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Determination of Total Arsenic in Environmental and Geological Samples by Electrothermal Atomic Absorption Spectrometry Using a Tungsten Furnace after Solvent Extraction and Cobalt(III) Oxide Collection

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A separation method, using solvent extraction and cobalt(III) oxide collection, has been studied for determining the total arsenic in environmental and geological samples by electrothermal atomic absorption spectrometry (ETAAS) using a tungsten furnace. After arsenic iodide was extracted into benzene, cobalt(III) oxide powder was added to the benzene solution to collect the extracted arsenic. The cobalt(III) oxide was separated from benzene by vacuum filtration and then suspended in 5 cm^3 of water. The slurry was introduced into the tungsten furnace and the determination of arsenic was performed. The relative standard deviation of the proposed method at the 0.20 mg dm^{-3} arsenic level was 2.4% ($n = 10$). The calibration curve obtained with the proposed method was linear up to 0.50 mg dm^{-3} (5.00 ng/10 mm^3), and the detection limit (3σ) was 12 μg dm^{-3} (0.12 ng/10 mm^3). The present method was applied to the analysis of some environmental and geological standard reference materials, and the concentrations of total arsenic obtained by the present method were in good agreement with the certified values or the reference values of those samples.

Arsenic is widely used in semiconductors, insecticides, pesticides, and pharmaceuticals, etc. However, industrial waste containing arsenic has attracted the attention of people concerned about environmental pollution. Arsenic plays an essential role in the human body; however, excess arsenic ingested and accumulated in the body leads to severe arsenic intoxication. Thus, the environmental concentration of arsenic is strictly regulated by several laws on environmental quality standards. Arsenic exists in the natural environment as various chemical species which have different levels of toxicity. Therefore, the determination of each arsenic species has been an important subject of recent studies. However, the establishment of a method for total arsenic determination is still especially important in order to grasp the behavior of arsenic in various environmental samples and to improve the reliability of the determination methods of each arsenic species.

A technique has been reported involving the absorptiometry of a complex formed between a color-development reagent and arsenic as a conventional method for arsenic determination.[1—3] Furthermore, a highly sensitive determination is possible when arsenic hydride is generated by the addition of a reducing agent, such as tin(II) chloride, zinc metal or sodium borohydride; the resulting arsenic hydride is then subjected to absorptiometry or electrothermal atomic absorption spectrometry (ETAAS).[4—7] In addition, a real-time determination by combining the above-mentioned equipment with pretreatment equipment has also been reported.[8,9]

The determination of arsenic using ETAAS is difficult, because the method lacks sensitivity and the results are highly dependent on the matrix component. Therefore, a chemical modifier is added to the sample to improve the sensitivity of ETAAS using a graphite furnace for arsenic determination, which has been reported previously.[5,10—18] However, the determination of trace amounts of arsenic in samples which have a high concentration of matrix components is difficult; a special pretreatment to separate arsenic is required.

Many solvent extraction methods that effectively separate arsenic from the matrix components have been studied.[19—23] However, examples of their application to environmental samples are quite few, because both the extractability and the sensitivities of the methods are insufficient.

We have studied the determination of lead,[24] bismuth,[24] and tellurium[25] by ETAAS using a tungsten furnace, and have reported the effects of using cobalt oxide as a chemical modifier and collector. We found that cobalt(III) oxide powder acts as a chemical modifier for arsenic when arsenic is determined by ETAAS using a tungsten furnace. In addition, it was found that cobalt(III) oxide powder also acts as an effective collector for arsenic iodide extracted into an organic phase. In this study, arsenic was separated from the matrix component using a solvent extraction method; the arsenic was then determined by ETAAS using a tungsten furnace in the presence of cobalt(III) oxide powder that acted as a chemical modifier and an arsenic collector.

Experimental

Reagents. An arsenic(III) standard solution was prepared by diluting an AAS-grade commercial arsenic standard solution (1000 mg dm^{-3}, As_2O_3 and NaOH in water of pH 5.0 with HCl, Wako Pure Chemical Industries, Ltd.) with water.

An arsenic(V) standard solution was prepared as follows.

Precisely 0.458 g of disodium hydrogenarsenate heptahydrate (99.0% < $Na_2HAsO_4 \cdot 7H_2O$, Wako Pure Chemical Industries, Ltd.) was dissolved in water to make a 100 cm^3 solution, and the resulting solution was established as a 1000 mg dm^{-3} standard solution of arsenic(V); this standard solution was diluted with water and used in the experiments.

Cobalt(III) Oxide. The requested amounts of cobalt(III) oxide powder (purity: 99.5%, Wako Pure Chemical Industries, Ltd.), which were passed through a 200 mesh (74 μm) sieve, were weighed and used for the experiments.

The acids used were of PMA-grade (Wako Pure Chemical Industries, Ltd.); the benzene and potassium iodide used were of gravimetric-analysis grade (Kanto Chemical Industries, Ltd.).

Ultrapure-grade water purified with a Milli Q-Labo filter (Nippon Millipore, Ltd.) was used throughout.

Apparatus. The analysis was conducted using an atomic absorption spectrometer (SAS 7500A) connected to a PS200A electrothermal atomizer (Seiko Instruments, Inc.).

An L-233 arsenic hollow-cathode lamp (Hamamatsu Photonics, Inc.) was used. A deuterium lamp was used for a background correction, and the furnace was a high-capacity U-type metal boat (50 mm^3) made of tungsten.

Procedure. Twenty cm^3 of the sample solution (total As $\leq$ 2.5μg), which was acidified with 9.0 M HCl (1 M = 1 mol dm^{-3}), was introduced into a separatory funnel, to which 5 cm^3 of 5 M KI was added to make a 25 cm^3 aqueous solution (Concentration of HCl: 7.2 M). An equal volume of benzene was added to this aqueous solution, and the funnel was placed on a shaker for 5 min to extract arsenic. After shaking, the benzene was separated from the aqueous solution into a 100 cm^3 PTFE beaker, to which 3 cm^3 of 4-methyl-2-pentanone (MIBK) and 30 mg of cobalt(III) oxide powder were added. The beaker was placed in an ultrasonic bath, and the organic phase was stirred for 10 min to collect arsenic adsorbed onto cobalt(III) oxide powder. Vacuum filtration was then performed using a PTFE membrane filter (diameter, 25 mm; pore size, 3.0 μm) to separate cobalt(III) oxide powder from the organic phase. The entire membrane filter, including the cobalt(III) oxide powder, was inserted into a plugged test tube, to which 5 cm^3 of water was added. The tube was shaken by hand to obtain a homogeneously dispersed slurry. Part of the slurry was introduced into the furnace, and the absorbance of arsenic (atomized under the conditions given in Table 1) was measured. Manual pipetting was employed for injecting the slurry.

Pretreatment of Solid Sample. To dissolve the solid sample, a mixed solution of HNO_3, $HClO_4$, and HF was used. When the weight of the collected sample ranged from 0.5 to 1.0 g, the volume ratio of the three acids was 5 : 5 : 3 (cm^3); when the weight collected ranged from 1.0 to 2.0 g, the volume ratio was 10 : 10 : 6 (cm^3). In addition, a blank test under acidic conditions was performed to confirm the blank value.

Table 1. Instrumental Operating Parameters for Arsenic

Parameter	Ramp time/s	Hold time/s	Temp/°C
Dry	10	20	130
Char	10	15	1000
Atomize	0	3	2500
Clean	0	1	2600

Wavelength: 193.7 nm, Spectral bandwidth: 0.5 nm, Lamp current: 10 mA, Gas flow rate: Ar: 5.0 $dm^3 min^{-1}$, H_2: 1.0 $dm^3 min^{-1}$.

We used the following procedure to dissolve the solid sample. A precisely weighed solid sample (from 0.5 to 2.0 g) was put into a Teflon® beaker, to which a mixed solution consisting of HNO_3, $HClO_4$ and HF was added. After the beaker was left standing for 15 min, it was placed on a hot plate (230 °C) to dissolve the sample; the sample was then solidified through evaporation. The resulting sample was dissolved in a 10 cm^3 HCl (1 + 10) solution and then filtered using No. 5B paper filter. Following removal of the residue, 37.5 cm^3 of concentrated HCl was added to the filtrate; water was then added to obtain a 50 cm^3 solution. The acidic concentration of the obtained solution sample was set at 9.0 M HCl for convenience in later use.

Results and Discussion

Measurement Conditions of ETAAS. In ETAAS using a tungsten furnace, the peak-area method showed poorer reproducibility and a higher detection limit compared with the peak-height (absorbance) method. Thus, the determination of arsenic in this study was employed by the peak-height method.

The influence of the charring temperature on the absorption behavior of arsenic(III) and arsenic(V) was surveyed by varying it from 200 to 1600 °C. Five cm^3 of slurries with the proposed method were used; the concentration of arsenic(III) or arsenic(V) was 0.20 mg dm^{-3} (1.0 μg/5 cm^3). At the same time, the following two solutions were used for a comparison experiment: 1) 0.20 mg dm^{-3} arsenic(III) and arsenic(V) standard solutions; 2) 5 cm^3 of 0.20 mg dm^{-3} arsenic(III) and arsenic(V) standard solutions into which 30 mg of cobalt(III) oxide powder was dispersed. The atomizing temperature was kept at 2500 °C. The obtained results are shown in Fig. 1. When only arsenic(III) and arsenic(V) standard solutions were used, although the absorbances of arsenic in a tungsten furnace decreased with increasing charring temperature above 800 °C, not all of the volatilization losses were admitted until 1600 °C. ETAAS using a graphite furnace has been reported to show different sensitivities of arsenic(III) and arsenic(V) with the same concentration.[23] However, the obtained absorbances of arsenic(III) agreed with that of arsenic(V) in a tungsten furnace.

In contrast, with respect to arsenic(III) and arsenic(V) standard solutions containing dispersed cobalt(III) oxide powder, the absorbance remained constant in the charring temperature range from 200 to 1100 °C, and exhibited the same value for both arsenic(III) and arsenic(V).

Regarding a slurry prepared by the proposed method, an absorbance slightly higher than that of the 0.20 mg dm^{-3} arsenic(III) and arsenic(V) standard solutions was obtained. In the charring temperature range from 200 to 1200 °C, constant absorbances were obtained, and the best relative standard deviation (<2.3%, n = 6) was observed at a charring temperature of 1000 °C.

Using slurries of arsenic(III) and arsenic(V) prepared with the proposed method, the influence of the atomization temperature of arsenic on the determination was tested from 2000 to 2700 °C under the condition where the charring temperature was kept at 1000 °C. The highest absorbance was then obtained at an atomization temperature of 2700 °C (R.S.D:

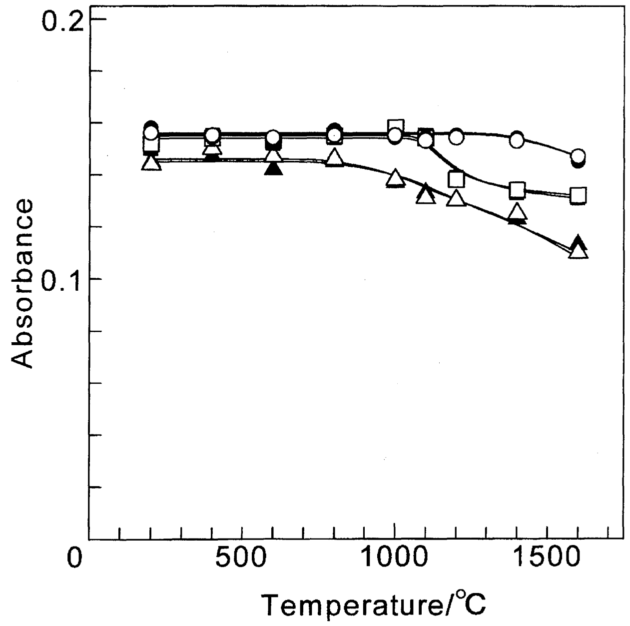

Fig. 1. Effect of charring temperature. ▲, △, As standard solution (0.20 mg dm^{-3}) only. ■, □, 5 cm^3 of As standard solution (0.20 mg dm^{-3}) containing dispersed cobalt(III) oxide powder. ●, ○, Slurry (As : 1.0 μg/5 cm^3) of the proposed method. ▲, ■, ●, As$^{\mathrm{III}}$. △, □, ○, As$^{\mathrm{V}}$. Injection volume: 10 mm^3.

3.5%); however, the best relative standard deviation was obtained at an atomization temperature of 2500 °C (R.S.D: 2.3%). Concerning the atomization time, 3 s was found to be optimal.

Extraction Conditions of Arsenic. Various references have reported the conditions under which arsenic(III) reacts with potassium iodide,[19—21] diethyldithiocarbamic acid,[1] or pyrrolidine dithiocarbamate in order to extract arsenic using an organic solvent. In this study, these methods were applied to collect arsenic using cobalt(III) oxide powder. The results indicate that arsenic is most effectively extracted in the form of arsenic iodide. The following discussion addresses the experimental conditions adopted in this study.

Effect of Acid Concentration. An aqueous solution (25 cm^3) containing 1.0 μg of arsenic(III) or arsenic(V) was acidified with 1.0—10.0 M HCl or 2.0—4.0 M H_2SO_4. Arsenic was then extracted into benzene to obtain the recovery of arsenic with cobalt(III) oxide powder. At the same time, 25 cm^3 of an aqueous solution with a potassium iodide concentration of 1.0 M was prepared to compare the arsenic recovery with that obtained above. The obtained results are presented in Figs. 2a and 2b for the arsenic(III) aqueous solution and arsenic(V) aqueous solution, respectively. The results are briefly described as follows.

As for arsenic(III), the recovery was approximately 90% for HCl concentrations of 8.0—10.0 M (Fig. 2a) and 0% for H_2SO_4 concentrations of 2.0—4.0 M (Fig. 2b). By adding potassium iodide to the aqueous solution, however, 100% recovery was obtained for both HCl concentrations of 6.0—10.0 M (Fig. 2a) and H_2SO_4 concentrations of 3.5—4.0 M (Fig. 2b).

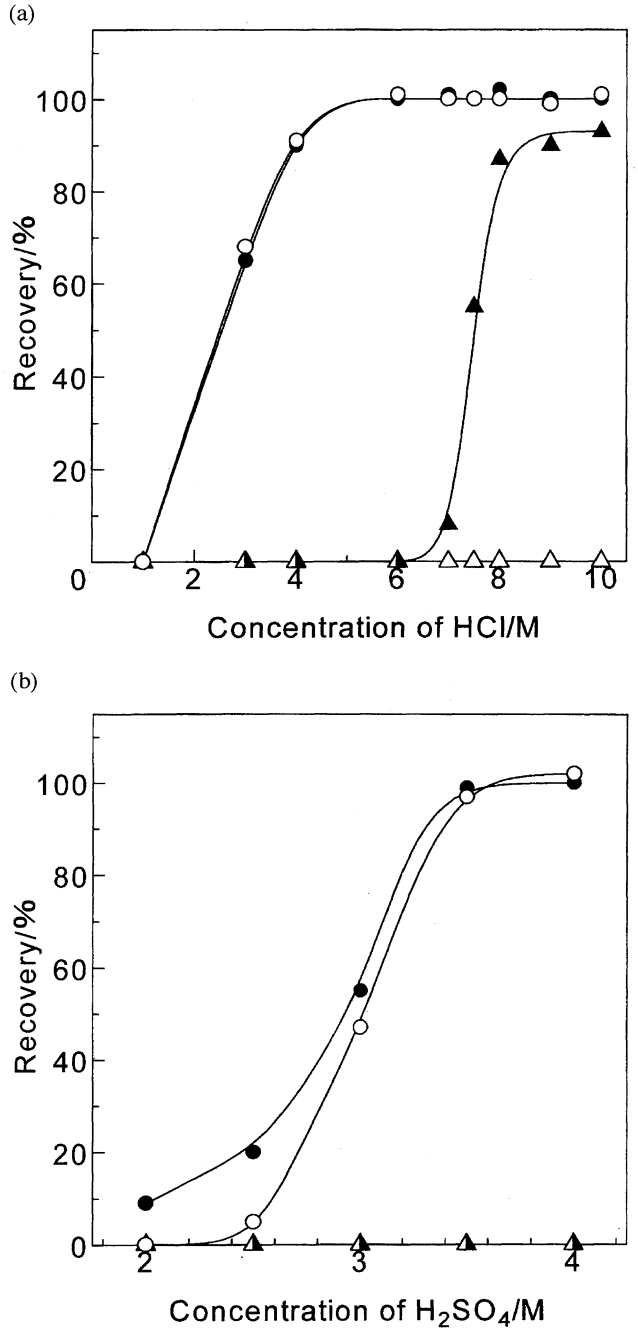

Fig. 2. (a) Recovery of As$^{\mathrm{III}}$ and As$^{\mathrm{V}}$ from extraction process as a function of HCl concentration. Benzene was used as solvent. ▲, △, Without KI. ●, ○, With 1.0 M KI. ▲, ●, As$^{\mathrm{III}}$. △, ○, As$^{\mathrm{V}}$. Cobalt(III) oxide powder: 30 mg.
(b) Recovery of As$^{\mathrm{III}}$ and As$^{\mathrm{V}}$ from extraction process as a function of H_2SO_4 concentration. Benzene was used as solvent. ▲, △, Without KI. ●, ○, With 1.0 M KI. ▲, ●, As$^{\mathrm{III}}$. △, ○, As$^{\mathrm{V}}$. Cobalt(III) oxide powder: 30 mg.

With respect to arsenic(V), the recovery was 0% for both HCl concentrations of 1.0—10.0 M (Fig. 2a) and H_2SO_4 concentrations of 2.0—4.0 M (Fig. 2b). As in the case of arsenic(III), when potassium iodide was added to the aqueous solution, 100% recovery was obtained for both HCl concentrations of 6.0—10.0 M (Fig. 2a) and H_2SO_4 concentrations of 3.5—4.0 M (Fig. 2b).

Based on the above results, we used an easy-to-handle HCl solution with a small calorific value. The HCl concentration for extraction was set at 7.2 M.

Selection of Organic Solvent. As the organic phase used for extraction, the following solvents were studied: 1) diethyl ether, 2) benzene, 3) MIBK, and 4) a mixed solution of the above solvents in equal volumes. Figure 3 shows the variation in the recovery when the HCl concentration was varied while the concentration of potassium iodide was kept constant at 1.0 M. The ratio of the aqueous to the organic phase was 1 : 1. The results presented in Fig. 3 are outlined as follows.

As for both arsenic(III) and arsenic(V), 100% recovery was achieved by benzene extraction for HCl concentrations of 6.0—10.0 M; 88 and 96% of arsenic(III) were respectively recovered by benzene/diethyl ether and benzene/MIBK mixed-solvent extractions for HCl concentration of 6.0 M. Regarding arsenic(V), the recovery was 99% when benzene/diethyl ether mixed-solvent extractions were used for a HCl concentration of 6.0 M, while 100% recovery was achieved by using benzene/MIBK mixed-solvent extractions for the same HCl concentration.

Based on the above results, it was found that benzene alone can extract arsenic(III) and arsenic(V) over a wide range of extraction conditions. However, when arsenic was collected using cobalt(III) oxide powder, a mixture of benzene and MIBK was superior to pure benzene during the operation. For these reasons, we employed the following procedure in this study: arsenic was first extracted into benzene, to which 3 cm^3 of MIBK was added; then, arsenic was collected using cobalt(III) oxide powder.

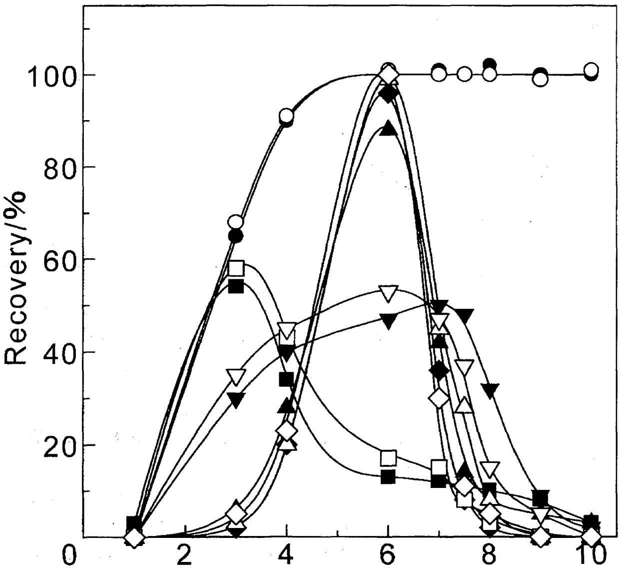

Fig. 3. Recovery of As^{III} and As^{V} from extraction process using various organic solvents in the case of HCl system. ●, ○, Benzene. ■, □, MIBK. ▲, △, Benzene/Diethyl ether mixed solvents. ▼, ▽, MIBK/Diethyl ether mixed solvents. ◆, ◇, Benzene/MIBK mixed solvents. ●, ■, ▲, ▼, ◆, As^{III}. ○, □, △, ▽, ◇, As^{V}. Concentration of KI: 1.0 M; Cobalt(III) oxide powder: 30 mg.

Effect of Concentration of Potassium Iodide. Potassium iodide (0.1—2.0 M) was added to an aqueous solution containing 1.0 μg of arsenic(III) or arsenic(V) to make 25 cm^3 of a 7.2 M HCl solution. The recoveries of the arsenic(III) and arsenic(V) were 100% for potassium iodide concentrations of 0.1—2.0 M. Therefore, we set the potassium iodide concentration at 1.0 M.

Effect of Extraction Time. Approximately 100% of arsenic iodide can be extracted by benzene in approximately 2 min, when the ratio of the aqueous to organic phase is 1 : 1. In this study, in order to completely extract arsenic in a single extraction operation, the extraction time was set at 5 min.

Collecting Condition of Arsenic on Cobalt(III) Oxide Powder. Effect of Stirring Time. Arsenic(III) and arsenic(V) were extracted into benzene; then, 30 mg of cobalt(III) oxide powder was added. The thus-prepared sample was stirred for various time periods and recovery was carried out. A recovery of approximately 50% was obtained for a stirring time of 1 min. The recovery was increased along with an increase in the stirring time; a recovery of 100% was obtained in the range of 5 to 30 min. Considering the requirements for rapid operation, the stirring time was set at 10 min.

Effect of Amounts of Cobalt(III) Oxide Powder. Five to 50 mg of cobalt(III) oxide powder was added to 25 cm^3 of organic phase containing arsenic(III) and arsenic(V), and the organic phase was stirred for 10 min; the recovery of the arsenic(III) and arsenic(V) was then determined. In the case of 10 to 50 mg cobalt(III) oxide powder being added, 100% recovery was attained; therefore, the amount of cobalt(III) oxide powder used in the proposed method was 30 mg.

Effect of Coexisting Ions. The effect of coexisting ions on the determination was studied in order to apply the method to environmental samples. Various kinds of ions coexisted in a 7.2 M HCl solution containing 1.0 μg of arsenic(III) or arsenic(V). According to a previously selected procedure, benzene extraction and collection of arsenic was performed using a prepared slurry with cobalt(III) oxide powder.

Table 2 shows the recoveries of arsenic for samples containing various kinds of ions. Because the pretreatment included benzene extraction and collection using cobalt(III) oxide powder, the recovery was 100±2% for every sample, regardless of the quantity of coexisting ions.

Calibration Curve. A calibration curve was obtained for a slurry sample prepared with the proposed method using a solution containing arsenic(III) or arsenic(V). The results indicate that the same calibration curve was obtained for arsenic(III) and arsenic(V), and that the dynamic range is 12-500 $\mu g\,dm^{-3}$.

Moreover, the method of concentrating the slurry onto the tungsten boat by repeating injection of the slurry sample was investigated; after a slurry containing arsenic (0.10 $mg\,dm^{-3}$) was added and dried on a tungsten furnace, the

Table 2. Effect of Foreign Ions on the Determination of Arsenic(III) and (V)

	Ion	Added^a)	Found/ng^b,c)		Recovery/%	
		mg	$\mathrm{As^{III}}$	$\mathrm{As^{V}}$	$\mathrm{As^{III}}$	$\mathrm{As^{V}}$
$\mathrm{As^{III}}$ $\mathrm{As^{V}}$	—	—	2.00	2.00	—	—
	$\mathrm{Na^{I}}$	150	2.02	2.00	101	100
	$\mathrm{K^{I}}$	150	2.01	1.97	101	99
	$\mathrm{Mg^{II}}$	150	2.00	2.00	100	100
	$\mathrm{Ca^{II}}$	150	2.04	1.98	102	99
	$\mathrm{Sr^{II}}$	1	2.01	2.01	101	101
	$\mathrm{Ba^{II}}$	5	1.99	2.00	99	100
	$\mathrm{Mn^{II}}$	3	2.03	2.04	102	102
	$\mathrm{Co^{II}}$	0.1	2.00	2.00	100	100
	$\mathrm{Ni^{II}}$	0.1	2.00	2.00	100	100
	$\mathrm{Cu^{II}}$	0.5	1.98	1.98	99	99
	$\mathrm{Zn^{II}}$	0.2	2.00	2.01	100	101
	$\mathrm{Cd^{II}}$	0.01	2.00	2.00	100	100
	$\mathrm{Sn^{II}}$	0.05	2.00	2.01	100	101
	$\mathrm{Pb^{II}}$	0.1	2.00	2.00	100	100
	$\mathrm{Al^{III}}$	200	2.03	2.02	102	101
	$\mathrm{Cr^{III}}$	0.2	2.03	2.02	102	101
	$\mathrm{Fe^{III}}$	200	1.97	1.97	99	99
	$\mathrm{Bi^{III}}$	0.1	2.00	2.00	100	100
	$\mathrm{Ti^{IV}}$	20	1.99	1.97	100	99
	$\mathrm{V^{V}}$	1	2.02	2.02	101	101
	$\mathrm{Mo^{VI}}$	0.01	2.00	1.97	100	99
	$\mathrm{SiO_3{}^{2-}}$	500	1.98	1.99	99	100
	$\mathrm{PO_4{}^{3-}}$	3	1.99	1.98	100	99

a) Sample volume: 25 cm^3; b) Slurry: 5 cm^3; 3) Injection volume: 10 mm^3.

Table 3. Analytical Results for Total Arsenic in Environmental and Geological Samples

Sample	Mean/μg g^{-1}	Reference value or Certified value/μg g^{-1}
JG-1a (Granodiorite)	0.41±0.02	0.43
JB-3 (Basalt)	1.65±0.04	1.84
JF-1 (Feldspar)	0.91±0.01	0.92
NIES No. 2 (Pond sediment)	11.5±1.0	12±2
NIES No. 9 (Sargasso)	117.3±2.8	115±9

addition and drying of the slurry on the tungsten furnace was repeated several times, and the absorbance was measured. The absorbance obtained by the repeated injection method from 1 to 5 times agreed with that by the one-time injection method, and the relative standard deviation was less than 3%. Consequently, the concentration method has been shown to be effective when the arsenic concentration in a sample is less than 10 μg dm^{-3}.

Application to Environmental and Geological Samples. The proposed method was applied to environmental samples from the National Institute for Environmental Studies (NIES) and geological standard rock samples from the Geological Survey of Japan (GSJ). These samples were dissolved in a sufficient volume of acid to make 50 cm^3; 10—20 cm^3 of the resulting solution was used for experiments. Six samples were collected from each of the environmental and geological samples, and arsenic determinations were performed three times for each dissolved sample solution. The determination of total arsenic employed a calibration curve obtained by the proposed method. The results revealed that the values determined by the proposed method agree well with the certified or reference value reported for each standard sample (Table 3).

In conclusion, the determination of trace amounts of arsenic in samples which have high concentrations of matrix components could be performed by ETAAS with a tungsten furnace following solvent extraction and collection of arsenic using cobalt(III) oxide powder as the pretreatment. The method was successfully applied to the determination of arsenic in several environmental and geological samples.

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