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Atomic Absorption Spectrophotometric Determination of Trace Cadmium after Preconcentration by Extracting Its 8-Hydroxyquinoline Complex into Molten Benzophenone

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A sensitive method for the determination of trace cadmium after the preconcentration by extracting its 8-hydroxyquinoline complex into a molten benzophenone was developed. Several experimental conditions such as the pH of solution, the amounts of 8-hydroxyquinoline and benzophenone, stirring time, and standing time were optimized. Trace cadmium in 100 mL water sample was chelated with 2.5 mL of 0.001 M 8-hydroxyquinoline at pH 8.0. After 0.07 g benzophenone was added, the solution was heated to about 70 °C and stirred vigorously for 1 minute to dissolve the complex quantitatively in a molten benzophenone, and stood for 30 minutes to reproduce the microcrystalline benzophenone. The benzophenone containing Cd-8-hydroxyquinoline complex was filtered and dissolved in acetone. Cadmium was determined by a flame atomic absorption spectrophotometry. The interfering effects of diverse concomitant ions were investigated and eliminated. This method could be applied to natural water samples and the recovery of more than 90% was obtained in the real samples.

Introduction

The determination of trace cadmium in a natural water is of importance in connection with water pollution. Cadmium is present in river or stream at the level of $\mu\text{g/mL}$ or less. So, cadmium should be separated and concentrated from the bulk matrix prior to an actual determination. Several preconcentration methods such as coprecipitation,¹ liquid-liquid extraction,^{2,3} flotation,⁴ non-boiling evaporation,⁵ ion-exchange resin sorption,⁶ adsorption by active carbon⁷ and electrolytic deposition⁸ have been used for the determination of cadmium.

In this work, the solid-liquid extraction which is based on a solid-liquid separation following a liquid-liquid extraction has been used on the separation and preconcentration of cadmium. The solid-liquid extraction has got several advantages over the liquid-liquid extraction.⁹ It is less tedious because the distribution of the nonpolar complex between an aqueous phase and a molten nonpolar organic phase is attained in equilibrium within a few minutes owing to a high temperature. And the concentration factor, that is, the sensitivity can be enhanced by the complete extraction of metal ions in a 100 mL aqueous solution with only small amount of the solid solvent (~ 0.07 g). Usually, common organic sol-

vents used in the liquid-liquid extraction are somewhat soluble in a water, but a solid crystal such as benzophenone is so nearly immiscible with a water that the crystal can be completely separated from the aqueous solution even at a room temperature. In a consequence, this method does not induce any error due to the change in the solvent volume. Therefore, this method seems to be very suitable for the extraction of a metal complex without any difficulties in a solid-liquid separation.

Owing to several advantages described above, the active studies have been performed in this field.^{10,11} Usually, the solid-liquid extraction has been used when the metal complexes are slightly soluble in liquid solvents employed in liquid-liquid extraction.^{9,12,13}

For cadmium, nonpolar complexes of 8-hydroxyquinoline,¹⁴ dithiocarbamate,¹⁵ or morpholine-4-carbothionate¹⁶ were formed and dissolved in a molten naphthalene at a high temperature. It was determined by UV-Vis spectrophotometry or polarography. In these studies, the calibration range was about 1.0-16.0 $\mu\text{g/mL}$ and the amounts of naphthalene used was 0.5-3.5 g. Cadmium of sub- $\mu\text{g/mL}$ level in real samples can not be determined in this calibration range, and also flame atomic absorption spectrophotometry can not be applied since such amounts of naphthalene often make the sample injection capillary tube clogged.

The cadmium-8-hydroxyquinoline complex of this work was insoluble in the organic solvents such as chloroform or benzene¹⁴ so that the benzophenone was used for the solid-liquid extraction. Finally, cadmium in the resulting solution was determined by a flame atomic absorption spectrophotometry.

Experimental

Instrumentation. GBC model 903 flame atomic absorption spectrophotometer was used with following conditions: 10 cm 1-slot burner, hollow cathode lamp of Photron Dty. Ltd., wavelength: 228.8 nm, air flowrate: 16.0 L/min., acetylene flowrate: 1.5 L/min., spectral bandwidth: 0.5 nm, burner height: 20 mm, lamp current: 4.0 A.

Bantax model 300A digital pH meter with a combined glass and calomel electrode was used to adjust the pH.

Reagents. All chemicals used were of analytical-grade or guaranteed-grade reagents. The deionized water by a Milli-Q water system (Millipore Co.) was used throughout all experimental procedures. Cadmium standard solution was made with 1000 $\mu\text{g/mL}$ stock solution prepared from cadmium nitrate by a dilution. The 8-hydroxyquinoline solution of several concentrations were made in 99.99% ethanol. The each 10^{-3} M or 10^{-5} M solution of Ce(III), Co(II), Cu(II), Ni(II), Mg(II), Fe(III), Mn(II), Zn(II), Pb(II) and CN^- was used for the study on the interfering effects.

General procedure. A 100 mL sample solution was taken in a 250 mL conical Erlenmeyer flask, and 2.5 mL of 0.001 M 8-hydroxyquinoline was added as a complexing agent. The pH was adjusted to 8.0 with 0.05 M NaOH for the complete complexation and 0.07 g benzophenone was added as a solid solvent. Then, this solution was heated in a waterbath to about 70 $^{\circ}\text{C}$ and stirred vigorously for 1 minute to dissolve the complex in the molten benzophenone, and allowed to stand for 30 minutes at room temperature

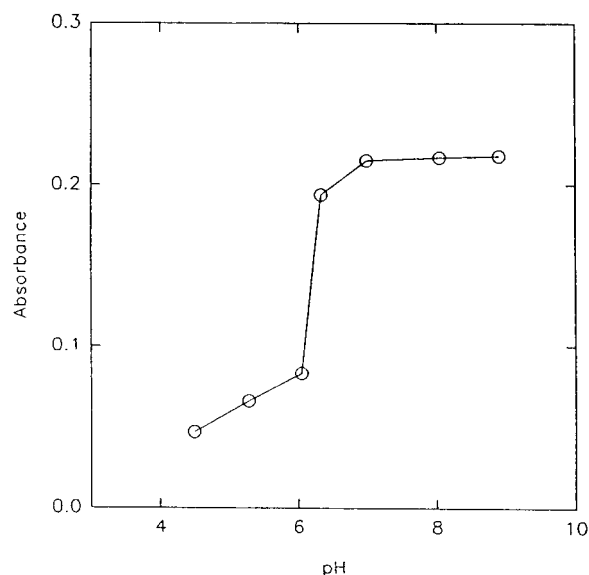


Figure 1. Effect of pH on the extraction of Cd(0.09 $\mu\text{g/mL}$).

to form microcrystalline benzophenone containing Cd-8-hydroxyquinoline complex. After filtered with fritted glass filter, this microcrystalline benzophenone was washed with deionized water and dissolved in a 10.0 mL volumetric flask with acetone. The absorbance of cadmium was measured on the base of Cd-free blank solution at 228.8 nm with flame atomic absorption spectrophotometer.

A calibration curve was prepared in the range 0.02-0.18 $\mu\text{g/mL}$ of cadmium as the general procedure.

A 100 mL aliquot of the real water sample was taken after the suspended matters or particles were filtered out with glass filter. A 4.0 mL of 0.010 M 8-hydroxyquinoline solution was added.

Results and Discussion

Effect of pH. The pH of the 100 mL solution containing 0.09 $\mu\text{g/mL}$ of cadmium and 2.5 mL of 0.001 M 8-hydroxyquinoline was carefully adjusted from 4.50 to 9.00 with 0.05 M HCl or 0.05 M NaOH to form the Cd-8-hydroxyquinoline complex quantitatively (Figure 1). Besides, the effect of pH on the extraction of Cd-8-hydroxyquinoline complex was investigated. As shown in Figure 1, the absorbance of cadmium extracted was dependent on the pH and the maximum absorbance was obtained in the range of pH 7.0-9.0. A pH 8.0 was chosen for the following measurements.

Amount of 8-hydroxyquinoline and benzophenone.

The extraction efficiency was investigated by adding the variable amount of 8-hydroxyquinoline to the solution containing 0.09 $\mu\text{g/mL}$ cadmium. Figure 2 shows that the cadmium could be quantitatively chelated on the addition of more than 1.5 mL of 0.001 M 8-hydroxyquinoline solution. Therefore, 2.5 mL of 0.001 M solution was used in this experiments.

The amount of benzophenone was varied from 0.01 to 0.16 g in order to investigate the efficiency that Cd-8-hydroxyquinoline complex was extracted into the molten benzophenone (Figure 3). The complex was quantitatively extracted on the addition of more than 0.05 g benzophenone. Below 0.05 g,

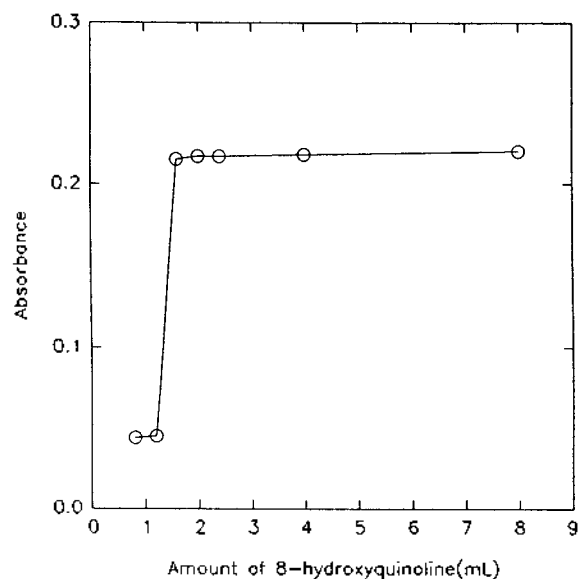


Figure 2. Extraction efficiency of Cd(0.09 µg/mL) in various amounts of 0.001 M 8-hydroxyquinoline.

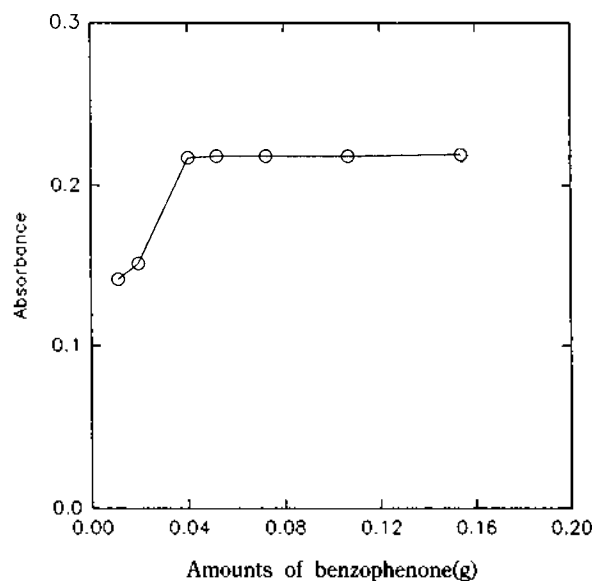


Figure 3. Variation in absorbance of Cd(0.09 µg/mL) according to the amounts of benzophenone.

the extraction was incomplete, and above 0.15 g, it was difficult to use because the capillary tube of flame AAS was often clogged. Hence, 0.07 g of benzophenone was used as the suitable amount.

Effect of stirring and standing time. The stirring time affects the distribution equilibrium in which nonpolar complex dissolves in a molten benzophenone at 70 °C. The extraction of Cd-8-hydroxyquinoline complex into a molten benzophenone at 70 °C was very rapid and the absorbance of Cd extracted was not changed between 30 seconds and 30 minutes. So, the sample solution was stirred vigorously for 1 minute.

To investigate the effect of standing time in reproducing the microcrystalline benzophenone after the extraction of Cd-

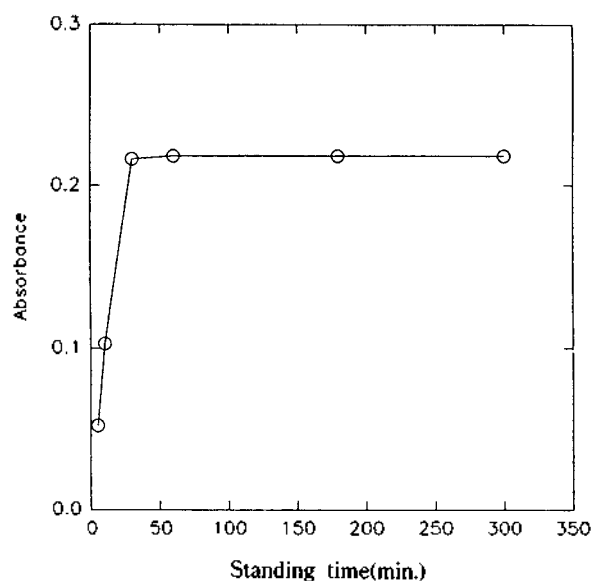


Figure 4. Effect of standing time on the extraction of Cd(0.09 µg/mL).

Table 1. Effects of diverse concomitant ions on the determination of 0.09 µg/mL cadmium

Ion ^a	Absorbance		Ion ^a	Absorbance	
	Mole ratio of ion to cadmium	change (%)		Mole ratio of ion to cadmium	change (%)
Ce(III)	10	-6.9	Fe(III)	10	-6.9
	100	-7.8		100	-7.8
	500	-5.5		500	-7.8
Co(II)	10	0.0	Mn(II)	10	-6.0
	100	-1.4		100	-6.0
	500	-2.3		500	-7.8
Cu(II)	10	-5.5	Zn(II)	10	-2.8
	100	-8.1		100	-3.7
	500	-44.5		500	-1.8
Ni(II)	10	-6.4	CN ⁻	10	-48.6
	100	-6.9		100	-50.5
	500	-7.8		500	-49.5
Mg(II)	10	-1.4	Pb(II)	10	-1.4
	100	-1.4		100	-53.7
	500	-42.7		500	-56.0

^aCations were added as nitrates or chlorides and an anion as sodium salt.

8-hydroxyquinoline complex into molten benzophenone at 70 °C in sample solution, it was allowed to stand at room temperature from 10 minutes to 5 hours (Figure 4). The absorbance of cadmium was remained constant at 30 minutes or more. The formation of microcrystalline benzophenone containing Cd-8-hydroxyquinoline complex was very fast even at room temperature. A standing time of 30 minutes was sufficient before the separation. It was observed that the microcrystalline benzophenone could be reformed more rapidly if the sample solution were vigorously stirred for approximately 1-2 minutes after the sample solution was cooled

Table 2. Figures of merit for calibration curves of cadmium

	without extraction	with extraction ^a	with extraction ^b
linear range ($\mu\text{g/mL}$)	0.20-1.80	0.020-0.180	0.020-0.180
regression equation ($y=b+mx$)	$-0.00535+0.23975x$	$-0.0114+2.5200x$	$-0.01865+2.5125x$
correlation coefficient (r)	0.99905	0.99566	0.99821
detection limit (ng/mL)		0.65806	

^a for the standard solutions without any interfering ions. ^b for the standard solutions with all concomitant ions of each 8.0×10^{-5} M and 4.0 mL of 0.010 M 8-hydroxyquinoline.

to about 30 °C.

Effects of concomitant ions. The possible interfering effects of concomitant ions on the determination of cadmium was investigated under the conditions given above. Sample solutions containing 0.09 $\mu\text{g/mL}$ cadmium, various metal ions and sodium cyanide were used for the investigation because they were assumed to prevent the Cd-8-hydroxyquinoline complex from forming. The results of interference studies are summarized in Table 1.

Cobalt(II) and zinc have not interfered for the extraction of Cd up to 500 : 1 mole ratio of this ion to cadmium, and magnesium up to 100 : 1 and lead up to 10 : 1 (that is, less than 3% effect on absorbance). Cerium(III), nickel, iron(III) and manganese(II) had the interferences to a small extent at the levels of 500 : 1. But magnesium at more than 500 : 1 mole ratio, copper(II) and lead at more than 100 : 1, and cyanide ion at even 10 : 1 caused to significant interferences. Such interfering effects are assumed to be caused by the complexation of those metal ions with 8-hydroxyquinoline prior to cadmium and the formation of more stable cyano cadmium complex than 8-hydroxyquinoline complex. To release the interferences by all ions at the 100 times concentration of cadmium, the added amount of 8-hydroxyquinoline was varied from 100 to 10,000 times moles of cadmium. The interferences could be sufficiently overcome by the addition of 4.0 mL of 0.010 M 8-hydroxyquinoline (~500 times).

Calibration curve and detection limit. A calibration curve was constructed with five standard solutions according to the general procedure described above. The calibration curve obtained was used to estimate the detection limit in accordance with the literature.¹⁷ Table 2 shows the linear range, the regression equation, the correlation coefficient(r), and the detection limit for the calibration curves. That is, the slopes were 0.23975, 2.5200 and 2.5125, and the correlation coefficient(r) were 0.99905, 0.99566 and 0.99821, for the case of no extraction, the extraction of the standard solutions, and the extraction of the standard solutions having all concomitant ions of each 8.0×10^{-5} M and 4.0 mL of 0.010 M 8-hydroxyquinoline, respectively. From these results, it could be known that three calibration curves had good linearity. Because the slope of the calibration curve constructed after the extraction of standard solution without any interfering ions was almost equal to that obtained after the extraction of the standard solution with those concomitant ions of each 8.0×10^{-5} M and 4.0 mL of 0.010 M 8-hydroxyquinoline in the same concentration range of cadmium (relative error : 0.3%), the former calibration curve was applied to determine cadmium in real sample.

The detection limit was defined as the sample concentra-

Table 3. Analytical data of cadmium in natural water ($\mu\text{g/mL}$)

spiked ($\mu\text{g/mL}$)	measured ($\mu\text{g/mL}$)	average ($\mu\text{g/mL}$)	coefficient of variation	s_r (%)	recovery
0.0000	0.0285	0.0284	4.95	0.0061	
	0.0269				
	0.0297				
0.1000	0.1228	0.1218	0.82	0.0011	93.4
	0.1217				
	0.1208				

tion giving a signal equal to the blank signal plus three times the standard deviation of blank.¹⁸ The detection limit obtained from a 10-fold concentrated cadmium solution was 0.65806 ng/mL .

Determination of cadmium in real samples. The absorbance of cadmium in water sample obtained from the contaminated Suwon stream was measured by flame atomic absorption spectrophotometer. The recovery in the real sample spiked with 0.1 $\mu\text{g/mL}$ of cadmium was determined by the proposed method in experimental section. The recovery was found to be 93.4% for cadmium as in Table 3. The coefficients of variation were 4.95% for 0.0284 $\mu\text{g/mL}$ of cadmium in a stream water sample and 0.82% for same water sample spiked with 0.1 $\mu\text{g/mL}$ cadmium. From these recovery and the coefficient of variation, this proposed method could be applied to the determination of cadmium in natural water sample.

Conclusion

The optimum values of experimental conditions such as the pH of sample solution, the amount of chelating agent (0.001 M 8-hydroxyquinoline), the amount of benzophenone, and standing time were 8.0, 2.5 mL, 0.07 g and 30 minutes, respectively. The sufficient addition of 8-hydroxyquinoline could eliminate the interfering effects by diverse ions coexisted. This proposed method could be applied to the determination of cadmium in natural water. Recovery was evaluated with 93.4%.

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Determination of Derivatives of Phenol with a Modified Electrode Containing β -Cyclodextrin

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Voltammetric determination of phenol derivatives, such as phenol, o-, m-, and p-cresols was studied with a β -Cyclodextrin (β -CD) modified-carbon paste electrode composing of the graphite powder and Nujol oil. Phenol derivatives were chemically deposited via the complex formation with β -CD by immersing the CME into a sample solution. The resulting surfaces were characterized with cyclic and differential pulse voltammetry. Treating the CME with 1 M nitric acid for five sec after a measurement could regenerate the electrode surface. Linear sweep and differential pulse voltammograms were recorded for the above system to optimize the experimental parameters for analysing the phenol derivatives. In this case, the detection limit for phenols was 5.0×10^{-7} M for 25 min of the deposition time with differential pulse voltammetry. The relative standard deviation was $\pm 5.2\%$ of 3.0×10^{-6} M (four repetitions). The interference effect of the following organic compounds was also investigated; Bezoic acid, hippuric acid, o-, m-, and p-methylhippuric acid. Adding the organic compounds into the sample solution reduces the peak current of the phenols to about 25%.

Introduction

A cyclodextrin (CD) is cyclic carbohydrates consisting of glucose units that associate with other organic compounds. The unique property of CD is that it forms the inclusion complex with the guest compounds in the cavity.^{1,2} Guest compounds incorporated in the CD cavity include various organic species of appropriate size, especially aromatic compounds. The mole ratio of the guest to host (CD) is usually 1:1 and 2:1. Exceptions include sometimes carboxylic acid and molecules which have long chains such as methyl orange.^{3,4} Another distinctive characteristic of CD is that it can form crystalline insoluble complexes with many hydrocarbons.⁵ While there are several studies for the chromatographic separation of organic species with CD via the inclusion complex formation,^{1,2,6} few studies of the electrochemical behavior of organic species in the presence of CD has been done so far.⁷⁻¹¹ Moreover, the direct analysis of organic spe-

cies using CD in electrochemical methods have been done less than that of the electrochemical behaviors of the CD derivatives.

Osa *et al.* reported that the effects of added α - and β -CDs on the half-wave potentials and the diffusion coefficients of o-, m-, and p-nitrophenols and determining the dissociation constants of CD-phenol complexes.⁹ Based on this, Matsue *et al.* investigated about a regioselective electrode system aimed at determining o-nitrophenol with a poly(perfluoro sulfonic acid)-coated electrode which was based on the regiorecognition ability of α -CD in the presence of p-nitrophenol.¹² They suggested that p-nitrophenol binded with α -CD in the Nafion layer. Nagase *et al.* developed the voltammetric anion responsive sensors based on ordered membrane assemblies containing cyclodextrin polyamine deposited on glassy carbon electrodes by the Langmuir-Blodgett method.¹³

We used the properties of β -cyclodextrin(β -CD), which is a cyclic carbohydrate consisting of seven glucose units¹ which can associate and capture the phenol derivatives. This was used to analyze these compounds in an aqueous solution

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