

Preconcentration and Determination of Cadmium by GFAAS after Solid-Phase Extraction with Synthetic Zeolite

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The solid-phase extraction (SPE) method for the preconcentration of trace amounts of cadmium using synthetic zeolite A-4 and its determination by graphite furnace atomic absorption spectrometry (GFAAS) was investigated. The preconcentration conditions, such as the optimum pH range of the sample solution for the adsorption of cadmium and the kind of acid solution for dissolving the cadmium-adsorbed synthetic zeolite A-4, as well as the measurement conditions for the determination of cadmium by GFAAS, *e.g.*, the ashing and atomizing temperature, were investigated. Quantitative recovery of cadmium onto zeolite A-4 from the sample solution over the pH range 2.0–9.0 was achieved by the batch method. After the solid-phase (cadmium-adsorbed zeolite A-4) was separated from the sample solution by a membrane filter, it was dissolved in 2.0 cm³ of 2.0 mol dm⁻³ nitric acid. An aliquot of the resulting solution was injected into the graphite furnace. In GFAAS measurements an alternate gas (Ar, 90%; O₂, 10%) was used as a sheath gas, and the ashing temperature and atomizing temperature were 400°C and 1600°C, respectively. The detection limit (3σ) for cadmium was 0.002 μg dm⁻³. The relative standard deviation at 0.010 μg dm⁻³ was 3.5–4.5% (*n* = 5). The proposed method has been successfully applied to the analysis of trace cadmium in environmental water samples.

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Cadmium and its compounds are environmental contaminants that accumulate in the human body, causing renal function disorder, lung cancer and prostate cancer. Thus, measurements of the cadmium concentration in environmental samples are of considerable interest. Owing to its high sensitivity, graphite furnace atomic absorption spectrometry (GFAAS) has been widely used for the determination of low-level metals in water samples. However, GFAAS is currently unable to detect cadmium because its concentration in water samples, such as river water, is generally extremely low. Therefore, an appropriate preconcentration and separation method is required prior to GFAAS analysis.

For measuring of low-level cadmium in water samples by GFAAS, solvent extraction,¹⁻⁴ coprecipitation,^{5,6} flotation,^{7,8} ion-exchange⁹⁻¹¹ and electrolysis¹² are effective preconcentration techniques. Solid-phase extraction (SPE)¹³⁻¹⁶ is another technique that is attractive because it uses no organic solvents. Many different types of adsorbents have been used for SPE. Afzali *et al.* used the natural analcime zeolite as an adsorbent of SPE for anodic stripping voltammetry analysis.¹⁷ On the other hand, a direct atomization method using metal-adsorbed adsorbents has employed a variety of adsorbents, such as activated carbon (AC),¹⁸ ion-exchange resin,^{19,20} chelating resin²¹ and chitin in GFAAS analysis.²² This method offers advantages: for example, it eliminates the need for any elution

procedure. However, various processing parameters, such as the grain size of the adsorbent, the kind and volume size of the dispersant, and the dispersant time of the suspension, need to be optimized because the homogeneity of the suspension is critical. Furthermore, the method has room for an improvement of analytical accuracy.

Synthetic zeolite is composed of a highly crystalline aluminosilicate framework comprising SiO₂ and Al₂O₃ tetrahedral units. The introduction of an overall negative surface charge requires counter ions, *e.g.*, Na⁺ and K⁺. Zeolite A-4 is one of the many types of synthetic zeolite. Zeolite A-4 has excellent properties, such as ion-exchange, adsorption, molecular sieve and catalysis, and is used in purification and separation processes.²³ However, there are few reports on the preconcentration of trace metal ions using synthetic zeolite by GFAAS.²⁴ Peña *et al.* reported on the on-line preconcentration of copper using synthetic zeolite and its determination by flame AAS.²⁵ The present study further exploits the properties zeolite A-4 for the preconcentration of trace cadmium and its determination by GFAAS. Once cadmium was collected from the water samples onto zeolite A-4, the solid-phase (cadmium adsorbed zeolite A-4) was dissolved in acid, even though zeolite A-4 is stable over a wide pH range. The resulting acid solution containing cadmium, and the concentration of cadmium in this resulting solution was measured by GFAAS. The proposed method has an advantage concerning the analytical accuracy compared with the direct atomization method (suspension method) because the metal

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Table 1 Instrumental operating conditions for Cd determination by graphite furnace atomic absorption spectrometry

Element	Cd
Wavelength	228.8 nm
Background correction	Zeeman effect
Slit width	1.3 nm
Lamp current	4.0 mA
Sheath gas (alternate gas)	Ar, 80%; O ₂ , 20%
Cuvette	Tube type pyrolytic graphite-coated cuvette
Injection volume	10 µl
Measurement mode	Peak height
Drying	100°C/30 s (ramp mode) 100°C/10 s (step mode)
Ashing	300°C/20 s (ramp mode) 300°C/10 s (step mode)
Atomization	2300°C/0 s (ramp mode) 2300°C/5 s (step mode)
Cleaning	2500°C/5 s (step mode)

concentration of the resulting solution is homogeneous.²⁶

In the present study, the preconcentration conditions of cadmium onto zeolite A-4, such as the solution pH and GFAAS measurement conditions, like the ashing temperature, were optimized. Moreover, the proposed method extends to the determination of trace amounts of cadmium in water samples.

Experimental

Instrumentation

A Hitach Model Z-5700 polarized Zeeman atomic absorption spectrometer equipped with a cadmium hollow-cathode lamp as the radiation source and Zeeman background corrector was used, and was combined with a tube-type pyrolytic graphite furnace to measure the atomic absorbance of cadmium. An automatic sampler was employed for injecting of the solution into the furnace by the proposed procedure. The operating conditions for the GFAAS are presented in Table 1.

X-ray diffraction (XRD) patterns of the zeolite A-4 and the residue on the graphite furnace were recorded with an RAD-B system (Rigaku Co.). Scanning electron microscope (SEM) images of the zeolite A-4 were obtained with a JSM-5400LUS SEM (Japan Spectroscopic Co., Ltd.). The elementary composition of the residue on the graphite furnace was analyzed with a JEP-2001 energy dispersive X-ray micro-analyzer (Japan Electron Co., Ltd.). A M-8L pH meter (Horiba Co.) and an SR-50 magnetic stirrer (Advantec Co.) were used for pH control of the sample solution and for the adsorption experiment, respectively. Furthermore, a TM-152 test tube mixer was used for dissolving the zeolite A-4 in an acid solution.

Reagents

Zeolite A-4 (Wako Pure Chemical Industries, Ltd., 200 mesh under) was used without purification because Zeolite A-4 is slightly soluble in a number of acid solutions. The chemical formula for zeolite A-4 is Na₂O·Al₂O₃·2SiO₂.

Further, zeolite F-9 (Wako Pure Chemical Industries, Ltd., 200 mesh under, Na₂O·Al₂O₃·2.5SiO₂), zeolite X-13 (Union Showa. K. K., powder, Na₂O·Al₂O₃·2.4SiO₂) and alumina (ICN Biomedicals, super grade I, Al₂O₃) were used for comparisons.

A cadmium working solution was prepared by appropriate dilution of the stock standard solution (AAS-grade; Cd 1000 mg dm⁻³ in 1.0 mol dm⁻³ hydrochloric acid; Wako Pure Chemical

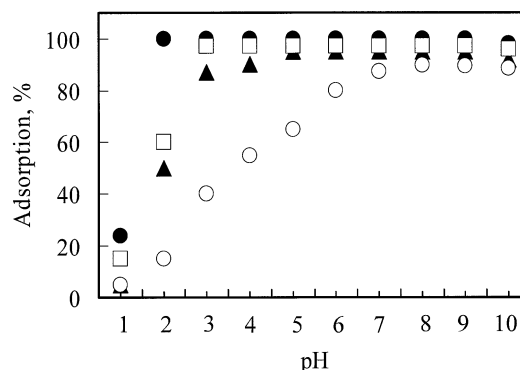


Fig. 1 Effect of pH on the adsorption of Cd(II) on the adsorbent. ●, A-4 zeolite; □, F-9 zeolite; ▲, X-13 zeolite; ○, alumina; Cd(II), 2.0 µg/100 cm³; adsorption time, 30 min.

Industries) with 1.0 mol dm⁻³ hydrochloric acid.

All other reagents were of analytical reagent grade and all solutions were prepared with ultra-pure grade water (out put of 18 MΩ cm⁻¹) using a Puric-S system (Organo).

Adsorption experiment

The adsorption of cadmium onto the zeolite A-4 was investigated. The adsorption experiment was carried out by a batch method. The zeolite A-4 (100 mg) was added into 100 cm³ of cadmium solution after its pH was adjusted to the optimum range. This solution was stirred for 60 min and separated with a membrane filter. The amounts of adsorbed cadmium on zeolite A-4 were determined by measuring the concentration of cadmium in the resulting filtrate using GFAAS. The adsorption capacities (q), *i.e.*, the amounts (mg) of adsorbed cadmium per weight (g) of zeolite A-4, were determined from the equation

$$q = (C_0 - C)/W$$

where C_0 and C are initial and final cadmium concentrations of the solution (mg/100 cm³), respectively, and W is the amount of zeolite A-4.

General procedure

A 100 cm³ aliquot of the sample solution containing less than 0.10 µg cadmium was placed in a beaker. The sample solution was adjusted to pH 6.0 with a diluted sodium hydroxide or nitric acid solution, and 100 mg of the synthetic zeolite A-4 was added as an adsorbent. The mixture was stirred for 20 min by a magnetic stirrer to adsorb cadmium onto the zeolite A-4, and the solid phase (cadmium-adsorbed zeolite A-4) was separated from the aqueous phase using a membrane filter (Millipore Co., Ltd.; diameter, 25 mm; pore size, 8.0 µm). The solid phase was carefully transferred into a stoppered centrifuge test tube (volume, 10 cm³) with a membrane filter. After the solid phase was dissolved in 2.0 cm³ of 2.0 mol dm⁻³ nitric acid using a test-tube mixer, the membrane filter was removed using tweezers. 10-µl volume of the resulting solution was slowly injected (2.0 mm³ s⁻¹) into the pyrolytic graphite cuvette by an automatic sampler. The atomic absorbance of cadmium was measured by GFAAS under the operating conditions given in Table 1. The measurement was repeated three times, and the absorbance readings were averaged.

Results and Discussion

Effect of pH on the adsorption of cadmium onto the adsorbent

It is very important to select the adsorbent in the proposed method. The pH range for the adsorption of cadmium, solubility, contamination and adsorption capacity of the adsorbent are important factors, and were thus examined using several types of inorganic adsorbents (*i.e.* zeolite A-4, zeolite F-9, zeolite X-13, and alumina). Based on these investigations, zeolite A-4 was used as an adsorbent in all subsequent experiments.

The optimum pH range of the sample solution for the adsorption of cadmium onto the adsorbent was investigated by varying the pH from 1.0 to 10.0. The results are shown in Fig. 1. Cadmium was quantitatively collected onto several types of inorganic adsorbents in the pH range of 3.0–7.0, except for alumina. The zeolite A-4 collected cadmium in a particularly wide pH range of 2.0–9.0. The recovery of cadmium decreased below pH 2.0 because zeolite A-4 partially dissolved. Below pH 0.5, zeolite A-4 dissolved completely. These results, suggest that the adsorption capacity of zeolite A-4 decreased in lower and higher pH ranges. Thus, the neutral pH range (pH 6.0) is optimal for the adsorption of cadmium onto zeolite A-4.

Dissolution of zeolite A-4

The feature of this method is direct injection of the sample solution (this solution containing cadmium and the dissolved zeolite A-4) into the graphite furnace.

Thus, the solubility of zeolite A-4 and the viscosity of the resulting solution were investigated: 100 mg of zeolite A-4 was added to 2.0 cm³ of hydrochloric or nitric acid, and dissolved using a test-tube mixer. If the resulting solution had a high viscosity, a portion of the resulting solution remained in the teflon tube of the automatic sampler, giving a negative error in the measurement of the cadmium concentration. Zeolite A-4 dissolved in both acid solutions, and the resulting solution had a low viscosity. Nitric acid was more effective for the dissolution of zeolite A-4, since the dissolution time was shorter and the acid concentration was lower than in the case of hydrochloric acid. The low acid concentration served to suppress the depletion of a graphite cuvette.

Furthermore, the metal contamination of the resulting solution (100 mg of zeolite A-4 dissolved in 2.0 cm³ of 2.0 mol dm⁻³ nitric acid) was examined, that is, the cadmium absorbance of the resulting solution was measured by GFAAS. The cadmium contamination in the resulting solution influences the cadmium concentration resulted in the proposed method. However, the cadmium contamination in the resulting solution was extremely low and could be neglected.

Although the small volume of nitric acid gave a high concentration rate, zeolite A-4 could not be decomposed in 1.0 cm³ of 2.0 mol dm⁻³ nitric acid. Thus, the cadmium-adsorbed zeolite A-4 was dissolved in 2.0 cm³ of 2.0 mol dm⁻³ nitric acid in subsequent experiments.

Effect of the amount of zeolite A-4 and the adsorption time for the preconcentration of cadmium onto zeolite A-4

According to the general procedure, the amounts of zeolite A-4 required for the preconcentration of cadmium was investigated using a solution (100 cm³) containing 0.005 µg of cadmium. Quantitative recovery of cadmium was achieved at above 50 mg of zeolite A-4. Therefore, 100 mg of zeolite A-4 was used for the collection of cadmium in this procedure.

Moreover, the effect of the adsorption time on the recovery of

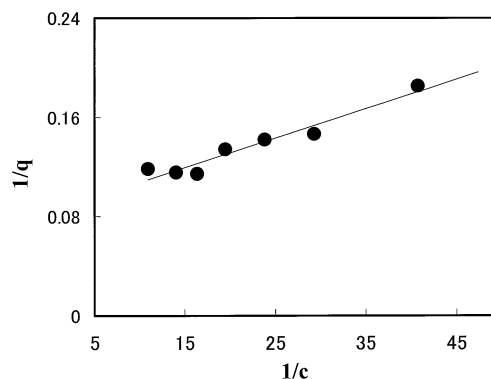


Fig. 2 Langmuir plots of the adsorption of cadmium(II). pH, 6.0; adsorption time, 60 min; sample volume, 100 cm³; A-4 zeolite, 100 mg.

cadmium was investigated. Cadmium was quantitatively collected onto the zeolite A-4 by stirring for more than 10 min with a magnetic stirrer. Therefore, an adsorption time of 20 min was used in the proposed procedure. SEM microphotographs and XRD patterns revealed no changes in the structure of zeolite A-4 (adsorption time, 20 min or 24 h), which indicates that zeolite A-4 is a stable adsorbent.

Adsorption of cadmium onto zeolite A-4

The recovery of cadmium from an aqueous solution was investigated according to the adsorption experiment. First, the recovery of cadmium from a low bulk metal concentration aqueous solution was examined. Zeolite A-4 quantitatively collected cadmium over 98% from these solutions. Secondly, the adsorption isotherms of cadmium onto zeolite A-4 in a wide bulk metal concentration aqueous solution at the optimum pH range was examined. The adsorption behavior can be described via the Langmuir adsorption equation:

$$\frac{1}{q} = \frac{1}{b} + \frac{1}{bKc}$$

where q (mg g⁻¹) is the amount of metal ions adsorbed onto the adsorbent at equilibrium, b (mg g⁻¹) is the maximal adsorption capacity, K (dm⁻³ mol⁻¹) is the adsorption equilibrium constant and c (mg cm⁻³) is the equilibrium concentration of metal ions in the residual solution. The Langmuir equation is an empirical equation, which is generally applicable to the monolayer adsorption of a single species from the liquid to the solid phase. The Langmuir adsorption isotherms (plots of $1/q$ versus $1/c$) of A-4 zeolite are approximately linear (Fig. 2). This shows that the Langmuir equation is a good fit for cadmium adsorption onto zeolite A-4 under the studied cadmium concentration range. From Fig. 2, the Langmuir equation parameters b and K were calculated to be 39.3 mg g⁻¹ and 53.1 dm⁻³ mol⁻¹, respectively. The value of K was high, indicating that the adsorbent used had a high adsorptive capacity. The b and K values obtained suggest that zeolite A-4 is an appropriate choice for an adsorbent. Thus, zeolite A-4 is effective for cadmium trace preconcentration due to its high adsorption capacity.

Optimization of operation conditions

In general, the pyrolytic graphite cuvette can be used repeatedly for about 200 times when a common aqueous sample solution is used. However, in the proposed procedure, the pyrolytic graphite cuvette could not be used for over 100 times

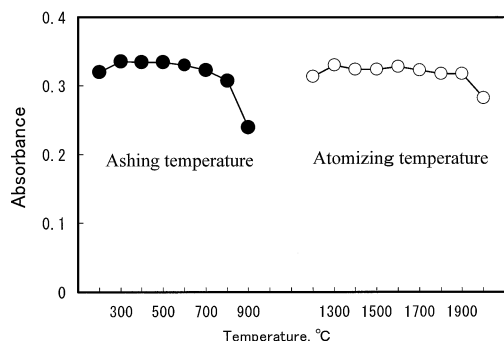


Fig. 3 Effect of the ashing and atomizing temperature on the absorbance of Cd.

because of the thermal decomposition product remaining after the measurement in the furnace, which caused a decrease in the analytical accuracy and an increase in the measurement error by repeated measurements. Although the structure of the residue (thermal decomposition product) was not determined by X-ray diffraction (XRD), its composition was Si, 21.6%; Al, 16.7%; Na, 12.0%; O, 39.7% as determined by elementary analysis. The residue could not be removed by any cleaning process. However, no residue remained in the furnace when a gas mixture of argon and oxygen was used as a sheath gas. Although argon gas is generally used to prevent the oxidation of a graphite cuvette, an alternate gas (mixture gas of Ar, 80%; O₂, 20%) proved to be effective in removing the residue in the present procedure. Thus, argon was used as a purge gas, and the alternate gas was used as a sheath gas in the present procedure.

Furthermore, it is very important to study the GFAAS measurement factors, such as the ashing and atomization temperatures, in order to achieve accurate atomic absorbance measurements for the analyte element. Thus, the effects of the ashing and atomization temperatures on the absorbance of cadmium were investigated using 2.0 cm³ of the resulting solution, according to the proposed procedure by varying the temperature from 200 to 900°C and from 1200 to 2000°C, respectively. The other conditions were kept constant, as given in Table 1. As shown in Fig. 3, a constant and maximum absorbance was obtained over the range from 300 to 800°C for the ashing temperature and from 1300 to 1900°C for the atomization temperature. The absorbance was observed to decrease below 300°C, which is attributable to incomplete thermal decomposition of the matrix in the ashing stage. The absorbance also decreased above 800°C, which is thought to be due to the considerable amount of cadmium volatilized before the atomization stage. In the case of the atomization temperature, the absorbance decreased below 1300°C because the atomization of cadmium was incomplete. The absorbance also decreased above 1900°C because the cadmium volatilized immediately, and could not be a sufficiently measurement of the cadmium absorbance.

Based on these results, an ashing temperature of 400°C and an atomization temperature of 1500°C were selected for cadmium analyses by the proposed procedure, and the graphite furnace was cleaned for 5 s at 1800°C after atomization.

Analytical performance

The calibration curves were obtained by applying the proposed procedure to a 100 cm³ of the sample solution. A straight line passing through the origin was obtained over the

Table 2 Effect of diverse ions on the determination of cadmium(II)

Ion	Amount added/ μg	Rec., %	Ion	Amount added/ μg	Rec., %
Ag(I)	100	101	Fe(III)	1000	102
Au(III)	100	96	Al(III)	1000	99
Bi(III)	100	105	Ca(II)	1000	100
Co(II)	100	97	K(I)	1000	100
Cr(III)	100	102	Na(I)	1000	102
Cu(II)	100	104			
Hg(II)	100	100	Cl ⁻	5000	100
Mn(II)	100	104	PO ₄ ²⁻	5000	98
Mg(II)	100	98	CO ₃ ²⁻	5000	100
Ni(II)	100	92	SO ₄ ²⁻	5000	102
Pb(II)	100	102	NO ₃ ²⁻	5000	102
Pd(II)	100	102	CO ₃ ²⁻	5000	100
Pt(IV)	100	95	SO ₄ ²⁻	5000	102
Sn(II)	100	98	NO ₃ ²⁻	5000	102
Zn(II)	100	101			

Cadmium(II) amount, 0.050 μg ; sample volume, 100 cm³; pH, 6.0; A-4 zeolite, 100 mg.

cadmium concentration range of 0.005 – 0.10 μg . The linear-regression equation (absorbance and cadmium concentration) was $y = 3.42x + 0.003$, and the correlation coefficient was 0.9993. The relative standard deviation was 3.7% for 0.010 μg of cadmium in a 100 cm³ sample solution (five observations), and the detection limit (3σ) was 0.002 μg for the cadmium in the initial sample solution.

In order to determine the appropriate volume of the sample solution, the volume of the aqueous phase was varied from 100 to 1000 cm³ containing 0.050 μg of cadmium. It was found that the recovery was constant up to 800 cm³ of the sample solution. At higher volumes (1000 cm³), the recovery decreased. Thus, a preconcentration factor of 400 could be achieved using 800 cm³ of the sample solution and dissolved with 2.0 cm³ of nitric acid.

Effect of diverse ions

The interference of foreign ions on the determination of cadmium was investigated by adding a known quantity of the desired ion to a 100 cm³ aliquot of aqueous solution containing 0.050 μg of cadmium under the recommended procedure. The obtained results are given in Table 2. The tolerance limit of foreign ions was taken as the value that caused an error of not more than $\pm 5\%$ in the absorbance.

No interference was found from common cations, such as Na(I), K(I), Ca(II) and Mg(II), and common anions, such as Cl⁻, NO₃⁻, CO₃²⁻, PO₄²⁻ and SO₄²⁻, over the investigation range, which were present at concentrations of 5000-times that of cadmium. Similarly, the other cations tested did not cause any serious interference, even when present at concentrations 500 times that of cadmium.

Application to determination of cadmium in water samples

The cadmium contents in several water samples were determined by the recommended procedure. The samples were immediately filtered through a membrane filter (pore size: 0.45 μm) to remove any suspended matter and adjusted to 1.0 mol dm⁻³ with nitric acid for storage in polyethylene bottles. Table 3 gives the results of analyses of the original sample solutions by the proposed procedure. In addition, known amounts of cadmium were spiked to the sample solutions. The quantitative recoveries of the spiked cadmium were obtained as shown in

Table 3 Determination of cadmium(II) in water samples

Sample	Sample volume/cm ³	Cd(II) added/ μg	Cd(II) found/ μg	Rec., %	R.S.D., % (n = 5)
Lake water (Noziriko, Nagano-pref.)	300	—	0.008	—	4.1
		0.010	0.019	102.7	4.4
		0.030	0.039	102.3	3.9
River water (Kitakamigawa, Iwate-pref.)	100	—	0.018	—	3.8
		0.010	0.027	98.4	3.8
		0.030	0.049	100.8	3.7
Experimental wastewater (Mimomi campas, Nihon University)	100	—	0.011	—	5.2
		0.010	0.021	99.4	5.1
		0.030	0.040	98.2	4.7

N.D. \leq 0.002 μg cadmium(II).

Table 3. The obtained results (Table 3) indicate that the proposed method is applicable to the analysis of water samples.

These results demonstrate the utility of the proposed method for the preconcentration and measurement of trace amounts of cadmium in water samples.

Conclusion

A solid-phase extraction method using zeolite A-4 for the preconcentration and determination of trace amounts of cadmium in water samples was investigated. Zeolite A-4 collected cadmium from sample solutions at pH 3.0–9.0, and the zeolite A-4 containing cadmium could be dissolved with nitric acid. The resulting solution was injected to the graphite furnace and its absorbance was measured by GFAAS. In this method, an alternate gas was effective for the measurement. Trace amounts of cadmium in natural water samples could be determined by the proposed procedure. The proposed method described here has the advantages of simplicity, rapidity, and a high concentration factor on the preconcentration procedure, and is applicable to the determination of trace amounts of cadmium in water samples.

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