

Large-Volume Injection Electrothermal AAS Combined with Tungsten-treated Pyrolytic Graphite Furnace: Determination of Cadmium in Tap, Snow and River Water Samples with Phosphate Modifier

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A large-volume (100 μ l) injection-ETAAS with W-treated PG furnace combined with a phosphate modifier was applied to the determination of unpolluted levels of Cd in tap, snow and river-water samples. The limit of detection of 1.1 ng l⁻¹ was observed for a 4 w/v% NH₄H₂PO₄ modifier. Matrix interference studies were tested for major ion species well found in fresh water. The direct determination of Cd in certified river water (12 \pm 2 ng l⁻¹) was carried out and the observed value was in agreement with the certified one. The good recoveries of Cd added to real environmental water samples were also observed. This method was applied to the determination of Cd in unpolluted environmental water samples.

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Introduction

The surface treatment of a graphite furnace with refractory element carbide is used as a sensitivity enhancement by means of controlling the reactivity of the graphite surface in electrothermal (ET) AAS. A single-drop injection method of W solution is a convenient method for a surface treatment.¹ It was found that the whole surface of the sample compartment was uniformly treated by W, but disordered graphite portions were found in the treated area.² The analytical effectiveness of a W-treated pyrolytic graphite (PG) furnace has been reported by Imai *et al.*, which provides for the stable injection of a large volume (100 μ l) of solution of Pb and As with high precision.^{3,4} Recently, it was found for Cd that a sample solution was condensed at the center of the sample compartment at any volume in 10 – 100 μ l, and was vaporized smoothly without the formation of any bubble during the dry stage only in the W-treated PG furnace.⁵ A distribution with a higher density of Cd in the center area after dry stage was observed by an atomic-absorption measurement of small cores collected from the furnace inner wall. The high precision resulted in the distribution of Cd during the dry process of the sample solution. This large-volume injection method made it possible to enhance the limit of detection (LOD) to 2.5 ng l⁻¹ with a Pd modifier by using a hollow-cathod lamp. Various modifiers made the following better LOD values: 15 ng l⁻¹ for 80 μ l injection with NaOH,⁶ 7.5 ng l⁻¹ with ammonium oxalate,⁷ 5 ng l⁻¹ for multiple injection (20 μ l \times 3) with (NH₄)₂HPO₄ + HNO₃,⁸ 3 ng l⁻¹ for 99 μ l with oxalic acid⁹ and 5 ng l⁻¹ with (NH₄)₂HPO₄ + NH₄NO₃.¹⁰ The electrodeless discharge lamp was usually employed as a high-power radiation source.¹¹

Cadmium is an important element because of its toxicity,

presenting a serious environmental and health hazard to humans and animals at low levels of exposure. The concentration levels were reported in the range 0.1 – 1000 μ g l⁻¹ for fresh water, 10 – 720 and 10 – 450 ng l⁻¹ for rain collected at inland and coastal, 20 – 760 ng l⁻¹ for snow, 10 – 9600 ng l⁻¹ for stream water, in which the maximum value was observed.^{11,12} It was reported in Japan that the background levels in river water were 16 – 350 ng l⁻¹.¹³⁻¹⁵ The ¹¹¹Cd concentration was reported to be in the range of 53 – 201 ng l⁻¹ in collected snow at the top of, or near the top of, mountains in North Japan.¹⁶ Recently, Kagaya *et al.*¹⁷ reported that an indium internal standard-assisted rapid coprecipitation with lanthanum phosphate was applied to the determination of Cd in river water. A LOD value of 0.63 ng l⁻¹ in 200 ml of sample solution was observed with an enrichment factor of 200 times. Highly sensitive and rapid analytical techniques of low levels of Cd without any pre-concentration process are also necessary for monitoring, public health and environmental studies. A rapid direct determination of Cd in environmental water samples without any pretreatment is effective to decrease in a contamination. Since a phosphate modifier well uses as a better sensitivity for Cd determination, a sensitivity enhancement would also be expected in the present technique. It was found that the large-volume injection ETAAS technique with a W-treated PG furnace for Cd with a NH₄H₂PO₄ modifier using a hollow-cathod lamp provided an improvement in the calculated limit of detection in environmental water samples.

Experimental

Instrumentation

Atomic absorption was observed with a Hitachi Model Z-7000 electrothermal atomic absorption spectrometer equipped with a Zeeman-effect background corrector and a Hitachi Model 180-0341 optical temperature controller (OTC) system (Hitachi

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Table 1 Standard operation conditions

Stage	Atomizer operation	Temperature/°C	Time/s	Ar/ml min ⁻¹
1	Dry	80–150	30	200
2	Pyrolysis	150–360	20	200
3	Pyrolysis	360–360	20	200
4	Atomizing ^a	2560–2560	5	0
5	Cleaning	2560–2560	3	200

a. Optical temperature controller was used.

Wavelength, 228.8 nm; bandwidth, 1.3 nm; time constant, 0.1 s.

Ltd., Marunouchi Tokyo, Japan). The maximum absorbance was monitored throughout the present study. The standard operation conditions are summarized in Table 1. A Cd hollow-cathode lamp of Hitachi 208-2008 was used as a radiation source. A pyrolytic graphite-coated graphite furnace (Part No. 190-6003, Hitachi) was utilized throughout. The furnace inner wall temperature during pyrolysis was observed with a Pt-Rh thermocouple. The maximum temperature during atomizing was measured by a Chino Model IR-AH1S radiation thermometer. Gilson micropipettes (Gilson Medical Electronics, Villier-leBel, France) were used for sample injection and to prepare solutions with the checking periodically by weighing. A portable clean booth of Iuchi Model PC-100S (Tenmann, Osaka, Japan) corresponding to class 100 with a HEPA filter was used for sample preparations. A Milli-Q Academic system after being deionized by an Elix 5 system (Millipore Co., Inc.) was used for water purification.

Reagents and samples

A commercially available stock solution of Cd was used (Kanto Chemical Co., Nihonbashi-cho, Tokyo, Japan). An aliquot of this solution was diluted as required before use. A reagent of $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ (Kanto Chemical Co.) was used as a chemical modifier. A blank test for the modifier solution was undertaken. Aqueous 0.1 mol dm^{-3} solutions of tungsten were prepared as a treatment solution. Sodium tungstate(VI) dihydrate (Kanto Chemical Co.) was used. Other solutions were prepared from analytical-reagent grade chemicals.

Tap-water samples were taken in Tokushima, Kitajima and Aizumi cities in Tokushima; the sample was taken after running the tap for a few minutes and analyzed without further treatment. Snow samples were taken on the campus of Iwate University in Morioka sited in North Japan and the campus of the University of Tokushima in Tokushima in South West Japan. No filtration was carried out. River-water samples were taken from the Sonose and Yoshino River in an unpolluted river in Tokushima.

A certified reference material of Ottawa River water SLRS-4 prepared by National Research Council Canada (NRC) was used.

Recommended procedure

The surface treatment was carried out by a single-drop coating method, *viz.*, $100 \mu\text{l}$ of a 0.1 mol l^{-1} solution of tungsten injected into the PG furnace and the atomization cycle was carried out.⁸ A $5\text{-}\mu\text{l}$ volume of phosphate modifier (4 w/v% $\text{NH}_4\text{H}_2\text{PO}_4$) was introduced additionally into a W-treated PG furnace by manual pipetting after a $100 \mu\text{l}$ portion of the sample solution had been introduced. The maximum and integrated absorbance values corresponding to Cd were obtained during atomizing in the

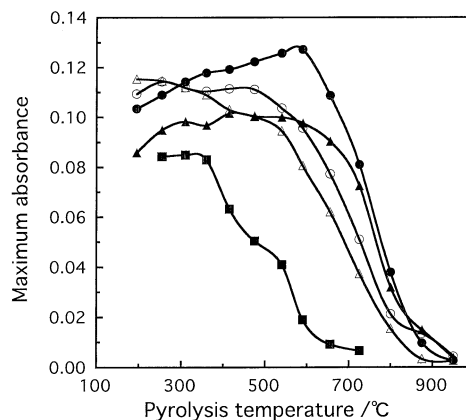


Fig. 1 Effect of the pyrolysis temperature on the maximum absorbance of 200 ng l^{-1} of Cd in the presence of a phosphate chemical modifier with the W-treated PG furnace. Sample, $100 \mu\text{l}$; modifier, $5 \mu\text{l}$. Matrix modifier: ■, no modifier; ●, 4 w/v% $\text{NH}_4\text{H}_2\text{PO}_4$; ▲, 1 w/v% $\text{NH}_4\text{H}_2\text{PO}_4$; ○, 4 w/v% $(\text{NH}_4)_2\text{HPO}_4$; △, 4 w/v% $(\text{NH}_4)_2\text{HPO}_4$.

standard atomization cycle. Sample operations were carried out in a clean booth. The blank solution was tested for Cd contamination from the experimental environment.

Results and Discussion

Figure 1 shows that the effect of the pyrolysis temperature on the maximum absorbance for 200 ng l^{-1} of Cd with the W-treated PG furnace with phosphate modifiers. When the modifier was absent, the maximum absorbance was decreased at temperatures above 360°C . When 1 and 4 w/v% $\text{NH}_4\text{H}_2\text{PO}_4$ was added, the maximum absorbance was decreased at temperatures above 540 and 600°C , respectively. When 1 and 4 w/v% $(\text{NH}_4)_2\text{HPO}_4$ was added, the maximum absorbance was decreased at temperatures above 360 and 480°C , respectively. At this time, 4 w/v% $\text{NH}_4\text{H}_2\text{PO}_4$ was selected as a working modifier because of its better tolerable pyrolysis temperature, relatively low background absorption and sensitivity enhancement. A pyrolysis temperature of 360°C was selected as an optimum one from the view point of a better standard deviation.

Table 2 shows the effect of the $\text{NH}_4\text{H}_2\text{PO}_4$ modifier on the maximum absorbance of Cd, which was examined in the presence of nitrate, chloride and sulfate of major alkaline and alkaline earth ions and in the presence of heavy metal ions, commonly found in snow, rain, river and tap water according to the recommended procedure. Up to the matrix concentration of NaNO_3 , KNO_3 , Na_2SO_4 and K_2SO_4 of 100 mg l^{-1} of cation, $\text{Mg}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, NaCl , KCl , and CaCl_2 of 50 mg l^{-1} , MgSO_4 of 20 mg l^{-1} , and $\text{Fe}(\text{NO}_3)_3$, MnCl_2 , $\text{Ni}(\text{NO}_3)_2$, and $\text{Co}(\text{NO}_3)_2$ of 1 mg l^{-1} , the relative absorbance for 200 ng l^{-1} of Cd was recovered in the range of 0.91 – 1.08 using each chemical modifier.

The slope of the calibration curve (sensitivity), the calculated limit of detection (LOD, 3σ) and the relative standard deviation (RSD) at 100 ng l^{-1} of Cd was obtained ($n = 5$) under the recommended procedure. The sensitivity, LOD and RSD were 0.807 ng l^{-1} , 1.1 ng l^{-1} and 2.0% for the $\text{NH}_4\text{H}_2\text{PO}_4$ modifier, respectively. The observed LOD was better than that (2.5 ng l^{-1}) with the Pd modifier and the W-treated PG. The dynamic

Table 2 Relative values of the maximum absorbance of 200 ng l⁻¹ Cd under the recommended procedure

Matrix	Conc./mg l ⁻¹ as cation	Relative absorbance
Cd only	Absence	1.00
NaNO ₃	100	0.97
KNO ₃	100	0.93
Mg(NO ₃) ₂	50	1.00
Ca(NO ₃) ₂	50	0.92
NaCl	50	0.99
KCl	50	0.99
CaCl ₂	50	0.91
Na ₂ SO ₄	100	0.97
K ₂ SO ₄	100	0.95
MgSO ₄	20	0.95
Fe(NO ₃) ₃	1	1.00
MnCl ₂	1	0.90
Ni(NO ₃) ₂	1	0.95
Co(NO ₃) ₂	1	1.08

Table 3 Determination of Cd in a certified reference material of river water (NRC, SLRS-4 Ottawa river)

Date	Mean ± standard deviation/ng l ⁻¹
1 <i>n</i> = 5	11 ± 2
2 <i>n</i> = 5	12 ± 1
3 <i>n</i> = 5	12 ± 3
4 <i>n</i> = 5	11 ± 1
5 <i>n</i> = 5	10 ± 1

range was 0 – 400 ng l⁻¹ for the maximum absorbance with large-volume injection. The sample water containing Cd over 400 ng l⁻¹ could be analyzed by using a smaller injection volume.

Table 3 gives the results of a direct determination of Cd of a certified reference material of Ottawa River water (SLRS-4) prepared by NRC according to the recommended procedure in different date. The mean value ± the standard deviation of the concentration was obtained to be 11 ± 1 ng l⁻¹ of Cd in all days, which is in agreement with the certified value of 12 ± 2 ng l⁻¹ of Cd. Thus, the recommended procedure proposed was very effective for the determination of Cd in unpolluted fresh-water samples.

Using the recommended procedure, the recoveries for 200 ng l⁻¹ of Cd, which is in the range of the background levels in fresh water, added to various water samples were studied for both chemical modifiers. The 900 µl of water sample was mixed with 100 µl of a Cd standard solution (0 or 2.0 µg l⁻¹). The concentration of Cd in this mixture was determined with a calibration graph. The recoveries of added Cd were to be 102 ± 4, 105 ± 2 and 101 ± 6% for the five tap-water samples, three river-water samples and five snow samples, respectively.

The determination of Cd in samples (28 of tap water, 12 of snow and 8 of river water) was carried out according to the recommended procedure. The analytical results are summarized in Table 4.

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Table 4 Analytical results of Cd in environmental water

Sample	Cd/ng l ⁻¹	Sample	Cd/ng l ⁻¹	Sample	Cd/ng l ⁻¹
Tap 1	6.8	Tap 17	ND ^a	Snow 5	40
Tap 2	6.3	Tap 18	3.4	Snow 6	337
Tap 3	5.4	Tap 19	9.9	Snow 7	104
Tap 4	6.4	Tap 20	ND	Snow 8	45
Tap 5	6.4	Tap 21	4.4	Snow 9	80
Tap 6	13	Tap 22	ND	Snow 10	4.7
Tap 7	9.5	Tap 23	3.1	Snow 11	15
Tap 8	16	Tap 24	3.9	Snow 12	ND
Tap 9	52	Tap 25	4.8	River 1	13.4
Tap 10	8.1	Tap 26	ND	River 2	10.0
Tap 11	34	Tap 27	ND	River 3	7.8
Tap 12	13	Tap 28	12	River 4	ND
Tap 13	3.1	Snow 1	9.5	River 5	ND
Tap 14	6.4	Snow 2	16	River 6	ND
Tap 15	9.5	Snow 3	26	River 7	ND
Tap 16	4.2	Snow 4	21	River 8	2.1

a. Non detected (< LOD).

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