Large Aliquot Injection Approach in the Electrothermal AAS Determination of Arsenic in Environmental Water Samples

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Determination of As by direct electrothermal atomization atomic absorption spectrometry with a pyropytically-coated graphite furnace treated with W by a single drop treatment technique was reported. The treated PG furnace made it possible to introduce a 100 μl aliquot of sample solution into the furnace with a high precision (RSD <4%). Use of a Pd-modifier made it possible to enhance the precision (RSD <3%) and the sensitivity. A good linearity (correlation factor >0.99) between integrated absorbance and injection volume was observed in the range 0 – 100 μl. The calculated detection limit and characteristic mass (sensitivity) for integrated absorbance were 22 ng l^{-1} and 16 pg and for maximum absorbance were 45 ng l^{-1} and 13 pg for a 100 μl injection with the Pd modifier at the optimum ashing temperature of 800 °C. An interference study for environmental matrices was also carried out. The recoveries of 2 and/or 4 μg l^{-1} of As added to various water samples, such as snow, cloud, river and tap waters, were 97 – 104%.

Arsenic is known to be a toxic agent which can accumulate in the human body over a lifetime. The determination of As at low concentration levels in water has become important in monitoring public health and for environmental studies. The mean concentration of As in rain and snow water in arctic catchments in northern Europe ranged from 0.08 to 5.1 μg l^{-1} and from 0.1 to 1.8 μg l^{-1}, respectively.[1] At the top or near the top of five mountains (700 – 1500 m altitude) in Akita in North Japan, located in the area along the Japan Sea, that in snow ranged from 0.17 to 0.99 μg l^{-1}.[2] Background levels of As concentration of stream water in the world are 0.1 – 4 μg l^{-1}.[1] Probably the most frequently used analytical techniques for As determinations in water are hydride generation atomic absorption spectrometry (HGAAS), inductively coupled plasma atomic emission (ICP-AES) and mass spectrometry (ICP-MS) because of its high sensitivity. The limits of detection (LODs) of various hydride generation analytical methods were reported, *e.g.* LODs of direct-HGAAS to be 0.058, 0.07 and 0.2 μg l^{-1};[3-5] LODs of preconcentration techniques 6 ng l^{-1} in 200 ml for ion-exchange HGAAS,[6] 60 ng l^{-1} in 10 ml for *in-situ* collection of hydride in graphite furnace atomizer with next ETAAS,[7,8] 12 ng l^{-1} for *in-situ* collection of hydride ETV-MIP-AES,[9] 60 ng l^{-1} in 50 ml for liquid absorption traps of hydride with next ETAAS[10,11] and 31 ng l^{-1} in 300 ml for chelate extraction HGAAS.[12] The ICP-MS is generally a highly sensitive technique, but the determination of As is complicated by the fact that the $^{75}ArCl^+$ ion has the same nominal mass as that of $^{75}As^+$. The determination of samples containing even small but variable levels of chloride may not therefore be possible using Ar plasma. The interference of Cl is one of the serious problems in the determination of the environmental water samples for As, such as snow, cloud, river and tap. In order to eliminate the $^{75}ArCl^+$ molecular interference within direct determination of As in fresh and saline waters, ETV-ICP-MS with a chemical modifer was examined. The improved LOD was 6.9 ng l^{-1} in the presence of chloride matrix up to 10000 mg l^{-1}.[13] Although ETAAS is a highly sensitive analytical technique extensively used in the direct determination of water for numerous elements because of its versatility, speed and specificity, determination of low-levels of metal in the water samples includes problems. The LOD for As in aqueous standard solution with direct determination is 1.0 μg l^{-1} for injection volume of 20 μl and improved LOD is approximately 0.2 μg l^{-1}.[14] Consequentry, highly sensitive and speedy ETAAS techniques are necessary to determine water samples including the low-levels of As for monitoring public health and for environmental studies.

The injection of a large sample volume can be used to minimize the analytical time and enhance the sensitivity without further contamination. It was reported for Pb that coating of a pyropytically-coated graphite (PG) furnace with a carbide refractory element was examined. The W-coated PG furnace was found to give a high precision (RSD <3%) for a 100 μl injection of sample solution and to give a good linearity (correlation factor >0.99) between the sample volume and integrated absorbance up to an injected volume of 100 μl.[15] Problems arise due to interference from the enriched matrix and also due to a memory effect.

Chemical modification is preferred as a simple approach to overcome the matrix interferences encountered especially in the direct analysis in samples with complex matrices.

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Bermejo–Barrera et al.[16] compared various chemical modifiers for determination of trace metal in seawater with an aliquot sample of 20 µl: $Pd(NO_3)_2$, $Mg(NO_3)_2$, $Pd(NO_3)_2–Mg(NO_3)_2$, $Pd(NO_3)_2$-ascorbic acid, $Pd(NO_3)_2–HONH_3Cl$, $Pd(NO_3)_2$–citric acid, $LaCl_3$, $ZrOCl_2$ and $AgNO_3$ to indicate characteristic mass values of 13, 32, 14, 12, 13, 14, 31, 20 and 21 pg, respectively. The LOD for those modifiers was 1.1 (22), 3.0 (60), 1.2 (24), 1.1 (22), 1.1 (22), 1.2 (24), 3.0 (60), 2.0 (60), and 2.2 µg l^{-1} (44 pg), respectively. Palladium modifier is an excellent modifer for As.

In this work it is reported that the W-coated PG furnace allowed the development of a valid and feasible analytical method for the direct determination of low levels of As in water samples, such as snow, cloud, river and tap waters, by using a 100 µl injection with a Pd modifier.

Experimental

Instrumentation and reagents

A Hitachi Model Z-7000 graphite furnace atomic absorption spectrometer equipped with a Zeeman-effect background corrector and an automatic data processor (Hitachi Ltd., Marunouchi, Tokyo, Japan) was used without an optical temperature controller system (Hitachi Model 180-0341). Collection of absorbance signals and absorbance integration were carried out by the data processor. Absorbance data (integrated absorbance and maximum absorbance) were printed out automatically. Pyrolytic graphite furnaces (Part No. 190-6003, Hitachi Ltd.) were utilized throughout. When a chemical modifier was used, it was injected separately from sample solutions. A Hitachi hollow cathode lamp (Hitachi Part No. 001-6103) was used as the light source. The time constant of 0.2 s for signal processing was used to reduce the noise from the optics. Current-controlled heating during atomizing was selected due to the slow signal processing. Gilson micropipets (Gilson Medical Electronics, Villiers-le-Bel, France) were used for sample injection and to prepare solutions. The accuracy of the dispensed volumes was periodically checked by weighing.

A commercially available stock solution of As was used (1000 mg l^{-1} of As as As_2O_3 with 0.05% NaCl in HCl solution: Kanto Chemical Co., Inc., Nihonbashihoncho, Tokyo, Japan). An aliquot of this solution was properly diluted before use. A commercially available stock solution of chemical modifier of Pd (10000 mg l^{-1} of Pd in 15% HNO_3: Kanto Chemical Co., Inc.) was used. The modifier stock solution was diluted ten times with water and used as a working modifier solution. Aqueous solutions including 0.1 mol l^{-1} of W was prepared as a treatment solution. Sodium tungstate(VI) dihydrate (Kanto Chemical Co., Inc.) was used. Other solutions were prepared from analytical-reagent grade chemicals. The water was purified by a Milli-Q Academic system after deionization by an Elix 5 system (Millipore Co., Inc.).

Recommended procedure

The recommended procedure for the determination of As is as follows: A 5 µl aliquot of matrix modifier (Pd: 1000 mg l^{-1} in 1.5% HNO_3) was introduced additionally into a W-treated PG furnace by manual pipetting after a 100 µl aliquot of sample solution was introduced. The integrated absorbance corresponding to As atomized was obtained during the standard atomization cycle which is summarized in Table 1. An Ar gas stop in the atomizing step was utilized for high sensitivity. The blank solution was tested for Pb contamination from the atmosphere and the contamination was monitored. No contamination was observed during the period of experiment.

The surface treatment of furnace was carried out by a one-drop coating method without soaking, viz., 100 µl of a 0.1 mol l^{-1} solution of W were injected into a PG furnace, and the furnace was heated according to the atomization temperature program given in Table 1.

Water samples

Four snow samples were taken in Akita city (Akita, Japan). Four snow samples were taken on the campus of the University of Iwate (Morioka, Japan). Three cloud water samples were collected along the mountainside of Mt. Mokkodake (1578 m altitude), a mountain ridge in the Hachimantai range (Akita, Japan), where is a clean area of north of Japan. Three river water samples were taken from the Katsuuragawa River (Tokushima, Japan). Three tap water samples were taken from the campuses of the University of Tokushima (Tokushima, Japan) and the University of Iwate (Morioka, Japan) and from a residential section in Komatsushima city (Tokushima, Japan). The tap water sample was taken after running the tap for a few minutes. The water sample was analyzed without further treatment.

Results and Discussion

Table 2 shows the integrated absorbance, maximum absorbance and relative standard deviation (RSD; $n = 5$) for 100 µl injections of 4 µg l^{-1} of As using the bare and W-treated PG furnace with and without a Pd modifier (5 µl of 1000 mg l^{-1}). Since the absorbance of As decreased above 500 (for 20 µl injection) and 1400°C for the bare PG furnace without and with

Table 1　Standard operation conditions

Atomizer operation Stage		Temperature/°C	Time/s	Ar/ml m^{-1}
1	Dry	80 – 120	30	200
2	Ashing	120 – 800	20	200
3	Ashing	800 – 800	20	200
4	Atomizing[a]	3000 – 3000	6	0
5	Cleaning	2800 – 2800	3	200
Wavelength 193.7 nm		Bandwidth 1.3 nm		Time constant 0.2 s

a. Current control.

Table 2　Integrated absorbance ($\int$abs), maximum absorbance (A_{max}) and precision for 4 µg l^{-1} As with 100 µl introduction

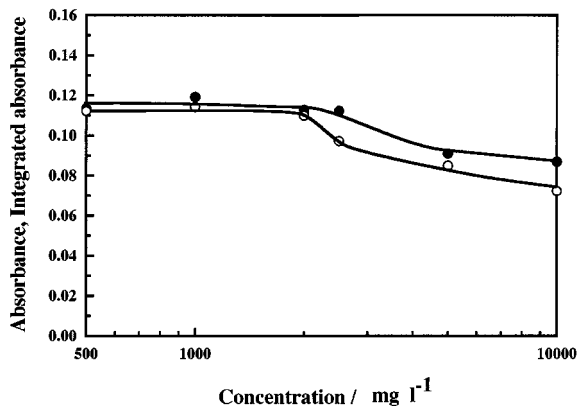| Furnace	Ashing temp. / °C	Pd-modifier	$\int$abs	RSD, %	A_{max}	RSD, %
Bare PG	500	non	0.0199 ± 0.0023	11	0.0192 ± 0.0023	12
Bare PG	800	added	0.0845 ± 0.0023	2.7	0.0867 ± 0.0006	0.7
W-PG	800	non	0.0946 ± 0.0015	1.6	0.0904 ± 0.0035	3.9
W-PG	800	added	0.1196 ± 0.0021	1.7	0.1138 ± 0.0031	2.7

Fig. 1   Effect of concentration of Pd modifier on integrated (●) and maximum (○) absorbances of 4 μg l⁻¹ of As with a W-treated PG furnace. Sample volume: 100 μl.

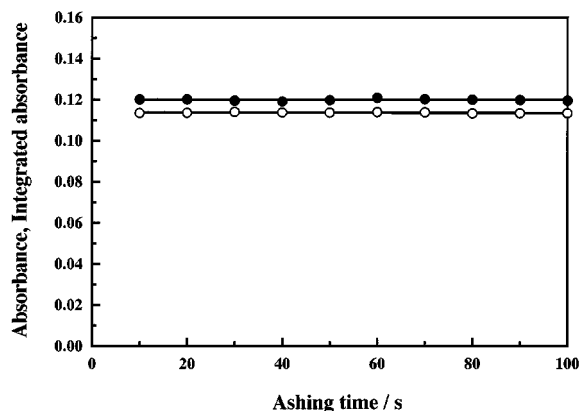
Fig. 3   Effect of hold time of ashing at 800°C of ashing temperature on integrated (●) and maximum (○) absorbances of 4 μg l⁻¹ of As with a W-treated PG furnace. Sample volume: 100 μl.
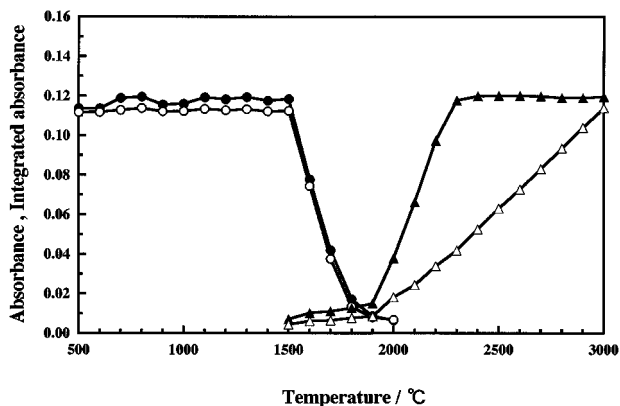

Fig. 2   Ashing and atomization temperature curves for 4 μg l⁻¹ of As with a W-treated PG furnace. Sample volume: 100 μl. Integrated absorbance, ● , ▲ ; maximum absorbance, ○ , △ . Ashing curve, ● ○ ; atomization curve, ▲ △ .
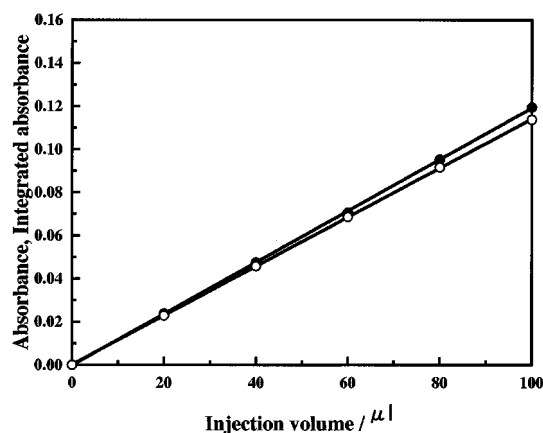

Fig. 4   Effect of injection volume on integrated (●) and maximum (○) absorbances of 4 μg l⁻¹ of As with a W-treated PG furnace.

Pd modifier, an ashing temperature of 500 and 800°C was used, respectively. When the absorbance of As decreased above 1700 and 1500°C for the W-treated PG furnace without and with Pd modifier, an ashing temperature of 800°C was used. The use of Pd modifier and W-treated PG furnace increased the integrated and maximum absorbance. The combination of Pd modifier and W-treated PG furnace gave the best improved sensitivity. The W-treated PG furnace was used as a working furnace with Pd modifier. The integrated and maximum absorbance were kept constant throughout the 5 – 350 and 50 – 350 firings, respectively.

Figure 1 shows the effect of concentration of Pd on integrated absorbance of As (4 μg l⁻¹) according to the recommended procedure. The maximum volume of modifier solution injected into the commercial PG furnace was 5 μl. Although the integrated and maximum absorbance slightly increased along with increases in the Pd concentration, the integrated and maximum absorbance reached a constant value in the ranges 500 – 2500 and 500 – 2000 mg l⁻¹ Pd, respectively. The lower concentration, 1000 mg l⁻¹ Pd, was selected as the working concentration to avoid contamination of the furnace.

Figure 2 shows the ashing temperature effect together with the atomizing temperature effect. A constant value of integrated and maximum absorbance was observed in the temperature range 500 – 1500°C and 500 – 1500°C; above 1500°C, which is

200° lower than that without the modifier, the absorbance decreased.   The temperature of 800°C was chosen as an optimum ashing temperature.   At this ashing temperature, a constant absorbance was observed with a hold time of 10 – 100 s, as can been seen in Fig. 3.   The atomizing temperature of 3000°C was selected to provide a maximum peak height with a maximum and constant integrated absorbance.   The atomizing time was selected and fixed to provide a maximum peak height and complete integration of the whole absorbance profile.

Using the recommended procedure, the characteristic mass and sensitivity of As detection, defined as the mass of As which yields an integrated and maximum absorbance of 0.0044, were 16 and 13 pg, respectively. The calculated limits of detection (LOD, 3σ) for the integrated and maximum absorbance were 22 (2.2) and 45 ng l⁻¹ (4.5 pg), respectively.   The limits of determination (10σ) for the integrated and maximum absorbance were 73 and 150 ng l⁻¹, respectively. When the bare PG furnace was used with the Pd modifier, the characteristic mass and sensitivity for the integrated and maximum absorbance were 21 and 20 pg, respectively and the LODs were 120 (12) and 110 ng l⁻¹ (11 pg), respectively.   The great improvement in LOD resulted from a decrease in RSD within the W-treated PG furnace.

Figure 4 shows the integrated and maximum absorbance observed with different injection volumes. The accuracy of the

Table 3   Relative values of integrated absorbance ($\int$abs) and maximum absorbance (A_{max}) of 4 µg l^{-1} As under the recommended procedure

Matrix	Conc. / mg l^{-1} as cation	$\int$abs	A_{max}	Matrix	Conc. / mg l^{-1} as cation	$\int$abs	A_{max}
As only		1.00	1.00	CaCl$_2$	10 – 200	1.01 ± 0.02	1.01 ± 0.02
NaCl	10 – 200	1.03 ± 0.01	1.03 ± 0.03	Ca(NO$_3$)$_2$	10 – 200	1.03 ± 0.01	1.03 ± 0.01
NaNO$_3$	10 – 200	1.02 ± 0.03	1.11 ± 0.06	MnCl$_2$	1	1.03	1.03
Ns$_2$SO$_4$	10 – 200	1.01 ± 0.01	1.04 ± 0.01	MnSO$_4$	1	1.01	1.03
KCl	10 – 200	1.01 ± 0.02	1.00 ± 0.02	FeCl$_3$	1	1.01	1.01
KNO$_3$	10 – 200	1.03 ± 0.01	1.02 ± 0.01	Fe(NO$_3$)$_2$	1	1.02	1.00
KSO$_4$	10 – 200	1.03 ± 0.02	1.00 ± 0.03	Ni(NO$_3$)$_2$	1	1.00	1.01
MgCl$_2$	10 – 200	1.00 ± 0.04	1.01 ± 0.03	ZnCl$_2$	1	1.00	1.00
Mg(NO$_3$)$_2$	10 – 200	1.01 ± 0.02	1.02 ± 0.02	Zn(NO$_3$)$_2$	1	1.00	1.01
MgSO$_4$	10 – 200	1.04 ± 0.02	1.04 ± 0.03	ZnSO$_4$	1	1.01	1.00

Table 4   Recoveries of As added into the various water samples

Sample	Blank-added / µg l^{-1} Observed	As-added / µg l^{-1} Spiked	As-added / µg l^{-1} Observed	Found / µg l^{-1}	Recovery, %
Snow Akita-1	0.12 ± 0.05	2	2.11 ± 0.03	1.99	100
Snow Akita-2	0.31 ± 0.04	2	2.37 ± 0.06	2.06	103
Snow Akita-3	0.07 ± 0.03	2	2.06 ± 0.04	1.99	100
Snow Akita-4	0.10 ± 0.04	2	2.14 ± 0.05	2.04	102
Snow Iwate-1	0.27 ± 0.05	2	2.31 ± 0.04	2.04	102
Snow Iwate-2	0.31 ± 0.03	2	2.31 ± 0.04	2.04	102
Snow Iwate-3	0.22 ± 0.04	2	2.29 ± 0.04	2.07	104
Snow Iwate-4	0.30 ± 0.05	2	2.32 ± 0.04	2.02	101
Cloud Akita-1	0.30 ± 0.03	2	2.33 ± 0.06	2.03	102
Cloud Akita-2	0.28 ± 0.03	2	2.36 ± 0.05	2.08	104
Cloud Akita-3	0.23 ± 0.03	2	2.29 ± 0.04	2.06	103
River-1	0.29 ± 0.02	2	2.34 ± 0.03	2.05	103
		4	4.39 ± 0.08	4.10	103
River-2	0.28 ± 0.02	2	2.35 ± 0.04	2.07	104
		4	4.42 ± 0.10	4.14	104
River-3	0.27 ± 0.04	2	2.28 ± 0.03	2.01	101
		4	4.31 ± 0.08	4.04	101
Tap-1 Tokushima	0.14 ± 0.01	2	2.08 ± 0.03	1.94	97
		4	4.04 ± 0.06	3.90	98
Tap-2 Iwate	0.21 ± 0.04	2	2.14 ± 0.06	1.93	97
Tap-3 Komatsushima	0.18 ± 0.04	2	2.14 ± 0.04	1.96	98
		4	4.11 ± 0.07	3.93	98

a. (Found/µg l^{-1}) = (As-added/µg l^{-1}) – (Blank-added/µg l^{-1}).

injecting volumes was periodically checked by weighing. As can be seen, a good linearity (correlation factor >0.99) between sample volume (0 – 100 µl) and absorbance was observed. The upper limit of dymanic range is extended up to 20 µg l^{-1}. When the sensitivity values based on mass of As achieved for the different injection volumes are identical with each other, the sample water containing As over 20 µg l^{-1} can be analyzed by the use of a smaller injection volume.

Table 3 shows relative values of integrated and maximum absorbance of As in the presence of various matrices under the recommended procedure, such as the chloride, sulfate and nitrate of Na, K and Mg and the chloride and nitrate of Ca, which are commonly found in snow, cloud, river and tap waters as a major ion species and also in the presence of heavy metal matrices, such as MnCl$_2$, MnSO$_4$, FeCl$_3$, Fe(NO$_3$)$_2$, Ni(NO$_3$)$_2$, ZnCl$_2$, Zn(NO$_3$)$_2$ and ZnSO$_4$, as a relative absorbance to that in the absence of matrix. For the major ion species in these water samples, the interference study was carried out at various concentrations (10, 50, 100 and 200 mg l^{-1}) in the range of 10 – 200 mg l^{-1} of cation. For the heavy metal ion species, the interference study was carried out at a concentration of 1 mg l^{-1} of cation. Good recoveries were observed for the maximum

absorbance except to NaNO$_3$ matrix. The tolerable concentration of NaNO$_3$ was 50 mg l^{-1} as Na, at which the recovery was 1.05. Since the use of integrated absorbance gave good recoveries for all matrices in the concentration range examined, the integrated absorbance mode was finally selected for signal processing.

Using the recommended procedure, the recovery test results of 2 and/or 4 µg l^{-1} of As added to water samples, *viz.*, snow, cloud, river and tap waters, were studied. The working sample was prepared by mixing 800 µl of water sample with 200 µl of an As standard solution (0, 10 or 20 µg l^{-1}). The As added to the sample was determined with a calibration graph according to the recommended procedure. The concentration of As observed in the samples with and without As added, together with the concentration of added As found and recovery of As, are shown in Table 4. The recoveries of As added to the eight snow samples were in the range 100 – 104%. For the cloud, river and tap water samples, the recovery was in the range 102 – 104, 101 – 104 and 97 – 98%, respectively. The As level in environmental water samples used was in the range 0.07 – 0.31 µg l^{-1}.

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