

Direct Simultaneous Determination for Ultratrace As, Se and Sb in River Water with Graphite-Furnace Atomic Absorption Spectrometry by TiO₂-Slurry Sampling

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A simple analytical method was established for the simultaneous multielement determination of As, Se and Sb in river water with GF-AAS using TiO₂-slurry sampling. Titanium dioxide (TiO₂, <0.5 µm) was applied as a sorbent to separate and concentrate these elements in a sample solution (100–300 ml); after filtration, a slurry was prepared with the solid phase and 5.0 ml of ultrapure water. In order to apply to river-water samples, the effect of TiO₂ in atomization, the effect of organic species of their metal and the interference of foreign ions were investigated. The proposed method was applied to JSAC 0302 and river water.

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In recent years, trace analysis for As, Se and Sb in all kinds of samples have received much attention. The main reasons are that the compounds of these elements are toxic; As and Se are also nutrient elements for the human's body.¹ Therefore, the contents of these elements in environment are strictly monitored by all countries. In a great many reports on direct determination, GF-AAS, ICP-AES² and ICP-MS³ are mentioned as being the main apparatus. ICP-MS with multielement determination and a lower detection limit is attractive, but the influence on As and Se caused by ⁴⁰Ar³⁵Cl and ⁴⁰Ar³⁷Cl has still not been completely solved. Moreover, it is too expensive for most researchers. ICP-AES, with multielement determination resembling ICP-MS, has a lower sensitivity for these elements. GF-AAS is generally employed to determine a single element. In addition, for some trace and ultra trace elements in actual samples, direct determination cannot be performed due to the effect of matrices and the limited sensitivity of the instrument. Hydride generation (HG), a technique of sample introduction, is an effective procedure by which these elements are separated from the matrix as their hydrides. This technique coupled with many analytical instruments (such as HG-AAS, HG-ICP-AES and HG-ICP-MS *etc.*) has been applied in analytical field,^{4–8} but it is necessary to keep the elements in solution in a low oxidation state and determination in the continuous mode. There have been a few lectures on *in-situ* trapping of hydrides on a graphite tube for ET-AAS.⁹ For this technology, the introduction of hydrides is difficult in actual operation.

Except for the HG technique, sorption, a pretreated procedure, is also often used for determining low-content elements in samples. The pretreated procedure is suitable for most instruments. Inorganic metal oxides, such as aluminum oxide,¹⁰ cobalt oxide¹¹ and titanium dioxide *etc.*, have been used to concentrate trace and ultra trace metallic elements as sorbents.^{12–17} TiO₂ can adsorb anions when the pH of the

solution is lower than pH 6.2 of the isoelectric point (IEP), according to Brunelle *et al.*¹⁴ The adsorption of Cr(VI) on TiO₂ under an acidic condition is also described by Vasileva *et al.*¹⁵ However, there are only a few reports on these oxides for As, Se and Sb.¹⁶ In our previous work, a new method was proposed with a simultaneous multielement graphite-furnace atomic-absorption spectrometer, in which the technologies of solid-phase extraction for TiO₂ and slurry sampling were used.¹⁷ The method with simultaneous multielement determination can save more time than that of a single element with a GF-AAS. Meanwhile, the slurry sampling simplifies the pretreated process. The fundamental adsorption conditions in the previous work¹⁷ were listed in the subsequent analytical procedure.

The aim of this study is to investigate detailed conditions concerning the determination of ultratrace As, Se and Sb in river water, such as the effect of TiO₂ in atomization, the influence of organic species of their metal and the interference of foreign ions. The proposed method was evaluated by a JSAC-0302 standard river-water sample, and applied to river-water samples.

Experimental

Reagents and chemicals

All of the reagents were of analytical grade. A multi element aqueous standard solution (100 µg l⁻¹) containing As(III), Se(IV) and Sb(III) was obtained on a daily basis by diluting appropriate aliquots of a 1000 mg l⁻¹ stock metal solution. Stock solutions (1000 mg l⁻¹) of As(V) and Se(VI) were separately prepared by dissolving the corresponding salts and adjusting the pH to 1.0 with nitric acid. These solutions were properly diluted for use. The standard solutions of Sb(III) with 20% HCl and Sb(V) were from SPEX CertiPrep, Ltd. Stock solutions of monomethylarsenic acid (MMA) (95%) and selenocystine (SeCyst) (SIGMA-aldrich, Inc., USA, 98%) were prepared by dissolving the corresponding solid in ultrapure

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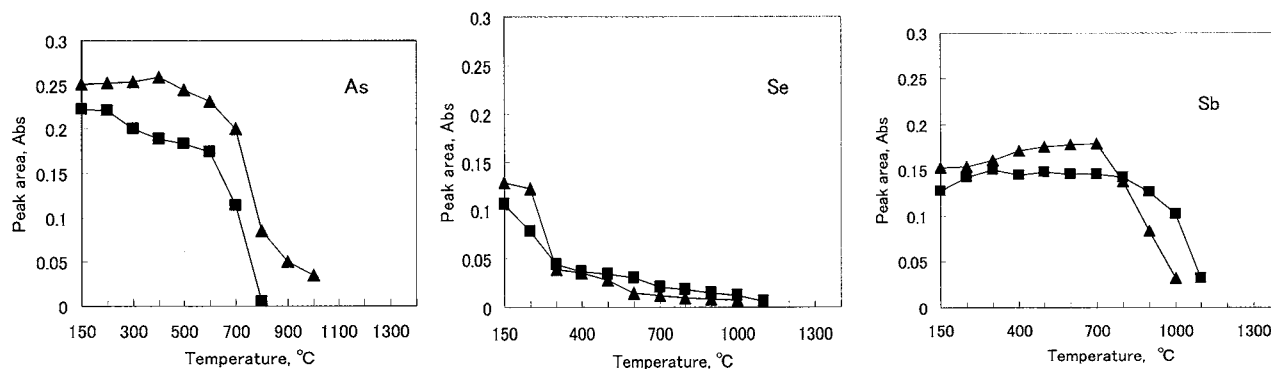


Fig. 1 Pyrolysis curves in two different media. $\blacktriangle$, TiO_2 slurry; $\blacksquare$, standard solution; atomization temperature, 2300°C ; concentrations of As, Se and Sb, $100\ \mu\text{g l}^{-1}$.

Table 1 Furnace program

Step	Temperature/ $^\circ\text{C}$	Time/s		Ar gas/ ml min^{-1}
		Ramp	Hold	
1 Dry 1	130	1	30	250
2 Dry 2	150	15	30	250
3 Atomization	2300	0	5	0
4 Clean up	2450	1	3	250

water. The nitric acid (60%) for poisonous metal analysis and sulfuric acid were from Kanto Chemical Co. Ing. Titanium(IV) dioxide (TiO_2 , anatase form, 99%, $<0.5\ \mu\text{m}$) was utilized as a sorbent. $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ was employed to coat the graphite tube. A river-water sample was collected in Edokawa river in Tokyo, filtrated with a $0.45\ \mu\text{m}$ pore size cellulose acetate membrane filter (ADVANTEC, Tokyo), and kept at 1.0 of pH with nitric acid. The above reagents without a source and the other reagents used in this work were from Wako Pure Chemical Industries, Ltd. in Japan.

Apparatus

A simultaneous multielement graphite-furnace atomic-absorption spectrometer (Model SIMAA 6000) from Perkin-Elmer Co. was used with a transversely heated graphite atomizer (THGA), longitudinal Zeeman-effect background correction and an AS-72 autosampler. Standard THGA graphite tubes (Part No. B0504033) and electrodeless discharge lamps (As, 193.7 nm, 380 mA; Se, 196.0 nm, 290 mA; Sb, 223.1 nm, 380 mA) were employed from EDL system 2 in Perkin-Elmer. The measurements were performed in a peak-area mode (integrated absorbance). A pH meter (HM-26S) manufactured by DKK-TOA Corporation and an electric balance (Sartorius Model BP301S-EA BR-1010) were employed. An ultrasonic (Branson 12, Branson) was used to dispend the slurry so as to improve its adsorption and homogeneity. A magnetic stirrer (ADVANTEC SR 506) was utilized to stir. A Milli-Q Water System, Millipore, was employed to produce ultrapure water. In addition, before being used, all glassware, pipette tips and storage bottles were soaked in dilute HNO_3 for 24 h and rinsed at least three times according to the order of water, pure water and ultrapure water.

Analytical procedure

The enrichment ratio (the ratio between the first sample volume and 5.0 ml of the slurry prepared according to the following procedure) of 20 was used for investigating the influential conditions on adsorption. One hundred milliliters of the sample solution with less than $5.0\ \mu\text{g l}^{-1}$ of As, Se and Sb were placed in a beaker; the pH was adjusted to 2.0 with 2.0 M HNO_3 . The sample solution containing 20.0 mg of TiO_2 was stirred by a magnetic stirrer for about 10 min, and was immersed in a sonication bath for about 10 min. After the solution was filtrated by a membrane filter, the remaining solid phase was transferred to a 15 ml centrifugal tube with ultrapure water, and then water was added to prepare 5.0 ml of a slurry sample. Then, $20\ \mu\text{l}$ of the slurry was injected into a graphite tube by an autosampler for each firing. As, Se and Sb in the samples were determined according to furnace conditions listed in Table 1.

Results and Discussion

Effect of the pyrolysis temperature

A graphite tube for the determination of As, Se and Sb was coated with zirconium nitrate.^{17,18} As shown in Fig. 1, the appropriate pyrolysis temperature for each element was different (300 to 500°C for As; 150 to 200°C for Se; 500 to 700°C for Sb). However, in order to be suitable for simultaneous determination, compromise conditions for these elements were necessary. In addition, because the determination for these elements was performed after concentration, the acids and other matrices had been mainly removed by filtration. TiO_2 as a sorbent had been the main matrix for determination with GF-AAS. In a previous paper, low-background absorbance for these elements in a TiO_2 slurry in favor of determination was proved at low temperature.¹⁷ Thus, the pyrolysis stage was abandoned and the temperature in dry 2 stage was set at 150°C , as listed in Table 1.

Stability of TiO_2 slurry

The stability of the TiO_2 slurry is affected by the pH value of the media.¹³ When the pH value of the solution is lower than the pH of the isoelectric point (IEP), the spontaneous adsorption of H^+ on titania results in a positive charge on the anatase surface.¹⁴ The action among these ions with the same positive charge can keep the slurry stable. It was proved that the TiO_2 slurry remained stable for 10 min at pH 1.0 in this work. In

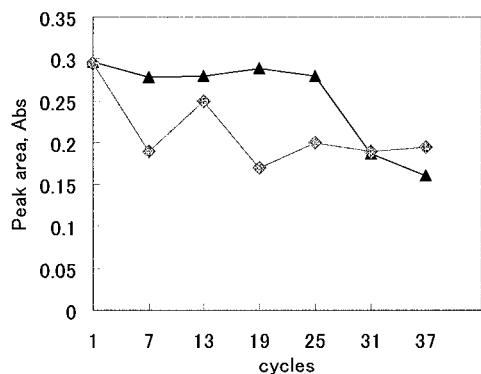


Fig. 2 Effect of a Zr-coating on the stability of a THGA tube for As in the TiO_2 slurry. Five firings were viewed as a cycle. $\blacktriangle$, Zr-coating THGA tube; $\blacklozenge$, THGA tube; injected volume, 20 μl /firing; TiO_2 , 80 μg /firing; concentration of As, 100 $\mu\text{g l}^{-1}$.

addition, due to the limitation of an autosampler capillary with AAS, the granularity of TiO_2 powder was limited in a definite range, so that the homogeneous slurry could be effectively controlled. Because of the smaller granularity of TiO_2 (<0.5 μm) used in this work, the instability resulted by the TiO_2 granularity was not obvious.

Effect of TiO_2 on the determination of As, Se and Sb

Two kinds of solution samples containing As, Se and Sb were used to investigate the effect. One was a standard solution obtained by diluting the stocked solution; another was a TiO_2 slurry prepared according to the recommended analytical procedure at an enrichment rate of 20. Injected into a graphite tube separately, these were atomized at 2300°C when the pyrolysis temperature was changed from 150 to 1100°C. The curves in Fig. 1 show that the sensitivity of As, Se and Sb in the TiO_2 slurry is higher than that of As, Se and Sb in the standard solution. As known, some compounds of these elements are easily volatile at low temperature, such as AsCl_3 (B.P. 130.2°C), SeOCl_2 (B.P. 176.4°C), SbCl_3 (B.P. 223.5°C). Owing to the adsorption of TiO_2 for some inorganic species of As, Se and Sb in acid condition, the loss of some species was reduced in a furnace at low temperature.

Effect of firings of a tube on the reproducibility

The poor reproducibility of results with a technology of slurry sampling is known with GF-AAS. One of the reasons is that the injected solid phase damages a graphite tube. Arsenic as an example was used to illustrate this effect. A cycle for 5 firings was monitored after every other 6 cycles, and the results were shown in Fig. 2. For a THGA tube, the reproducibility of the results for a cycle was good ($\text{RSD}\% < 5\%$). Nevertheless, the absorbance sometimes became high and sometimes low after 6 cycles. Meanwhile, $\text{RSD}\%$ for the high-absorbance monitoring dots was less than 15%, but was over 30% for the low type in 120 firings. Except for the difference in the absorbance, similar phenomena occurred for Se and Sb. As known, the reaction of TiO_2 with carbon is used in the industrial production of TiC when exceeding 900°C.¹³ The reaction results in damage to the surface of the graphite tube, which results in poor reproducibility. With increasing firings, the surface of tube was damaged by the slurry for a THGA tube, which made the reproducibility to become poor. In order to obtain more stable results, a Zr-coating THGA tube was used in the experiment. The curve for a Zr-coating THGA tube (Fig. 2)

Table 2 Recovery test for total As, Se, and Sb from different concentration ratios of low/high oxidation states

Total added/ $\mu\text{g l}^{-1}$	Concentration ratio (low/high oxidation state)	Found/ $\mu\text{g l}^{-1}$		
		As(III, V)	Se(IV, VI)	Sb(III, V)
5.0	4:1	4.9	5.0	5.2
5.0	3:2	4.7	4.8	5.1
5.0	2:3	4.6	4.8	5.0
5.0	1:4	4.5	4.8	5.0

shows that the detected results were stable and the $\text{RSD}\%$ for the monitoring dots was less than 5% in 120 firings. This is because a layer of ZrC delays any damage of the surface of the graphite tube caused by the form of TiC . With increasing firings for the tube, however, the ZrC layer was destroyed step by step, and thus the reproducibility became increasing worse over 120 firings.

Effect of different oxidation states of As, Se and Sb on the recovery

Vasileva *et al.*¹⁴ further point 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. A change in the pH can have an impact on the adsorption of these elements on TiO_2 , which has been proved in previous research; the optimal condition of the pH is 2.0.¹⁷ In order to further investigate the effect of different oxidation states, mixed solutions were prepared according to the different ratio given in Table 2, and used to carry out determinations for these elements according to the analytical procedure at pH 2.0. The obtained results show that the total recoveries for the total Se and Sb are independent of any change of the low/high oxidation states; with decreasing the concentration ratio, the recoveries of As show only a small decrease. The decreasing cause of recovery for As is unknown at present.

Effect of organic species on the total recovery of each element for As, Se and Sb

Since organic species of As, Se and Sb were also contained in environmental samples used in this study, two organic species, monomethylarsenic acid (MMA) and selenocystine (SeCyst), were utilized to investigate the effect on the total recovery of each element. Stable and high-purity organic species of Sb were not found, so the effect of the organic species of Sb was not investigated in this work. Organic species in actual river samples are far lower than inorganic species in content. Therefore, a small quantity of the two organic compounds was together added with inorganic species to investigate the effect. The results given in Table 3 show that the added organic species had only a small effect on total recovery for each element. Further investigations show that when the two compounds were separately added, the recoveries of MMA and SeCyst were 93 and 52%, respectively. Obviously, the recovery for SeCyst is difficult. In fact, for river-water samples, the effect on the total recovery for each element may become smaller, owing to lower content for the two organic species.

Effect of foreign ions

To investigate the influence of many ions on the analyte ions, an artificial river-water sample was prepared by diluting chloride salts and nitrates, containing Na^+ of 1000 mg l^{-1} , K^+ of 10 mg l^{-1} , Ca^{2+} of 50 mg l^{-1} , Fe^{3+} of 10 mg l^{-1} , Mg^{2+} of 50 mg l^{-1} ,

Table 3 Effect of organic compounds of As and Se on the total recovery of each element in 100 ml of ultrapure water

Added/ $\mu\text{g l}^{-1}$				Found/ $\mu\text{g l}^{-1}$			Rec., %	
Total As		Total Se		As	Se		As	Se
As(III)	MMA ^a	Se(IV)	SeCyst ^b	3.6	3.3		90	94
3.0	1.0	3.0	0.5					
—	4.0	—	4.0	3.7	2.1		93	52

a. MMA, monomethylarsenic acid.

b. SeCyst, selenocystine.

Table 4 Effect of foreign ions

Sample	Added/ $\mu\text{g l}^{-1}$			Found/ $\mu\text{g l}^{-1}$			Recovery, %		
	As	Se	Sb	As	Se	Sb	As	Se	Sb
An artificial river water ^a	4.0	4.0	4.0	4.2	4.1	3.9	105	102	98
60 mg l ⁻¹ SO ₄ ²⁻ , 30 mg l ⁻¹ PO ₄ ³⁻	4.0	4.0	4.0	2.1	2.2	3.9	52	55	97
20 mg l ⁻¹ SO ₄ ²⁻ , 10 mg l ⁻¹ PO ₄ ³⁻	4.0	4.0	4.0	2.9	3.0	4.0	72	75	100
10 mg l ⁻¹ SO ₄ ²⁻	4.0	4.0	4.0	3.4	3.8	3.8	85	96	96
5 mg l ⁻¹ PO ₄ ³⁻	4.0	4.0	4.0	3.7	3.9	3.9	94	98	98

a. An artificial river water was composed of: Na⁺, 1000; K⁺, 10; Ca²⁺, 50; Fe³⁺, 10; Mg²⁺, 50; Cu²⁺, 1.0; Zn²⁺, 1.0; Al³⁺, 1.0; Pb²⁺, 1.0 mg l⁻¹.

Cu²⁺ of 1.0 mg l⁻¹, Zn²⁺ of 1.0 mg l⁻¹, Al³⁺ of 1.0 mg l⁻¹, and Pb²⁺ of 1.0 mg l⁻¹. Some solutions containing Na₂SO₄ and Na₃PO₄ were prepared. By adding the determined elements in the prepared samples, the recoveries were obtained, as listed in Table 4. The recoveries of As, Se and Sb in an artificial river-water sample were over 95%, which indicates that the coexisting cations had no influence on adsorption. The decrease in the recoveries of these elements in other samples shows that the two anions obviously impact on the adsorption of As, Se and Sb on TiO₂. Except for As, the recoveries were over 95% up to 10 mg l⁻¹ SO₄²⁻ and 5 mg l⁻¹ PO₄³⁻. Because Cl⁻ and NO₃⁻ are highly present in the solutions, the effect on the recoveries has not been specially investigated.

Preparation of calibration curves

Under the same operating conditions for the graphite furnace, the integrated absorbances of a multielement aqueous standard solution of As(III), Se(IV) and Sb(III) were lower than that of a TiO₂ slurry prepared according to the recommended analytical procedure. That is, TiO₂ had effects on As(III), Se(IV) and Sb(III), as discussed above. Therefore, it is not suitable to determine the contents of As(III), Se(IV) and Sb(III) in actual samples with the calibration curves of the standard solution of these elements. To determine accurately the actual sample, the calibration curves (As, $y = 0.0550x$, $R^2 = 0.999$; Se, $y = 0.0240x$, $R^2 = 0.998$; Sb, $y = 0.0332x$, $R^2 = 0.999$) made by the TiO₂ slurry were used. In addition, the calibration curves of a multielement aqueous standard solution of As(III), Se(IV) and Sb(III) correspond to those of As(V), Se(VI) and Sb(V). The calibration curves were linear up to 5.0 $\mu\text{g l}^{-1}$. When a 2.0 $\mu\text{g l}^{-1}$ multi-element solution was applied, the detection limits (3σ) were found to be 0.14 $\mu\text{g As l}^{-1}$, 0.12 $\mu\text{g Se l}^{-1}$ and 0.10 $\mu\text{g Sb l}^{-1}$, respectively, with an enrichment rate of 30.

Table 5 Analysis results of the standard reference material (JSAC 0302) for As and Se

Element	Found $\pm \sigma$ / $\mu\text{g l}^{-1}$ ($n = 3$, parallel)	Certified value/ $\mu\text{g l}^{-1}$
As	5.1 ± 0.3	5.3 ± 0.2
Se	4.9 ± 0.2	5.0 ± 0.1
Sb	—	—

Analysis of river-water samples

The determination of trace elements in water samples from the environment with the present method is very important and necessary. Because of the absence of reference materials with As, Se and Sb, an evaluation on the applicability was performed by examining the recoveries of As and Se in a JSAC (0302) standard river-water sample. For an enrichment ratio of 20, these metals in the sample (100 ml) were preconcentrated according to the recommended analytical procedure. The obtained results given in Table 5 show that the recoveries of As and Se are up to 95%. The concentrations of these elements determined by the present method were in good agreement with the certified values. Subsequently, the procedure was applied to river-water samples. As discussed concerning effect of foreign ions, SO₄²⁻ and PO₄³⁻ have effects on the recoveries. Thus, the concentrations of SO₄²⁻ and PO₄³⁻ in the samples were determined first by ion-chromatography.¹⁹ It was found to be 30 mg l⁻¹ for SO₄²⁻ and nothing for PO₄³⁻. Therefore, the river-water samples were diluted twofold to minimize the interferences from the anion. That is, 150 ml of the river-water samples was diluted up to 300 ml, and then preconcentrated according to the recommended analytical procedure at an enrichment ratio of 60. The results ($\mu\text{g l}^{-1}$) were 0.90 ± 0.05 for As, not found for Se and 0.70 ± 0.06 for Sb. Compared with the determined results ($\mu\text{g l}^{-1}$) (0.85 ± 0.04 for As; not found for Se; 0.66 ± 0.03 for Sb) with the undiluted river water, obviously, the obtained results with the diluting river water are more reliable.

TiO₂-slurry sampling is an effective preconcentration procedure for the simple storage and measurement of trace levels of As, Se and Sb in environmental water samples by GF-AAS. The method allows one to determine simultaneous inorganic compounds of As, Se and Sb in a short time. The simultaneous foreign ions interferences and influence of organic compounds in environmental water sample show that the method is suitable for complicated matrix solutions. The method has been applied to the determination of As, Se and Sb in JSAC 0302 and river-water samples. During the future course of our studies, the speciation of these elements will be carried out by separating different oxidation states with GF-AAS.

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