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## Determination of the Trace Amounts of Total Arsenic by Hydride Generation-AAS in Environmental Samples Using a Mixed Nitric-Perchloric- Sulfuric Acid as Pretreatment Agent

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### Abstract

Arsenic in environmental samples, pretreated with the mixed acid of nitric-perchloric-sulfuric, was subjected to hydride generation using sodium tetrahydroborate (III) solution. The arsine, evolving from the hydride generation system, was determined by atomic absorption spectrometry (AAS). Using the mixed acid of nitric-perchloric- sulfuric as pretreatment agents at 250°C, the time for the decomposition could be shortened and the blank value of arsenic from reagents used was reduced. The mixed acid of nitric-perchloric-sulfuric was also found to be effective pretreatment agent for organic arsenic compounds in which a dimethylated compound, sodium cacodylate has been known as one of the most indecomposables. The present approach was proven to be satisfactory as pretreatment of the quantitative analysis of the trace amounts of total arsenic in environmental samples.

### Introduction

It is well known that arsenic and its compounds vary in their toxicity according to the oxidation states and chemical forms of the arsenic<sup>1)</sup>. Not only in the study of environmental chemistry, but also in the geochemistry, as background of the former, the arsenic contained in environmental samples is necessary to be examined in its existing chemical forms and determined its concentration and distribution according to its chemical forms.

An analytical method using atomic absorption spectrometry in which the water sample containing arsenic is sprayed directly into flame is quite low in sensitivity. It has been applied only to a limited number of samples. In recent years, the following method has been widely used because of its high sensitivity: arsenic is transformed into arsine by use of a sodium tetrahydroborate (III) solution and introduced into the argon(nitrogen)-hydrogen flame or a heated quartz cell to atomize for atomic absorption spectrometry<sup>2)-7)</sup>.

The authors<sup>8)</sup> reported previously an analytical method to determine arsenic contained in geothermal water as follow: after the acidify of a geothermal sample has been adjusted, the arsenic concentration of it is transformed into arsine by use of sodium tetrahydroborate (III) solution, introduced into the nitrogen-hydrogen flame to atomize for atomic absorption spectrometry, and thus subjected to differential determination of inorganic arsenic (III) and the sum of arsenic (III+V) species using a calibration curve based on the relation between the peak height of corresponding spectral lines and the concentration of arsenic.

For the determination of arsenic contained in solid samples, pretreatment of the samples is necessary. In the pretreatment of solid samples, mixed acid<sup>9)</sup> of nitric-sulfuric-perchloric is generally used. In the case of samples such as soil, sediment and living body, for instance, which contain in a large amount of organic substances, loss of

arsenic<sup>10)</sup> can possibly take place when the nitric acid has been consumed before the organic substances are decomposed completely. To avoid such a trouble, chemical agents such as potassium permanganate and perchloric acid are added to keep the arsenic in a form of arsenic (V) during the decomposition period.

Terashima *et al.*<sup>11)</sup> used a Teflon beaker for the decomposition of a sample containing arsenic, and reported a wet decomposition method using the mixed acid of perchloric acid-nitric acid-potassium permanganate. For the decomposition of a sample containing silicates, they added the need of further addition of hydrofluoric acid. Yamamoto *et al.*<sup>6)</sup> used a Kjeldahl flask in the sample decomposition operation, and reported a decomposition method using the mixed acid of nitric-sulfuric-hydrochloric acid. Maeda *et al.*<sup>12)</sup> reported such an arsenic analytical method as follows: a sample was added with magnesium nitrate, subjected to wet decomposition, dissolved in an aq. solution of hydrochloric acid and potassium iodide, and back-extracted in chloroform, which was then subjected to total arsenic determination by the use of the carbon tube atomizer-AAS system. Jin *et al.*<sup>13)</sup> examined not only *p*-arsanilic acid, but also arsenobetaine by a mixed acid of nitric-perchloric-sulfuric. However, the detailed conditions, such as temperature and time of decomposition, were not reported. The authors investigated in detail the temperature and decomposition time using inorganic, organic arsenic environmental standard samples, such as sediment and biological samples.<sup>14)</sup>

This study reported below was to establish the pretreatment method of the solid samples such as sediments and biological samples for total arsenic determination inclusive of organic arsenic.

Using samples of inorganic and organic arsenic compounds and solid samples, the temperature and decomposition time for the pretreatment were done in detail for the wet decomposition methods using nitric-perchloric-sulfuric mixed acids. As a result, a good enough sample pretreatment method was found for the determination of total arsenic in such solid samples such as of sediments and biological samples.

## Experimental

### Apparatus

Atomic absorption measurement was performed using Nippon Jarrel-ash Model AA-855, equipped with a heated quartz cell supplied with nitrogen, and with Hamamatsu T.V. hollow-cathode lamp. Absorbances were recorded with a Shimadzu U-125 MN recorder. A Shimadzu Arsenic Analyzer (Model ASA-1) arsine generation system and a Nippon Jarrel-ash arsine generation system (Model HYD-20) were used. In this study, sodium

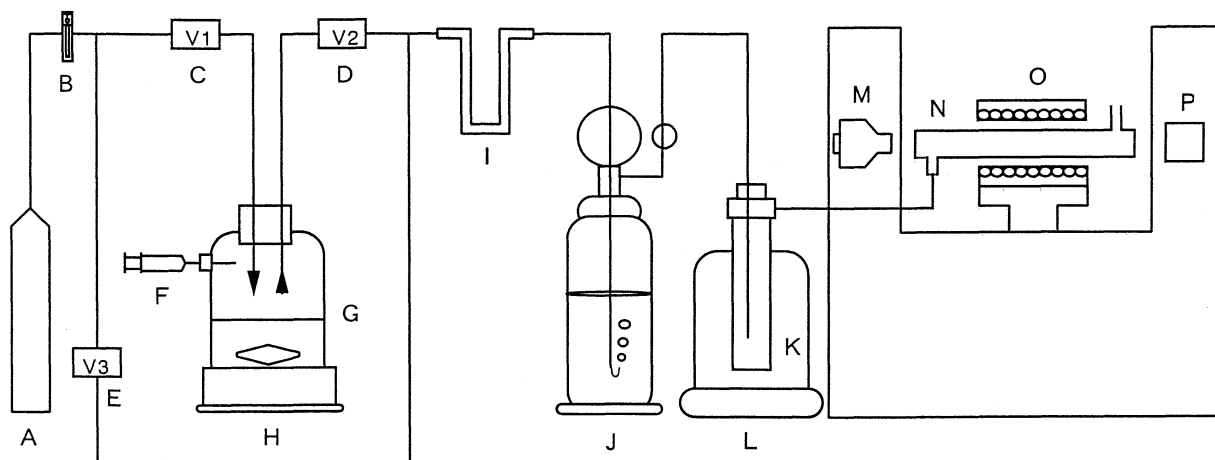


Fig. 1 Schematic diagram of analytical apparatus: A. Nitrogen cylinder, B. Flow meter, C, D, E. Magnetic valve, F. Syringe, G. Reaction vessel, H. Magnetic stirrer, I. U tube (packed with glass wool wetted by a 10% aq. soln. of lead acetate), J. Washing bottle, K. Dehumidication vessel, L. Cold trap, M. Hollow-cathode lamp, N. Heated quartz cell, O. Electric furnace, P. Atomic absorption spectrophotometer.

tetrahydroborate (III) was used as a solution which was injected through a silicone rubber stopper of a side arm of the vessel by syringe. The schematic diagram of analytical apparatus is given in Fig. 1. The hydride generation system was assembled with a switch, a timer, a magnetic valve, a magnetic stirrer, U-tube *etc.* The U-tube was packed with glass wool wetted by a 10% aq. solution of lead acetate to remove hydrogen sulfide. The hydrogen chloride gas evolved from the hydride generator was excluded with water in a gas washing bottle. The cold trap after the gas washing bottle was used for dehumidification.

The reaction vessel was glass-made, and the packing was made of silicone rubber. The carrier gas used was nitrogen. As the atomizer of arsine, heated quartz cell was used.

#### *Reagents*

Standard solution of arsenic (III), 1,000 mg l<sup>-1</sup>. A commercially available arsenic (III) for atomic absorption was obtained from Nacalai tesque Co.. A working solution (0.1 mg l<sup>-1</sup>) were prepared by dilution this solution with 0.1 M hydrochloric acid.

Standard solution of arsenic (V), 1,000 mg l<sup>-1</sup>. An amount of 2.40 g of potassium dihydrogen arsenate (V) was dissolved in pure water and then diluted to 1,000 ml with pure water.

Standard solution of organic arsenic, 1,000 mg l<sup>-1</sup>. An amount of 0.291 g of *p*-arsanilic acid was dissolved in pure water and then diluted to 1,000 ml with pure water.

Standard solution of organic arsenic, 1,000 mg l<sup>-1</sup>. An amount of 0.295 g of sodium cacodylate trihydrate was dissolved in pure water and then diluted to 1,000 ml with pure water.

Sodium tetraborohydride solution, 3% solution containing 0.1 M sodium hydroxide. An amount of 6 g of sodium tetrahydroborate (III) was dissolved in 200 ml of 0.1 M sodium hydroxide solution.

The acids (hydrochloric acid, nitric acid, sulfuric acid, perchloric acid), potassium permanganate and potassium peroxodisulfate were used for the measurement of toxic metals.

All other reagents used were of analytical reagent grade purity and ultrapure water was prepared by purifying distilled water with a Milli-Q SP system just before use.

#### *Determination of the sum of inorganic arsenic (III+V) species*

The standard procedure for the determination of arsenic species are as follows, instrumental conditions are given in Table 1.

A volume of 40 ml of a sample solution (As(III+V) ≤ 0.5 µg) was taken, and added with 5 ml of concentrated hydrochloric acid and 5 ml of 40% potassium iodide solution into the hydride generation vessel. The vessel in the hydride generation system was then set-up. The magnetic stop cock was turned to open, and the system was flushed with the nitrogen gas for 40 s to replace air, agitating the solution with a magnetic stirrer. Then the magnetic stop cock was turned to by-pass and inject 2 ml of 3% Sodium tetrahydroborate (III) solution within 20 s. After 60 s of the gas sampling time, the magnetic stop cock was turned to open automatically and introduce arsine into the heated quartz cell. The arsenic was determined by AAS.

Table 1 Instrumental conditions for arsenic determination

Wavelength (nm)	193.7
Spectral band width (nm)	0.68
Hollow cathode lamp current (mA)	5
Measurement mode	AA
Carrier gas (N <sub>2</sub> ) flow rate (l min <sup>-1</sup> )	0.6
Heated quartz cell temperature (°C)	1,000
Recorder range (mA)	100
Chart speed (mm min <sup>-1</sup> )	10

### Determination of total arsenic

Total arsenic determination of environmental samples (sediments, biological samples *etc.*) was done using the decomposition methods described later which were applied also to the samples of organic arsenic compounds and solid samples. For the determination of total arsenic, the method for the determination of the sum of arsenic (III+V) species was used. As to the solid samples, they were used after having been ground into a form of powder by use of a agate mortar.

## Results and Discussion

### Calibration curves

The calibration curves for arsenic (III) and arsenic (V) in the determination of the sum of inorganic arsenic (III+V) species are shown in Fig. 2.

The calibration curves for arsenic (III) and arsenic (V) used in the arsenic determination method were obtained with good accordance within the concentration range from 0 to 0.5  $\mu\text{g}/40\text{ ml}$ . Therefore, the sum of arsenic (III) and arsenic (V) can be determined by this method. However, using *p*-arsanilic acid organic was determined only 10% of the total concentration, and sodium cacodylate was hardly determined. Therefore, a pretreatment is necessary in order to determine the organic arsenic quantitatively as well as the inorganic arsenic.

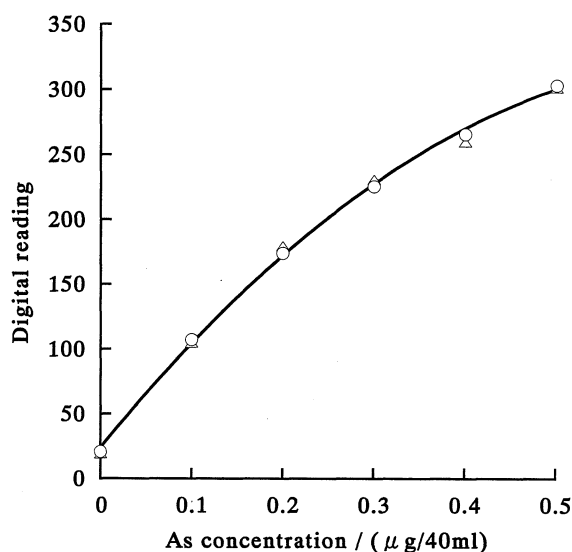


Fig. 2 Calibration curves for inorganic arsenic (III) and arsenic (V).  
Symbols: ○, arsenic (III), △, arsenic (V).

### Sample pretreatment for total arsenic determination

Using the method for the determination of the sum of inorganic arsenic (III) and arsenic (V) species verified as above, standard solutions of arsenic (III) and samples of *p*-arsanilic acid and sodium cacodylate as reference materials for organic arsenic compounds were subjected to arsenic determination without sample pretreatment, results are shown in Fig. 3. A method aimed for the determination of inorganic arsenic (III+V) species was found to be impossible to determine organic arsenic. This fact led to the idea that the solid samples containing organic arsenic should be pretreated by some means to transform any organic arsenic to inorganic form. In the group of methylated arsenic compounds, a dimethylated compound sodium cacodylate is known to be one of the most indecomposables. It was therefore presumed that, if any method could be found to decompose sodium cacodylate completely, all other organic arsenic compounds could be also decomposed.

As the sample decomposition vessel, Teflon and a volumetric flask were used. Using a mixed acid of nitric-

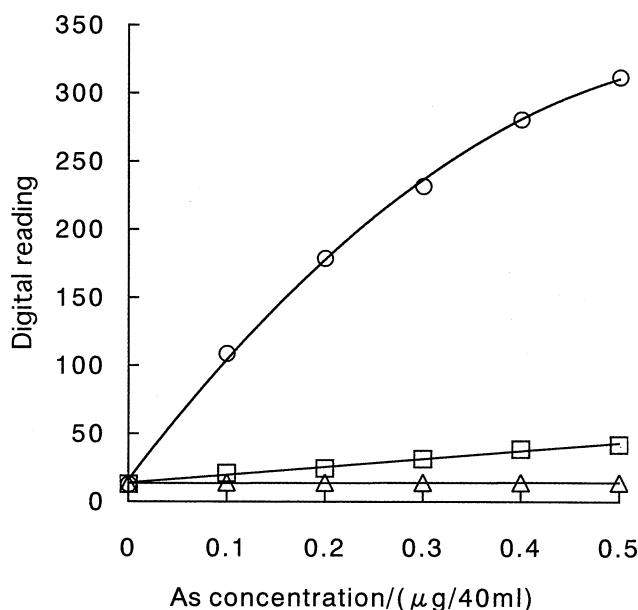


Fig. 3 Calibration curves for inorganic and organic arsenic using the method for determination of sum of arsenic (III) and arsenic (V).

Symbols:  $\circ$ , arsenic (III),  $\square$ , *p*-arsanilic acid,  $\triangle$ , sodium cacodylate.

perchloric-sulfuric combined with potassium permanganate or potassium peroxodisulfate, a detailed study was done on the wet pretreatment methods from (1) to (3) as described below.

#### *Sample pretreatment method (1)*

A sample (of inorganic arsenic (III) or of *p*-arsanilic acid or sodium cacodylate as organic arsenic standard materials) was placed in a Teflon vessel, added with 2 ml mixture of nitric acid-perchloric acid in a 1:1 volume ratio and 5 ml of 5M sulfuric acid, and heated on a hot plate at 120°C for 60 min to undergo decomposition. After cooled down, it was added with 0.5 ml of 10% hydroxyl ammonium chloride, and made into a definite constant volume (100 ml) by addition of pure water. The sample thus pretreated, was put in the reaction vessel in an amount of 40 ml and then subjected to arsenic determination using the verified method for determination of the sum of inorganic arsenic (III+V) species.

#### *Sample pretreatment method (2)*

A sample was put in a Teflon vessel, added with 20 ml of 2.5% potassium peroxodisulfate and 5 ml of 5M sulfuric acid, and heated on the hot plate at 200°C for 60 min to decompose. After cooled down, it was added with 1 ml of 20% ascorbic acid, and then treated similarly to the case of pretreatment method (1).

#### *Sample pretreatment method (3)*

A sample was put in a 50 ml long-necked flask, added with 2 ml mixture of nitric acid-perchloric acid in a 1:1 volume ratio and 5 ml of concentrated sulfuric acid and heated on the hot plate at 250°C for 70 min to decompose. After cooled down, it was made to a definite constant volume (50 ml) by addition of pure water, and then treated similarly to the case of pretreatment method (1).

The samples of inorganic arsenic (III) and those of *p*-arsanilic acid and sodium cacodylate as reference materials for organic arsenic compounds were treated by sample pretreatment methods from (1) to (3) and then subjected to arsenic determination using of the verified method for determination of the sum of inorganic arsenic (III+V) species, the results are shown in Table 2.

It was proven from these results, that in solution with *p*-arsanilic acid, 100% recovery of arsenic was found in the sample pretreatment methods (1) to (3), while in solution with sodium cacodylate insufficient decomposition

Table 2 Recovery of arsenic from standard sample by several pretreatment methods

	Added (as As) $\mu\text{g}$	Found <sup>a</sup> (as As) $\mu\text{g}$		
		Method 1 <sup>b</sup>	Method 2 <sup>c</sup>	Method 3 <sup>d</sup>
As (III)	0.25	0.25 (100) <sup>e</sup>	0.25 (100) <sup>e</sup>	0.25 (100) <sup>e</sup>
	0.50	0.49 (98.0)	0.50 (100)	0.50 (100)
<i>p</i> -Arsanilic acid	0.25	0.25 (100) <sup>e</sup>	0.24 (96) <sup>e</sup>	0.25 (100) <sup>e</sup>
	0.50	0.49 (98.0)	0.49 (98.0)	0.50 (100)
Sodium cacodylate	0.25	<0.01 (< 4) <sup>e</sup>	0.04 (16) <sup>e</sup>	0.25 (100) <sup>e</sup>
	0.50	<0.01 (< 2)	0.07 (14)	0.50 (100)

a. Mean of 5 determinations.

b. Added 2 ml of  $\text{HNO}_3\text{-HClO}_4$  mixture (volume ratio of 1:1) and 5 ml of 5M  $\text{H}_2\text{SO}_4$ , and heated on a hot plate at  $120^\circ\text{C}$  for 60 min to undergo decomposition.

c. Added 20 ml of 2.5%  $\text{K}_2\text{S}_2\text{O}_8$  and 5 ml of 5M  $\text{H}_2\text{SO}_4$ , and heated on a hot plate at  $200^\circ\text{C}$  for 60 min to undergo decomposition.

d. Added 2 ml of  $\text{HNO}_3\text{-HClO}_4$  mixture (volume ratio of 1:1) and 5 ml of concentrated  $\text{H}_2\text{SO}_4$ , and heated on a hot plate at  $250^\circ\text{C}$  for 70 min to undergo decomposition.

e. Figures in parentheses indicate recovery percentage.

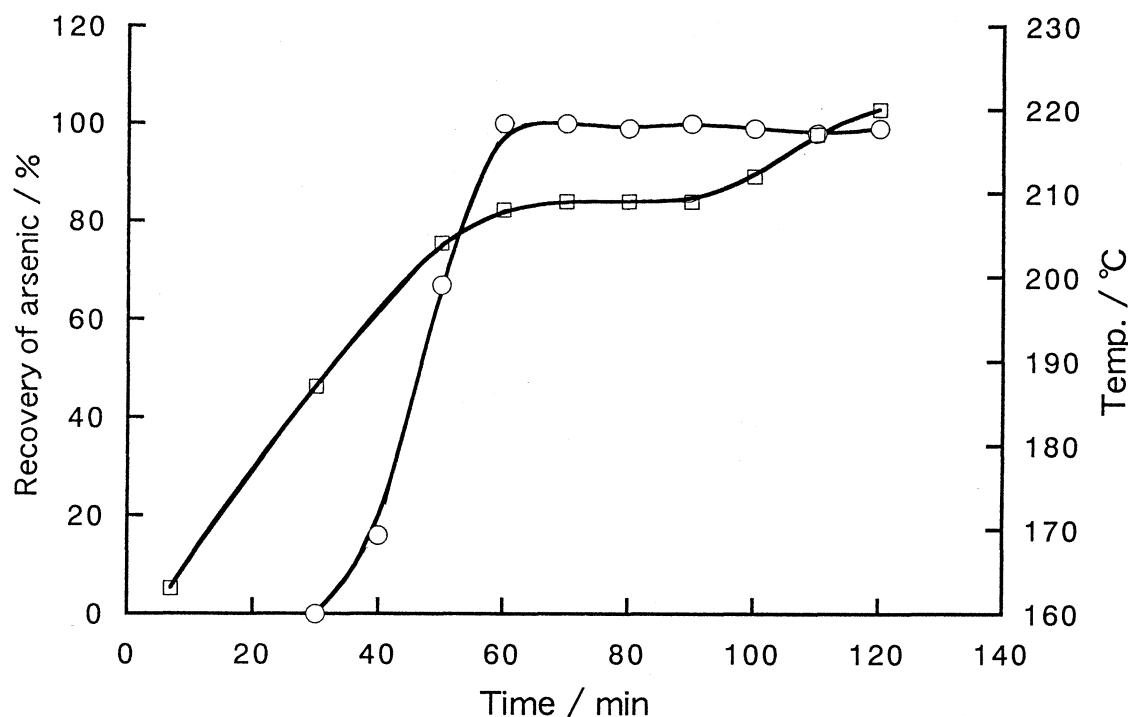


Fig. 4 Effect of the heating temperature and time on the recovery of arsenic.

Symbols: ○, recovery percentage of arsenic[sodium cacodylate (As 0.10  $\mu\text{g}$ )], □, temperature of solution.

was found in the methods (1) and (2). It was proven from these that the use of sample pretreatment method (3) can give 100% recovery of arsenic for the samples of inorganic arsenic (III) as well as *p*-arsanilic acid and sodium cacodylate use as reference materials for organic arsenic compounds.

#### *Effect of heating temperature and time on the recovery of arsenic*

Using sample of sodium cacodylate containing 0.10  $\mu\text{g}$  of arsenic, the sample pretreatment method [shown in (3)] was examined in terms of the effect of heating temperature and time on the recovery of arsenic. The results are shown in Fig. 4. Heating the solution on a hot plate at *ca.*  $250^\circ\text{C}$  increased the temperature inside the

decomposition vessel rapidly to 220°C for *ca.* 60 min, while after 90 min the temperature gradually increased with time. As can be seen from Fig. 4, the recovery of arsenic from sodium cacodylate was constant (100%) irrespective of the time from 60 min to 120 min. Therefore, subsequent experiments were conducted at *ca.* 210°C for the solution temperature and 90 min for the heating time. It was also found that, with use of the sample pretreatment method (3), arsenic contained in sodium cacodylate can be determined by the verified method for the determination of inorganic arsenic (III+V) species.

#### Reproducibility

Table 3 shows the reproducibility for standard arsenic solutions in several arsenic forms using a pretreatment method (3) with a mixed acid of nitric-perchloric-sulfuric under the optimum conditions. The table indicates that 0.30 and 0.50 µg of arsenic (inorganic and organic arsenic) were determined with an excellent reproducibility by the pretreatment method (3).

The detection limit (base on S/N=2) in the determination for arsenic analysis was found to be 0.015 µg/40 ml. In five times repetitive measurements of samples containing 0.3 and 0.5 µg of arsenic, the average value and the relative standard deviation were 0.28-0.29, 0.48-0.50 µg and 2.7-4.0%, 2.0-2.2%, respectively.

Furthermore, in a comparison between the calibration curves obtained by peak area (RSD 1.9 %) and peak height methods (RSD 4.3 %) the former gave a smaller relative standard deviation at each of concentrations than the latter, indicating the higher reproducibility for the former. In the experiment hereafter, preparation of a calibration curve was therefore done by use of the peak area method.

Using the standard samples of pond sediments<sup>15)</sup> and vehicle exhaust particulates<sup>16)</sup> now available to produced

Table 3 Reproducibility of data for arsenic in standard solutions using the HNO<sub>3</sub>-HClO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> pretreatment method

Sample	Taken/µg	Found <sup>a</sup> /µg	SD <sup>b</sup> /µg	RSD <sup>c</sup> , %
As (III)	0.30	0.29	0.008	2.7
	0.50	0.50	0.010	2.0
<i>p</i> -Arsanilic acid	0.30	0.28	0.009	3.0
	0.50	0.49	0.011	2.2
Sodium cacodylate	0.30	0.29	0.012	4.0
	0.50	0.49	0.011	2.2

a. Mean of 5 determinations.

b. Standard deviation.

c. Relative standard deviation.

Table 4 Determination of total arsenic in standard reference materials using several pretreatment methods

Decomposition method	As content/mg kg <sup>-1a</sup>	
	Pond sediment NIES <sup>b</sup> No.2	Vehicle exhaust particulates NIES <sup>b</sup> No.8
Method 1 <sup>c</sup>	3.7	1.5
Method 2 <sup>d</sup>	9.4	2.9
Method 3 <sup>e</sup>	13.3	2.8
Certified values	12 ± 2	2.6 ± 0.2

a. The content of arsenic is converted to these values when samples are heated at 110 °C for 6 hr.

b. The sample is produced by National Institute for Environmental Studies.

c. Added 2 ml of HNO<sub>3</sub>-HClO<sub>4</sub> mixture (volume ratio of 1:1) and 5 ml of 5M H<sub>2</sub>SO<sub>4</sub>, and heated on a hot plate at 120°C for 60 min to undergo decomposition.

d. Added 20 ml of 2.5% K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and 5 ml of 5M H<sub>2</sub>SO<sub>4</sub>, and heated on a hot plate at 200 °C for 60 min to undergo decomposition.

e. Added 2 ml of HNO<sub>3</sub>-HClO<sub>4</sub> mixture (volume ratio of 1:1) and 5 ml of concentrated H<sub>2</sub>SO<sub>4</sub>, and heated on a hot plate at 250 °C for 70 min to undergo decomposition.



Table 5 Recovery of total arsenic from spiked samples using the  $\text{HNO}_3\text{-HClO}_4\text{-H}_2\text{SO}_4$  pretreatment method

Sample	Sample weight/g	Taken (as As) / $\mu\text{g}$		Found <sup>a</sup> As/ $\mu\text{g}$
		As <sup>3+</sup>	Me <sub>2</sub> AsO <sub>2</sub> Na <sup>b</sup>	
Marine sediment <sup>c</sup>	0.100	-	-	0.98
	0.100	1.00	0.00	2.00 (101) <sup>i</sup>
	0.100	0.00	1.00	1.86 (93.9)
Spring sediment <sup>d</sup>	0.200	-	-	1.08
	0.200	0.50	0.00	1.55 (98.1) <sup>i</sup>
	0.200	0.00	0.50	1.43 (90.5)
Volcanic ashes <sup>e</sup>	0.500	-	-	1.20
	0.500	0.20	0.00	1.43 (102) <sup>i</sup>
	0.500	0.00	0.20	1.34 (95.7)
Marine algae <sup>f</sup>	0.100	-	-	10.7
	0.100	1.00	0.00	11.9 (102) <sup>i</sup>
	0.100	0.00	1.00	11.9 (102)
Shellfish meat <sup>g</sup>	0.200	-	-	1.58
	0.200	0.50	0.00	2.14 (103) <sup>i</sup>
	0.200	0.00	0.50	2.05 (98.6)
Fish meat <sup>h</sup>	0.200	-	-	0.82
	0.200	0.50	0.00	1.33 (101) <sup>i</sup>
	0.200	-	0.50	1.28 (97.0)

a. Air dry basis, b. Sodium cacodylate, c. Kagoshima Bay, d. Kurino Yahata jigoku, e. Mt. Sakurajima, f. NIES No.9 Sargasso, g. NIES No.6 Mussel, h. Trachurus captured at outside of Kagoshima Bay, i. Figures in parentheses indicate recovery percentage.

NIES (National Institute for Environmental Studies), the sample pretreatment methods from (1) to (3) were compared in terms of total arsenic determination, of which results are given in Table 4. As seen in Table 4, the sample pretreatment methods (1) and (2) gave smaller values than the certified values, while the method (3) gave values close to the certified values.

#### *Application to actual samples*

Using the sample pretreatment method for total arsenic determination, actual samples added with inorganic arsenic (III) and organic arsenic (sodium cacodylate) were subjected to wet decomposition, which were then brought to arsenic analysis using of the verified method for determination of the sum of inorganic arsenic (III+V) species and studied in terms of recovery of arsenic.

As can be seen in Table 5, the results were obtained with good recovery of arsenic for almost all samples. From these, it is concluded that the present method is applicable enough to actual samples.

## Conclusion

The method for determination of inorganic arsenic (III+V) species by means of atomic absorption spectrometry using a heated quartz cell hydride generation system can analyze arsenic contained in a liquid samples at a concentration level of 0.25 to 7.5  $\mu\text{g l}^{-1}$ .

With the aim of total arsenic determination of solid environmental samples, various sample pretreatment methods were studied in detail. By combined use of the nitric-perchloric-sulfuric mixed acid as a pretreatment agent with heating at 220°C (solution temperature) for 30 min, the sample of sodium cacodylate, which is well known as a indecomposable organic compound, was decomposed completely. From these, it was proved that, heating the solution on a hot plate at 250°C, with use of mixed acid (nitric-perchloric-sulfuric acid), the solid environmental samples of sediments and biological samples can be determined in terms of total arsenic by means of the verified method for the determination of the sum of inorganic arsenic (III+V) species in liquid samples using

the atomic absorption spectrometry which utilizes the hydride generation-heated quartz cell system.

Further, the proposed pretreatment method was successfully used for the determination of trace amounts of total arsenic in environmental solid samples.

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