l^{-1}$).

3.12. Application to water sample

The proposed method was applied on the determination of As, Se and Sb in water samples. The standard calibration method was made according to the analytical procedure. The results of determination of As, Se and Sb were given in Table 3. The results indicate that the recoveries of these elements in tap water sample are suitable for trace analysis, but the recovery of As in river water sample is less than 80%. The low recoveries of As may be due to the competitive sorption of the anions (SO_4^{2-} or PO_4^{3-}) discussed in the above effect of interference ions.

4. Conclusions

In the present work, a relatively simple and rapid method for simultaneous determination of total As, Se and Sb was established and has been applied for determination of As, Se and Sb in tap water and river water samples. The conditions for GFAAS and adsorption on titanium dioxide were discussed in detail in this paper. The proposed method is also applicable to the determination of trace amount of other metal ions as resembling the determined elements in water sample. In the course of the studies, the speciation analysis of these elements will then be carried out by separation of different oxidation states with GFAAS.

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