

Determination of Cadmium and Lead in Tap Water by Graphite-Furnace Atomic Absorption Spectrometry after Preconcentration on a Finely Divided Ion-Exchange Resin as the Pyrrolidinedithiocarbamate Complexes

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A rapid and simple preconcentration method based on the combined use of ammonium pyrrolidinedithiocarbamate (APDC) and a finely divided anion-exchange resin has been described for the determination of trace amounts of cadmium and lead by graphite-furnace atomic absorption spectrometry (GFAAS). Cadmium- and lead-APDC complexes were extracted simultaneously on the resin at pH 6. The resin particles holding the cadmium- and lead-APDC complexes were separated by filtration and dispersed in 1.0 ml of 0.1 mol l⁻¹ hydrochloric acid containing 100 µg of palladium(II). The resulting suspension was introduced directly into the graphite furnace by an automatic sampler. The detection limits of cadmium and lead in a 150-ml sample aliquot were 0.17 and 5.7 ng l⁻¹, respectively, based on three-times the standard deviation of blank values. The proposed method was applied to the determination of nanograms per liter levels of cadmium and lead in tap water.

Keywords Cadmium, lead, tap water, ion-exchange resin, graphite-furnace atomic absorption spectrometry

Graphite-furnace atomic absorption spectrometry (GFAAS) is one of the most widely used techniques for the determination of trace elements in water. However, its sensitivity for cadmium and lead is not sufficient for a direct determination of these elements in drinking water. So far, many techniques have been used for the enrichment of trace elements in water samples. One of the most important conditions of the enrichment techniques is simple connection to the subsequent determination techniques. When the desired trace elements can be quantitatively extracted on a small amount of fine particles, a method based on the collection of particles by filtration, the preparation of a suspension in a small volume and the determination by suspension-introduction GFAAS is favorable. Chelating ion-exchange resins¹⁻⁷ and ion-exchange resins⁸ and activated carbon⁹⁻¹² with complexing agents have been used for this purpose. Another technique was recently reported in which a part of the resin thin layer was cut and inserted in a cuvette for the determination by electrothermal AAS.¹³

The aim of this work was to develop a simple preconcentration method for the determination of cadmium and lead in tap water with the combined use of a finely divided ion-exchange resin and APDC. Fine resin particles are well suited for the rapid collection of the desired trace elements from a large sample of aliquots.⁸

Since the ion-exchange resin particles have both hydrophilic and hydrophobic properties, they can act as a hydrophilic organic solid in the bulk solution, and can extract species with hydrophobic properties. APDC was selected for the simultaneous extraction of cadmium and lead on the resin particles. The proposed method was applied to the determination of cadmium and lead in tap water supplied to our laboratory.

Experimental

Apparatus

A Hitachi Zeeman-effect GFAAS (Model Z-8270) equipped with an auto-sampler (Model SSC-300) was used for measuring the atomic absorption of cadmium and lead. The instrumental operating conditions are summarized in Tables 1 and 2. A Toyo KG-25 filter holder with a membrane filter of cellulose nitrate (0.45 µm pore size, 25 mm in diameter) was used for collecting the resin particles by filtration under suction. A Branson Ultrasonic Cleaner B-42 was used for preparing the resin suspension.

Reagents

All reagents used were of analytical grade. A Yamato Model WAR-30 and a WB-21 Auto-Still were employed to purify the water used; the water was first passed through a reverse-osmosis membrane and then

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Table 1 Instrumental and working conditions for the determination of cadmium by GFAAS

Lamp current	7.5 mA			
Wavelength	228.8 nm			
Slit width	1.30 nm			
Furnace programmer settings				
	Dry	Ash	Atomize	Cleaning
Temperature/°C	80 - 140	600	1500	2800
Time/s	40	30	5	8
Argon/ml min ⁻¹	200	200	0	200
Mode	ramp	step	step	step

Table 2 Instrumental and working conditions for the determination of lead by GFAAS

Lamp current	7.5 mA			
Wavelength	283.3 nm			
Slit width	1.30 nm			
Furnace programmer settings				
	Dry	Ash	Atomize	Cleaning
Temperature/°C	80 - 140	900	2400	2800
Time/s	40	40	5	4
Argon/ml min ⁻¹	200	200	0	200
Mode	ramp	step	step	step

distilled twice. A 20 mmol l⁻¹ APDC solution was prepared by dissolving a reagent of special grade for AAS (Wako Pure Chemical) in water. Working solutions of cadmium (20.0 ng ml⁻¹) and lead (300 ng ml⁻¹) were prepared from the AAS standard solutions (100 µg ml⁻¹ in 0.1 mol l⁻¹ nitric acid, Wako Pure Chemical) by dilution with 0.1 mol l⁻¹ hydrochloric acid. A 1000 µg ml⁻¹ palladium solution was prepared by dissolving palladium(II) chloride (99.9%, Wako Pure Chemical) in 1 mol l⁻¹ hydrochloric acid. A working solution of 100 µg ml⁻¹ palladium in 0.1 mol l⁻¹ hydrochloric acid was prepared from the stock solution by dilution with water. An anion-exchange resin suspension (ARS) was prepared from a macroreticular-type Diaion PA318 (Mitsubishi Kagaku), according to the reported method:⁸ The resin was conditioned in the usual way for preparing the chloride form. The wet resin was crushed in a PTFE mortar with a PTFE pestle to make a slurry, which was then diluted appropriately with water. The resin suspension was filtered through a G-3 glass filter with a nominal pore size ranging from 20 - 30 µm. The exchange capacity of the resin suspension in the resulting filtrate was 5.4 µequiv. ml⁻¹, which was determined by conductometric titration with a standard silver nitrate solution.

General procedure for the determination of cadmium and lead

A 150-ml aliquot of the solution containing less than 2.00 ng of cadmium and 40.0 ng of lead was placed in a 300-ml polypropylene beaker. The solution pH was adjusted to 2 with the addition of 0.17 ml of 6 mol l⁻¹ hydrochloric acid, and 4.0 ml of ARS, 1.5 ml of 20 mmol l⁻¹ APDC and 1.5 ml of 3 mol l⁻¹ sodium perchlorate solutions were added successively. The pH was then adjusted to 6 with the addition of 2 ml of a 1:1 mixture of 1.0 mol l⁻¹ ammonium acetate and 1.0 mol l⁻¹ sodium hydroxide solutions. The whole was stirred for 10 min; then, the resin particles were collected on a membrane filter by filtration under suction. A disk of resin thin layer of approximately 17 mm diameter and 0.03 mm thick was thus prepared. The membrane filter holding the resin thin layer was placed in a 10-ml beaker and a 1.0 ml portion of 0.1 mol l⁻¹ hydrochloric

acid containing 100 µg of palladium was added. The beaker was covered with a piece of Sealone film (Fuji Photo Film) and subjected to ultrasonic irradiation for 60 s. The resulting resin suspension was then placed in a cup for the auto-sampler and the cup was covered with a Sealone film. The mixture in the cup was shaken by hand just before automatic sampling and a 20-µl portion of the suspension was injected to the graphite cuvette.

Determination of cadmium and lead in tap water

A tap-water sample was collected after running the water for more than 1 h. A 150-ml portion of the sample water was placed in a 300-ml polypropylene beaker and the pH was adjusted to 2 with the addition of 0.17 ml of 6 mol l⁻¹ hydrochloric acid; then, the pH was adjusted to 6 with the addition of 3.0 ml of 1 mol l⁻¹ trisodium citrate. The following procedures were the same as in the general procedure.

Results and Discussion

Effect of the ashing temperature

To find the optimum ashing temperature, the effect of an ion-exchange resin and palladium as the matrix modifier was examined by preparing four solutions without an extraction step, as shown in Figs. 1 and 2. The absorbance of cadmium and lead was seriously suppressed in the presence of palladium (curve B in Figs. 1 and 2), while the ion-exchange resin particles did not show any appreciable effects on the determination of cadmium and lead (curve C in Figs. 1 and 2). On the other hand, in the presence of both palladium and ion-exchange resin (curve D in Figs. 1 and 2), the optimal ashing temperature was shifted to a higher region and found to be in the range 600 - 700 °C and 900 - 1200 °C for cadmium and lead, respectively. The ashing temperature was fixed to 600 °C for cadmium and 900 °C for lead by considering the lifetime of the graphite cuvette. Although the reason for the synergic effect due to the ion-exchange resin and palladium is not clear, a 1.0 ml portion of 0.1 mol l⁻¹ hydrochloric acid containing 100 µg ml⁻¹ of palladium was selected

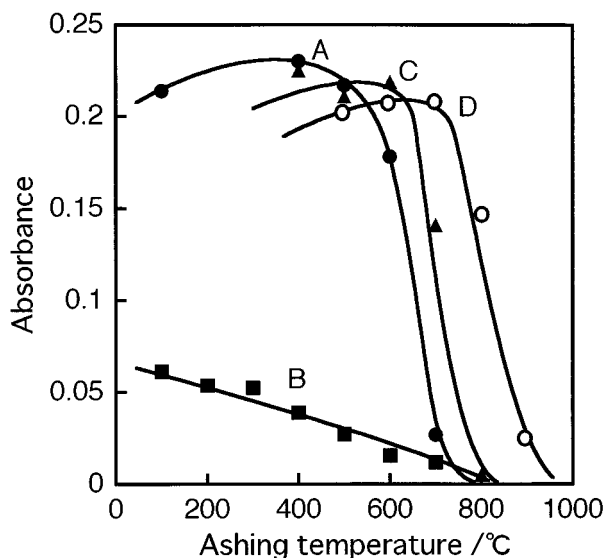


Fig. 1 Effect of the ashing temperature on the absorbance of cadmium. A, 0.1 mol l⁻¹ hydrochloric acid containing 2.00 ng ml⁻¹ of cadmium and 30.0 ng ml⁻¹ of lead; B, A containing 100 µg ml⁻¹ of palladium; C, A containing 21.6 µequiv.ml⁻¹ of anion exchange resin; D, A containing 100 µg ml⁻¹ of palladium and 21.6 µequiv. ml⁻¹ of anion exchange resin.

as the medium for preparing the resin suspension.

Effect of pH

The effect of the pH was investigated in the pH range 2–8. The constant and maximum absorbance of cadmium was observed above pH 4, while that of lead was obtained above pH 5, as shown in Fig. 3. Therefore, the solution pH was fixed at 6 for the simultaneous extraction of cadmium- and lead-APDC complexes on the ion-exchange resin.

Effect of amount of APDC

The effect of the amount of APDC on the extraction of cadmium and lead was examined with the addition of different amounts of 20 mmol l⁻¹ APDC solutions of up to 3.0 ml. The maximum and constant absorbance of 2.00 ng of cadmium and 30.0 ng of lead were obtained with the addition of a 20 mmol l⁻¹ APDC solution above 1.5 ml.

Effect of amount of ARS

The maximum and constant absorbances of 2.00 ng of cadmium and 30.0 ng of lead in 150 ml of solution were obtained with the addition of ARS in the range 1.0–6.0 ml for cadmium and 4.0–6.0 ml for lead, respectively. When the amounts of ARS were increased from 4.0 to 6.0 ml, the reproducibility of the absorbance measurements was found to decrease, which is probably due to the insufficient ashing under the conditions given in Tables 1 and 2. Therefore, the amounts of ARS were fixed at 4.0 ml for the simultaneous extraction of cadmium- and lead-APDC complexes.

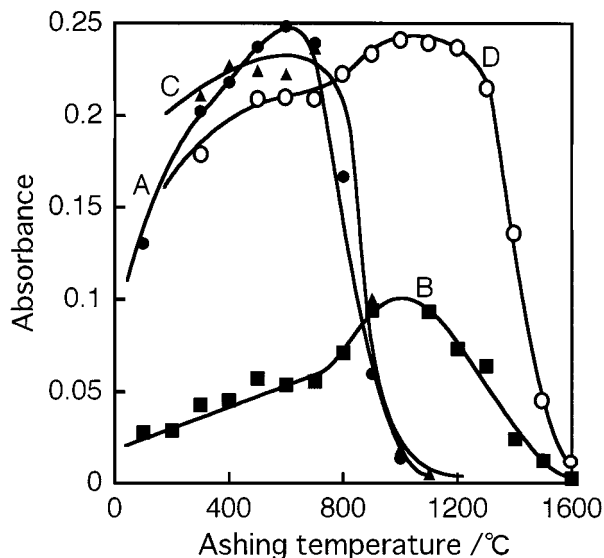


Fig. 2 Effect of the ashing temperature on the absorbance of lead. The other conditions were the same as in Fig. 1.

Effect of the stirring time

The effect of the stirring time on the extraction of cadmium and lead-APDC complexes on the ion-exchange resin was investigated. The maximum and constant absorbances of cadmium and lead were obtained after stirring for more than 5 min.

Effect of sodium perchlorate

Without the addition of sodium perchlorate, more than 1 h was required for collecting ion-exchange resin particles from 150 ml of the bulk solution by filtration.

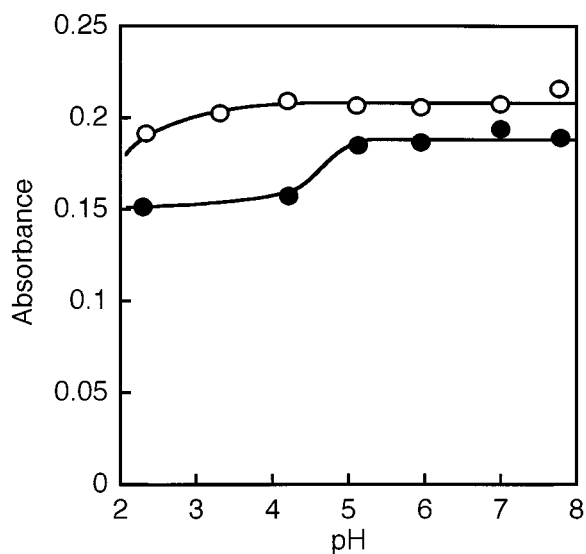


Fig. 3 Effect of the pH on the resin-phase extraction of cadmium-APDC (○) and lead-APDC (●) complexes. Amount of ARS (5.4 µequiv./ml) 4.0 ml; cadmium, 1.50 ng; lead, 30.0 ng; sample volume, 150 ml.

With the addition of 1.0 ml of 3 mol l⁻¹ sodium perchlorate solution, however, the filtration was completed within 3 min. This was probably because perchlorate ions were fixed to the ion-exchange sites, and the resulting resin particles would partly coagulate with each other.

Effect of ultrasonic irradiation time

The resin particles collected on the membrane filter were dispersed in a 1.0 ml of 0.1 mol l⁻¹ hydrochloric acid containing 100 µg of palladium by ultrasonic irradiation. Irradiation for more than 30 s was required to make a suspension. About 70–80% of cadmium and lead in the resulting suspension was found in the solution, which showed that the cadmium- and lead-APDC complexes were mostly decomposed in 0.1 mol l⁻¹ hydrochloric acid.

Effect of sample volume

The recovery of cadmium- and lead-APDC complexes was investigated with varying sample volumes. The maximum and constant absorbances of cadmium and lead were obtained from different sample volumes of up to 300 ml.

Calibration graph

The calibration graphs for the determination of cadmium and lead were prepared according to a general procedure. Good linearity was obtained for up to 2.00

ng of cadmium and 40.0 ng of lead. The absorbance and the standard deviation of the blank value for cadmium and lead were 0.0263±0.0008 (*n*=6) and 0.0344±0.0017 (*n*=6). The limit of detection for cadmium and lead in a 150-ml sample aliquot was 0.17 and 5.7 ng l⁻¹, respectively, based on three-times the standard deviation of the blank values.

Effect of foreign ions

The results of the effect of foreign ions are summarized in Table 3. The effect of iron(III) was successfully eliminated with the use of a buffer solution containing citrate. Since the solutions prepared from sodium chloride for the volumetric analysis and 99.9% calcium carbonate (both Wako Pure Chemical) contained appreciable amounts of metal impurities, these solutions were purified by resin-phase extraction of the impurities with the combined use of APDC and ARS.

Results of the determination of cadmium and lead in tap water

The recovery of added amounts of cadmium and lead were found to be quantitative in the presence and absence of citrate, as shown in Tables 4 and 5. The recovery of cadmium and lead from 150 ml of the sample water was also examined by re-extracting cadmium and lead in the filtrate of the first extraction. Since

Table 3 Effect of foreign ions on the recovery of 1.50 ng of cadmium and 30.0 ng of lead from 150 ml of the sample solution

Ion	Added as	Amount added/ µg	Recovery, %	
			Cadmium	Lead
Na(I)	NaCl	2070000	104	102
		690000	97	96
		60000	97	98
		60000	104	95
Si(IV)	Na ₂ SiO ₃	300	97	101
Fe(III)	FeCl ₃	2.0	104	98
		5.0	92	77
		5.0 ^a	102	103
		10.0 ^a	105	101
Cu(II)	CuSO ₄	0.6	95	99
Co(II)	CoCl ₂	0.3	99	102
Ni(II)	Ni(NO ₃) ₂	0.6	100	98
Mn(II)	MnCl ₂	0.6	104	96
Al(III)	AlK(SO ₄) ₂	0.6	98	96
Zn(II)	ZnCl ₂	0.6	103	99
		1.5 ^a	103	101
V(V)	NH ₄ VO ₃	0.3	97	95
		0.6 ^a	98	104
Cr(III)	CrK(SO ₄) ₂	0.6	103	98
Cr(VI)	K ₂ Cr ₂ O ₇	0.3	96	102
		0.6 ^a	103	98

a. The pH of the acidified sample was adjusted to 6 with the addition of 3 ml of 1 mol l⁻¹ trisodium citrate.

Table 4 Results of the determination of cadmium in tap water

Date	Sample volume/ml	Cd added/ ng	Cd found/ ng	RSD, %	Recovery, %
'97/8/6	100 ^a	0.00	0.88	5.8	
	100 ^a	0.80	1.66	2.3	98.3±4.4
'97/8/10	100 ^b	0.00	1.03	3.9	
	100 ^b	0.80	1.83	4.2	100.0±7.4

Number of analyses; *n* = 5.

The pH of the acidified sample was adjusted to 6 with the addition of (a) 2 ml of a 1:1 mixture of 1.0 mol l⁻¹ ammonium acetate and 1.0 mol l⁻¹ sodium hydroxide solutions and (b) 3 ml of 1 mol l⁻¹ trisodium citrate.

Table 5 Results of the determination of lead in tap water

Date	Sample volume/ml	Pb added/ ng	Pb found/ ng	RSD, %	Recovery, %
'97/8/6	100 ^a	0.0	15.3	3.6	
	100 ^a	10.0	25.2	2.8	99.6±4.6
'97/8/10	100 ^b	0.0	22.6	8.6	
	100 ^b	10.0	32.4	3.0	99.3±4.3

Number of analyses; *n* = 4 or 5.

The pH of the acidified sample was adjusted to 6 with the addition of (a) 2 ml of a 1:1 mixture of 1.0 mol l⁻¹ ammonium acetate and 1.0 mol l⁻¹ sodium hydroxide solutions and (b) 3 ml of 1 mol l⁻¹ trisodium citrate.

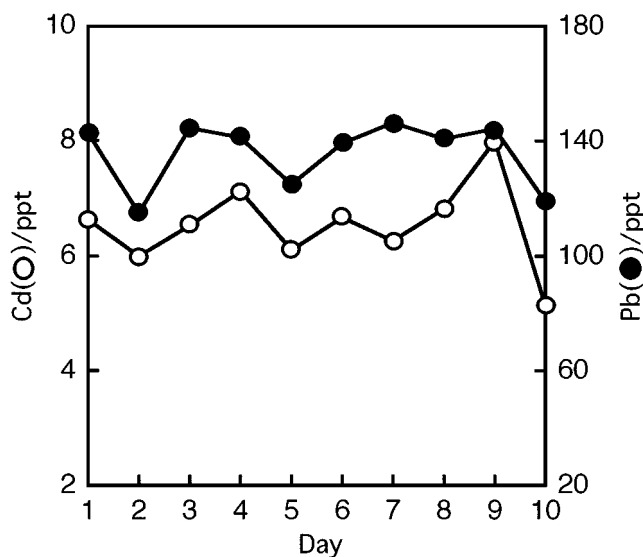


Fig. 4 Results of the determination of cadmium (○) and lead (●) in tap water supplied to our laboratory during the period from 9th and 18th September, 1997. Sample volume, 150 ml. Each plot was the mean of three or four runs. The relative standard deviations were in the ranges 2.4 - 11.4% and 2.8 - 8.7% for the determination of cadmium and lead, respectively.

none of the cadmium and lead was found in the filtrate, it was also concluded that they were quantitatively recovered. The results of the determination of cadmium and lead in tap water supplied to our laboratory during the period from 9th to 18th September, 1997, are summarized in Fig. 4. A calibration graph prepared daily. The means along with the standard deviations of the concentration of the metal ions for 10 days were

6.52±0.75 ppt for cadmium and 136±12 ppt for lead, respectively.

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