

Determination of Cadmium(II) and Copper(II) by Flame Atomic Absorption Spectrometry after Preconcentration on Column with Pulverized Amberlite XAD-4 with Bismuthiol I

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A column preconcentration method with pulverized Amberlite XAD-4 loaded with bismuthiol I (BI) has been developed for the determination of trace Cd(II) and Cu(II) in various real samples by flame atomic absorption spectrophotometry. Various experimental conditions, such as the size of XAD-4, adsorption flow rate, amount of bismuthiol I, stirring time for adsorbing bismuthiol I on XAD-4, pH of sample solution, amount of XAD-4-BI, desorption solvent, and desorption flow rate, were optimized. Also, the adsorption capacity and the adsorption rate of Cd(II) and Cu(II) on XAD-4-BI were investigated. The interfering effects of various concomitant ions were investigated, Bi(III), Sn(II) and Fe(III) were found to affect the determination. But the interference by these ions was completely eliminated by adjusting the amount of XAD-4-BI resin to 0.70 g, although the adsorption flow rate was slower. For Cd(II) our proposed technique obtained a dynamic range of 0.5-40 ng mL⁻¹, a correlation coefficient (R²) of 0.9913, and a detection limit of 0.3 ng mL⁻¹. For Cu(II), the corresponding values were 2.0-120 ng mL⁻¹, 0.9921 and 1.02 ng mL⁻¹. To validate this proposed technique, the aqueous samples (stream water, reservoir water, tap water and wastewater), the diluted brass sample and the plastic sample, as real samples, were used. Recovery yields of 91-103% were obtained. These measured data were not different from ICP-MS data at 95% confidence level. Our proposed method was also validated using rice flour CRM (normal, fortified) samples. From the results of our experiment, we found that the technique we present here can be applied to the determination of Cd(II) and Cu(II) in various real samples.

Key Words : Cadmium(II), Copper(II), Adsorption, Amberlite XAD-4, Bismuthiol I (BI)

Introduction

Cd(II) is used extensively in the manufacturing of batteries, paints, and plastics. In addition, iron products, such as nuts and bolts, are plated with it to prevent corrosion. Plating operations are the major source of the cadmium that reaches the water environment, which at extreme concentrations causes an illness called "Itai-Itai", which is characterized by brittle bones and intense pain. Low levels of exposure to cadmium over prolonged periods causes high blood pressure, sterility among males, kidney damage, and flu-like disorders. Recent findings show that significant amounts of cadmium are contained in cigarette smoke.

While being a gastrointestinal tract irritant, Cu(II) is generally not harmful to humans at low $\mu\text{g mL}^{-1}$ concentrations. In surface water, however, Cu(II) can be toxic to aquatic plants and some fish species at concentrations less than 1.0 $\mu\text{g mL}^{-1}$. Thus, Cu(II) tends to be much more of an environmental hazard than a human hazard.¹ Most environmental, biological and alloy samples generally have a trace amount of Cu(II) at the ng mL⁻¹ level. Therefore, the accurate and precise determination of trace Cd(II) and Cu(II) is becoming increasingly important.

In the determination of Cd(II) and/or Cu(II), various methods, including UV-Vis spectrophotometry,² FAAS,³ ET-AAS,⁴ ICP-AES,⁵ ICP-MS,⁶ stripping voltammetry,⁷ ion chromatography,⁸ potentiometry,⁹ spectrofluorimetry¹⁰ and

polarography¹¹ have been used.

ET-AAS, ICP-MS, and stripping voltammetry can measure directly at the ng mL⁻¹ level. However, some of these methods are time-consuming, require complicated and expensive instruments, have complex operational conditions, encounter various types of interference or have high maintenance cost.

If instruments with high sensitivity are not required when the concentration of Cd(II) and Cu(II) to be determined is at the level of ng mL⁻¹, UV-Vis spectrophotometry, FAAS and polarography, which are commonly employed in general laboratories, could be used. However, the main problem with these methods is a low sensitivity for trace metal ions at the ng mL⁻¹ level. This limitation can be overcome with some preconcentration techniques.

Liquid-liquid extraction¹² and a solid phase extraction are two methods by which trace Cd(II) and Cu(II) in aqueous solution can be preconcentrated. Although solid phase extraction has severe limitations under which metal ions or metal chelates can be adsorbed or desorbed on solid adsorbents, it has many advantages, including the availability and easy recovery of the solid phase, the attainability of large preconcentration factors, the facility for separation and enrichment, using systems with continuous flow, and the absence of the need for toxic organic solvents.¹³

Activated carbon,¹⁴ chitosan,¹⁵ silica,¹⁶ naphthalene,¹⁷ thiol cotton fiber,¹⁸ alumina,¹⁹ polyurethane foam,²⁰ and Am-

berlite XAD resin²¹ are present in common solid adsorbents.

Among solid adsorbents, Amberlite XAD resins have been widely used to develop several chelating resins for preconcentration procedures because of its good physical properties, including porosity, high surface area, durability and purity.²²

Chelating resins can be used to preconcentrate the metal ions after a chelating agent is adsorbed²³ or bonded chemically²⁴ on Amberlite XAD resin surface. Chelating resin in which a chelating agent is bonded chemically is so stable that it can be used repeatedly. But, its adsorption capacity on metal ions is only in the medium range because of the steric effect of the chelating agent.²⁵ It also presents limits when selecting a desorption solvent, because the desorption of electrostatically bound metal ions is expected to be achieved only by proton exchange from concentrated acidic solution. On the other hand, although the adsorbed chelating resin is less stable than the bonded chelating resin, the former has more capacity sites and is more effective for desorption because of the option of utilizing either a common organic solvent or acidic solution to remove the adsorbed metal chelates or the bound metal ions. Therefore, if an appropriate chelating agent that adsorbed stably were selected, the adsorbed chelating resin would be seen rather favorably as separating and enriching the metal ions.

Enhanced adsorption capacity of the chelating resin can be achieved by increasing the number of chelating sites on the resin as well as their accessibility. This can be obtained by using a resin with a relatively high surface area and by selecting a chelating agent of small molecular size.²⁶ Amberlite XAD-4, a type of polystyrene divinylbenzene, has a hydrophobic surface and macroporous surface, a relatively high surface area ($725 \text{ m}^2 \text{ g}^{-1}$), and is widely used as a good adsorbent for organic substances containing π electrons.²⁷ Bismuthiol I (BI) is relatively small in size and has π electrons. Therefore, we expected that Cd(II) and Cu(II) would be well preconcentrated selectively if a XAD-4 resin loaded with bismuthiol I and a mixed Cd(II) and Cu(II) solution with optimized pH were used.

The aim of the present work is to develop and validate a method for preconcentration and separation from matrix constituents of ng mL^{-1} levels of Cd(II) and Cu(II) in real samples, such as aqueous solutions, brass, plastics, and rice flour CRM samples, using a glass column filled with pulverized XAD-4 loaded with bismuthiol I.

Experimental

Instrumentation and apparatus. For the determination of preconcentrated Cd(II) and Cu(II), a GBC model 903 flame atomic absorption spectrometer was used under the following conditions: 10 cm 1-slot burner, cadmium and copper hollow cathode lamp of Photron Dty. Ltd., wavelength: 228.8 nm for Cd and 324.7 nm for Cu, air-acetylene flame, burner height: 10 mm, lamp current: 3.0 mA for both Cd and Cu, and spectral bandwidth: 0.5 nm. Cd(II) and Cu(II) in real samples was determined directly with a HP

4500 ICP-MS spectrometer. A Bantex model 300A digital pH meter with a combined glass and calomel electrode was used to adjust the pHs of all sample solutions.

To pulverize Amberlite XAD-4 resin, a Vibratory Micro Mill (Model Pulverisette 0, Taemyoung Co., Korea), and a mortar and pestle were used. A CEM Microwave oven (Mars 5 model, vessel type XP 1500 plus) was used to convert the rice flour CRM samples and the plastic samples to solution samples. A glass column (10 cm \times 10 mm i.d.) with a glass filter (1-G-1) and a Teflon stopcock at the bottom was used to preconcentrate Cd(II) and Cu(II) in sample solutions.

To determine bismuthiol I, which remained after being adsorbed on XAD-4 resin, a Hewlett-Packard 8453 UV-Vis spectrophotometer was used. To investigate optimum flow rate, a peristaltic pump (Micro tube pump MP-3, EYELA Tokyo Rikakikai, Japan) was used.

Reagents and solutions. All chemicals used in this experiment, which included Cd(NO₃)₂·4H₂O (Aldrich Co.), Cu(NO₃)₂·7H₂O (Aldrich Co.), and bismuthiol I (2,5-dimercapto-1,3,4-thiadiazole, Aldrich Co.), were of analytical grade and guaranteed grade reagents unless otherwise specified. Amberlite XAD-4 (20-60 mesh) was purchased from Aldrich Co. Cd(II) and Cu(II) standard solutions were prepared with 1000 $\mu\text{g mL}^{-1}$ stock solution prepared from cadmium(II) nitrate and copper(II) nitrate by a suitable dilution. Water deionized by a Barnstead E-Pure 3-module deionization system was used throughout all experimental procedures. The concentration of stock solution of various species used in investigating the interfering effects was 1000 $\mu\text{g mL}^{-1}$. Korea Research Institute of Standards and Science (KRISS) supplied rice flour certified reference materials (normal and fortified).

Pulverization of Amberlite XAD-4 resin. XAD-4 resin (20-60 mesh, 0.25-0.85 mm) was purified with an ethanol : hydrochloric acid : water (2:1:1) solution, washed with deionized water until the resin was free from acid, and dried at 110°C for 3 hours. In one method for pulverizing XAD-4 resin, the resin, 0.075-0.106 mm in size, was gathered with 150 mesh and 200 mesh sieves after being dried and ground with a mortar and pestle. The other technique was cryogenic grinding, accomplished by using a cryogenic mill with a self-container liquid nitrogen bath (Vibratory Micro Mill). XAD-4 resin was ground into fine particles (500-800 mesh, 0.015-0.025 mm).

Preparation of Amberlite XAD-4 loaded with bismuthiol I. For the adsorption of bismuthiol I on XAD-4, 3.0 g of the cleaned and pulverized XAD-4 resin (150-200 mesh) was added to 50 mL of ethanol solution containing 250 mg of bismuthiol I and stirred for 3 hours. Thereafter, XAD-4 resin loaded with bismuthiol I was filtered with filter paper (Whatmann No. 41) in a glass funnel, washed with deionized water, and dried at 40 °C for 3 hours in a drying oven, and stored in a desiccator.

Preconcentration of Cd(II) and Cu(II) in column. A 0.50 g sample of XAD-4-BI (0.075-0.106 mm) was packed in a glass column (10 cm \times 10 mm i.d.). A 1000 mL sample

Table 1. Decomposition conditions of microwave digestion system for plastic powder and rice powder samples

Step	Plastic Powder			Rice Powder		
	Ramping time (min.)	Temperature (°C)	Holding time (min.)	Ramping time (min.)	Temperature (°C)	Holding time (min.)
1	3.0	120	0.0	3.0	120	5.0
2	3.0	150	0.0	3.0	150	5.0
3	3.0	180	10.0	3.0	200	20.0
4	5.0	200	25.0			
Cooling		room temperature	60.0		room temperature	60.0

solution containing Cd(II) and Cu(II) was taken into a 1000 mL Erlenmeyer flask, and adjusted to pH 6.0 with 0.1 M HCl or 0.1 M NaOH. This sample solution was passed through the column packed XAD-4-BI resin at a flow rate of 5.0 mL min⁻¹ by simply controlling the stopcock in the glass column. The desorption of Cd(II) and Cu(II) retained on XAD-4-BI was carried out with 10 mL of 4 M HNO₃ warmed to 50°C at a flow rate of 0.5 mL min⁻¹, and the desorbed Cd(II) and Cu(II) solution was collected to a 10 mL volumetric flask and then filled with 4 M HNO₃ to the mark. Cd(II) and Cu(II) content in the collected solution was measured on the base of Cd- and Cu-free blank solution at 228.8 nm and 324.7 nm, respectively, with a flame atomic absorption spectrometer.

Calibration curve and detection limit. The calibration curves were prepared in the concentration range of 0.5–40 ng mL⁻¹ for Cd(II) and 2.0–120 ng mL⁻¹ for Cu(II) standard solutions, according to “Preconcentration of Cd(II) and Cu(II) in column,” by simultaneously using several columns. The regression equation and the correlation coefficient (R²) of the calibration curve were obtained with the method of least squares. The detection limit was obtained from the signals of twenty-five blank samples and the slope of the calibration curve. The detection limit is defined as the sample concentration giving signals equal to three times the standard deviation of the blank signal.²⁸

Preparation of aqueous samples. The 1000 mL aliquots of stream water (Hwangguchicheon, Suwon, Korea), reservoir water (Botongri, Hwaseong, Korea), tap water (The University of Suwon, Korea), and the untreated wastewater (Suwon Environmental Production Office, Korea) were taken after the suspended matter or particles were filtered out with a glass filter (1-G-4) and used as real samples.

Preparation of diluted brass sample. The surface of the brass sample was washed with acetone and deionized water to remove impurities. A 0.1000 g brass sample was weighed accurately and transferred to a 250 mL Erlenmeyer flask to which 10 mL of 6 M HNO₃ was added. The flask was heated in a fume hood until the contents dissolved completely and cooled to room temperature. This brass solution was transferred to a 1000 mL volumetric flask and diluted by filling to the mark. A 0.5 mL aliquot of the solution was diluted further to 1000 mL with deionized water in a volumetric flask and used as a real sample.

Preparation of plastic sample. A 0.5 g portion of the finely ground plastic sample was taken to a high-pressure digestion vessel. Then 9 mL of concentrated HNO₃ and 2

mL of H₂O₂ were added, and these materials were mixed well. The plastic sample decomposed in the CEM microwave oven (Mars 5 model) according to the digestion program in Table 1. The dissolved sample solution and the solution used to wash the digestion vessel were collected to a 1000 mL volumetric flask and diluted with deionized water to the mark.

Preparation of rice flour CRM samples. A 1.0 g rice-flour sample (CRM 108-01-001 (normal), CRM 108-01-002 (fortified)) was taken to a high-pressure digestion vessel, and 7 mL of concentrated HNO₃ were added and mixed well. The rice flour CRM sample was decomposed in a CEM microwave oven (Mars 5 model) according to the digestion program in Table 1. The dissolved sample solution and the solution used to wash the digestion vessel were collected to a 1000 mL volumetric flask and diluted with deionized water to the mark.

Results and Discussion

Size of Amberlite XAD-4 and adsorption flow rate. Amberlite XAD-4 resin was prepared as the original resin (20–60 mesh, 0.25–0.85 mm), pulverized by a mortar and pestle (150–200 mesh), and ground by a Vibratory Micro Mill (500–800 mesh).

Each 0.50 g of size-different XAD-4-BI resin was taken to a glass column, 1000 mL of 15 ng mL⁻¹ Cd(II) or 30 ng mL⁻¹ Cu(II) standard solution adjusted to pH 6.0 was passed through the glass column to enrich Cd(II) or Cu(II) in accordance with “Preconcentration of Cd(II) and Cu(II) in column.” Thereafter, it was compared with the preconcentration efficiency, according to the size of XAD-4-BI resin and the flow rate of the sample solution. The result is shown in Figure 1.

For Cd(II), XAD-4-BI resin with 20–60 mesh was adsorbed quantitatively below the 2 mL min⁻¹ flow rate, but as the flow rate was increased above 2 mL min⁻¹, the adsorption yield slowly decreased. Cu(II) was also adsorbed quantitatively below the 3 mL min⁻¹ flow rate. In both cases, we assumed the results reflected a flow rate faster than the equilibrium adsorption rate.²⁹ And for both Cd(II) and Cu(II), it is known that the smaller the particle size, the bigger the specific adsorbing surface area and the higher the desorption of analyte on the resin. Therefore, preconcentration efficiency is higher in the column prepared with 150–200 mesh resin compared with 20–60 mesh resin.³⁰ XAD-4-BI resin with 500–800 mesh was so fine that a peristaltic

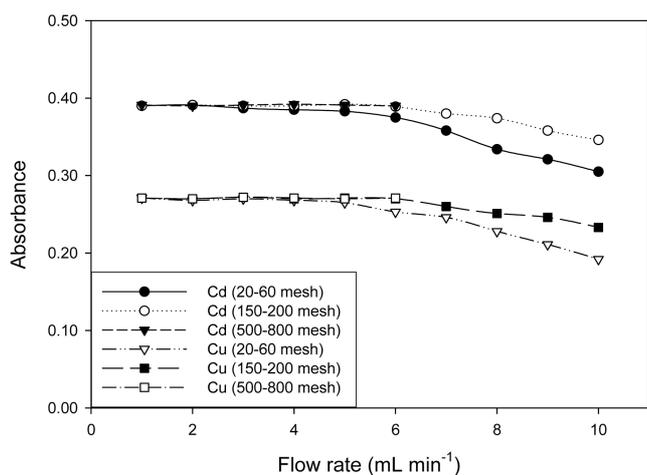


Figure 1. Effect of XAD-4 size and flow rate on the preconcentration of Cd(II) (15 ng mL^{-1}) and Cu(II) (30 ng mL^{-1}) at pH 6.0.

pump had to be used at even 1 mL min^{-1} , and the pump could not be used above 6 mL min^{-1} because of high back-pressure. Smaller resin particles would have good preconcentration yield at higher flow rates, but they would have increased back-pressure on the glass column, making it necessary to reduce the flow rate, subsequently increasing preconcentration time. Therefore, XAD-4-BI with 150-200 mesh, for which the flow rate, could be maintained at 5 mL min^{-1} by controlling the stopcock conveniently, was used in this experiment.

Amount of bismuthiol I. The amount of bismuthiol I dissolved in 20 mL ethanol was varied from 5 mg to 55 mg, with the bismuthiol I loaded in several 0.5 g portions of 150-200 mesh XAD-4 resin and stirred for 3 hours. To analyze the supernatant solution of each sample, aliquots of 5.0 of the solution were removed by a measuring pipet. The concentration of bismuthiol I in the supernatant solution was determined by a UV-Vis spectrophotometer, and then the amount of bismuthiol I adsorbed on XAD-4 resin was calculated. The result is shown in Figure 2. The amount of

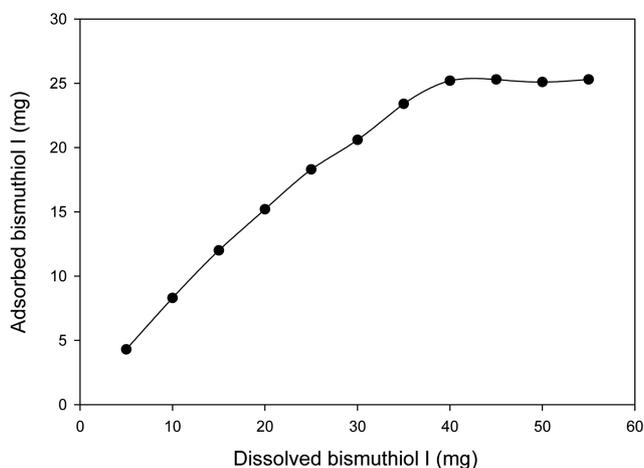


Figure 2. The amount of bismuthiol I adsorbed on 0.50 g XAD-4 according to the amount of dissolved bismuthiol I.

actually adsorbed bismuthiol I was maximized and varied slightly when the amount of bismuthiol I in ethanol solution was above 40 mg. So, the optimum amount of bismuthiol I was selected at 40 mg. But when the actually adsorbed amount of bismuthiol I in 40 mg was measured by UV-Vis spectrophotometry ($\lambda_{\text{max}} = 336 \text{ nm}$, $\epsilon_{\text{max}} = 1.44 \times 10^4$), the value was 25.2 mg. This corresponds to $(0.335 \text{ mmole}) (\text{g XAD-4})^{-1}$. In the experimental section "Preparation of Amberlite XAD-4 loaded with bismuthiol I", the amount of XAD-4 and bismuthiol I was taken to be 3.0 g and 250 mg, respectively. In this case, the adsorbed amount of bismuthiol I was $(0.342 \text{ mmole bismuthiol I}) (\text{g XAD-4})^{-1}$ similar to the previous result. So, when XAD-4 resin was loaded with bismuthiol I, we used the method in the experimental section.

Stirring time for loading with bismuthiol I on XAD-4 resin. Leaving the macroporous resins in contact with the reagent solution for a longer period of time assures that the reagent is quantitatively adsorbed.³¹ After 0.50 g of dried XAD-4 resin and 40 mg bismuthiol I in 20 mL ethanol were added to a 50 mL beaker, bismuthiol I coated the XAD-4 resin in variance with stirring time. The adsorption degrees of bismuthiol I on XAD-4 resin as a function of stirring times are shown in Figure 3. Bismuthiol I was adsorbed quantitatively and stably on XAD-4 resin above 180 minutes. Therefore, stirring time was optimized to 180 minutes.

pH. A sample solution was investigated to find the effect of its pH on the adsorption degrees of Cd(II) or Cu(II) in column. When a specific metal ion was separated and preconcentrated by using resin loaded with the chelating agent at optimum pH, the selectivity and the efficiency of resin loaded with chelating agent could be maximized.

After 0.50 g of XAD-4-BI was added to each glass column, 1000 mL of 15 ng mL^{-1} Cd(II) or 30 ng mL^{-1} Cu(II) solution varied in pH from 3.0 to 11.0 by using 0.1 M HCl or 0.1 M NaOH was passed. We investigated at which pH there was quantitative preconcentration, and the results are shown in Figure 4. We found that both Cd(II) and Cu(II) were adsorbed quantitatively at pH ranging from 6.0 to 8.0.

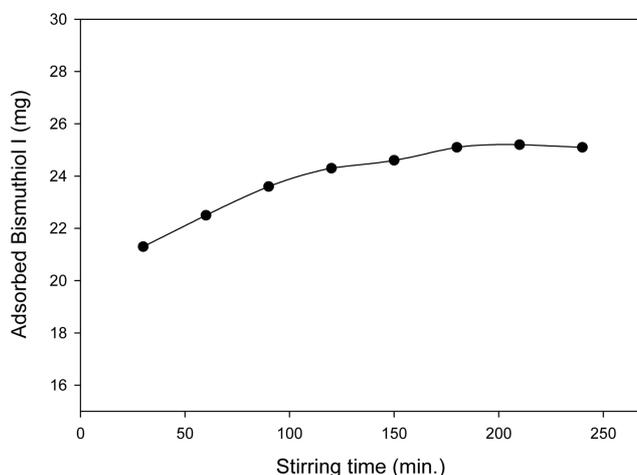


Figure 3. Effect of stirring time on the adsorption of bismuthiol I (40 mg) on XAD-4 (0.5 g).

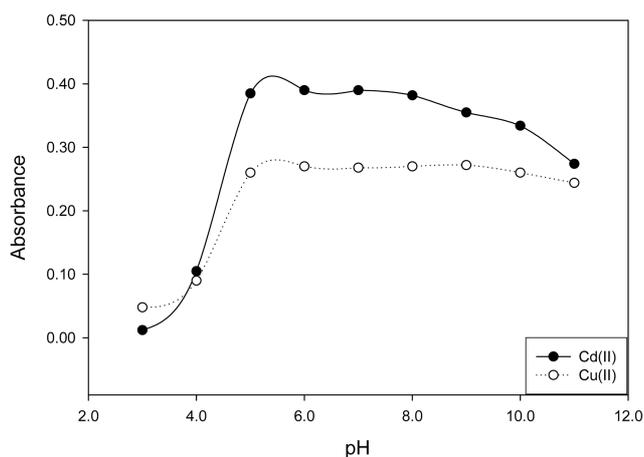


Figure 4. Effect of pH on the adsorption of Cd(II) (15 ng mL^{-1}) and Cu(II) (30 ng mL^{-1}) on XAD-4-BI resin.

Cd(II) and Cu(II) were not preconcentrated quantitatively above pH 10.0. We concluded that the adsorption process competed with the process forming the hydroxide precipitate. When the pH of the Cd(II) or Cu(II) solution was adjusted to 6.0, a buffer solution was not used. The concentrated phosphate buffer ($\text{KH}_2\text{PO}_4 + \text{NaOH}$) used to prepare the buffer solution of pH 6.0 might interfere with the preconcentration of Cd(II) or Cu(II). Therefore, pH 6.0 was selected as the optimum pH, and it was adjusted using 0.1 M HCl or 0.1 M NaOH.

Adsorption capacity. The adsorption capacity (maximum amount of metal adsorbed per gram of resin) of the resin is important to determine how much resin is required to quantitatively adsorb a specific metal ion from the solution. The adsorption capacity of resin on a metal ion was determined by saturating 1.0 g of chelating resin with metal ion solution. Several factors, including surface area, pore diameter, distribution surface polarity, chelating agent, and solvent polarity, contribute to a chelating resin's capacity for a given solute.³²

The adsorption capacities of XAD-4-BI resin on Cd(II) or Cu(II) were determined by the batch process. A 0.50 g XAD-4-BI resin was added to 50 mL of 2.0×10^{-4} M Cd(II) or Cu(II) solution at pH 6.0 and at 25 °C in a 50 mL beaker. After it was stirred for 1 hour, this solution was filtered. Cd(II) or Cu(II) in the filtrate was determined by flame atomic absorption spectrometry. The adsorption capacity of XAD-4-BI resin for Cd(II) or Cu(II) was calculated from Cd(II) or Cu(II) concentration difference between the original solution and filtrate. The adsorption capacity Q_r was calculated as follows³³:

$$Q_r = (C_0 - C_e)V/W,$$

where Q_r is the adsorption capacity (mmole g^{-1}). C_0 and C_e are the initial and the equilibrium molar concentration of Cd(II) or Cu(II). V is the volume of Cd(II) or Cu(II) solution (mL). W is the mass of XAD-4-BI (g). For Cd(II), the adsorption capacity of XAD-4-BI resin was $0.0043 (\pm 0.0005)$ ($\text{mmole Cd(II)} (\text{g resin})^{-1}$), or $0.483 (\pm 0.061)$ (mg

Cd(II)) ($\text{g resin})^{-1}$ for 7 measurements. For Cu(II), it was $0.0067 (\pm 0.0008)$ ($\text{mmole Cu(II)} (\text{g resin})^{-1}$), or $0.423 (\pm 0.047)$ (mg Cu(II)) ($\text{g resin})^{-1}$ for 7 measurements.

Adsorption rate of Cd(II) and Cu(II). The adsorption rate of Cd(II) or Cu(II) on XAD-4-BI was determined by batch method. A 0.50 g of XAD-4-BI was added to a 50 mL beaker containing 50 mL of 2.0×10^{-4} M Cd(II) or Cu(II) solution at pH 6.0 and then the solution was stirred at 25 °C for predetermined times. To sample the supernatant solution at predetermined times, we used fourteen batch systems were used. Also, at predetermined time intervals, aliquots of 5.0 mL solution were removed for analysis. The concentration of Cd(II) or Cu(II) in the supernatant solution was determined by FAAS, and then the amount of Cd(II) or Cu(II) adsorbed on XAD-4-BI resin was calculated. The adsorption half time $t_{1/2}$, defined as the time needed to reach 50% of the resin adsorption capacity, was estimated from the curves (Figure 5). From Figure 5, we observed that an equilibrium time of about 30 minutes was required for more than 95% adsorption. However, the time of 50% adsorption was less than 4 min. The faster adsorption of Cd(II) or Cu(II) on XAD-4-BI probably reflects better accessibility of Cd(II) or Cu(II) to the chelating sites in the resin.

Amount of Amberlite XAD-4-BI. Quantitative retention can be obtained only with an appropriate amount of XAD-4-BI. An insufficient amount of resin may induce the loss of analytes. A reasonable excess amount of resin can prevent the desorption of retained metal chelates and metal ions when an appropriate volume of desorption solvent is used.²⁵ For this reason, the amount of resin should be optimized. The amount of XAD-4-BI added to each glass column was varied from 0.05 g to 0.70 g, then 1000 mL of 15 ng mL^{-1} Cd(II) or 30 ng mL^{-1} Cu(II) solution adjusted to pH 6.0 was passed through the glass column at a flow rate of 5 mL min^{-1} . We found the amount of XAD-4-BI that was well preconcentrated, and the result is shown in Figure 6. For both Cd(II) and Cu(II), we found that when the amount of XAD-4-BI was above 0.20 g, the degree of adsorption was high and varied slightly. For a 1000 mL sample solution contain-

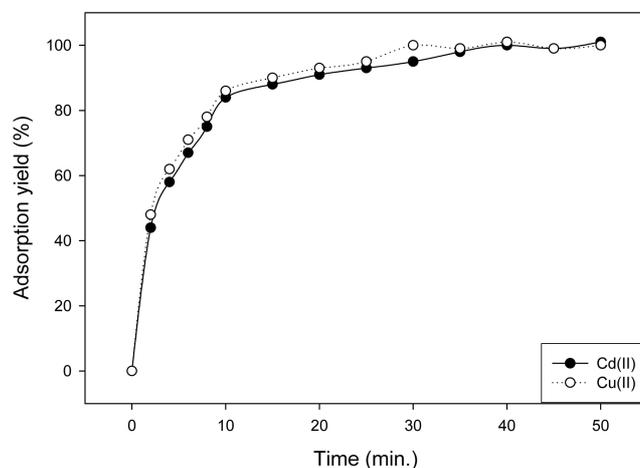


Figure 5. Kinetics of Cd(II) and Cu(II) adsorption on XAD-4-BI resin at pH 6.0.

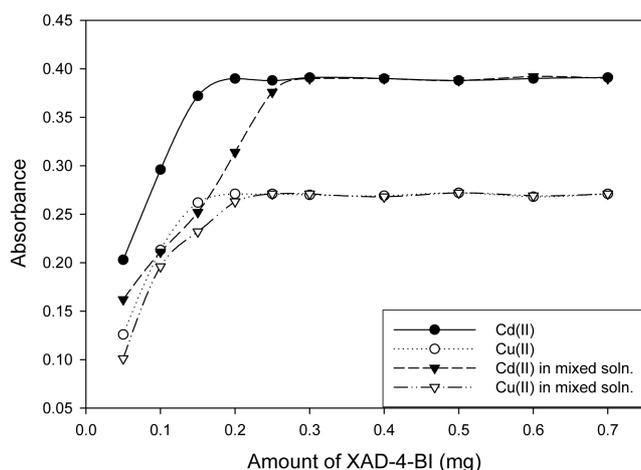


Figure 6. Effect of the amount of XAD-4-BI on the pre-concentration of Cd(II) (15 ng mL^{-1}) and Cu(II) (30 ng mL^{-1}) at pH 6.0 and flow rate 5 mL min^{-1} .

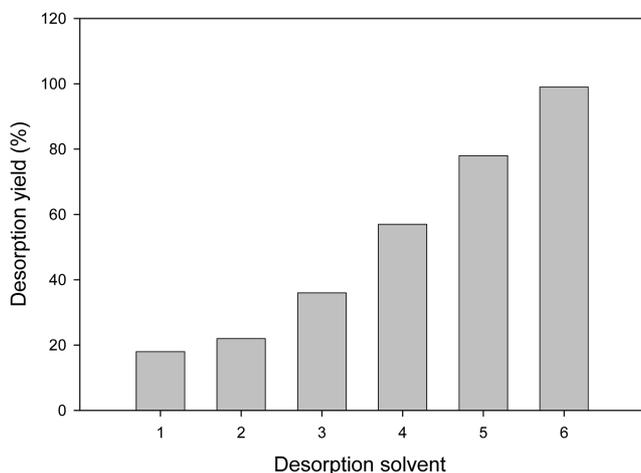


Figure 7. Desorption yields of various solvent on the desorption of pre-concentrated Cd(II) and Cu(II) at desorption flow rate 0.5 mL min^{-1} . 1 acetone; 2. ethanol; 3. 1.0 M KCN; 4. 4 M HCl; 5. 4 M HNO₃; 6. 4 M HNO₃ at 50 °C.

ing 15 ng mL^{-1} Cd(II) and 30 ng mL^{-1} Cu(II), the adsorption was 0.25 g for Cd(II) and 0.30 g Cu(II). Therefore, in consideration of the real sample containing diverse species and the flow rate of the sample solution, the amount of XAD-4-BI was optimized to 0.50 g.

Desorption solvent and desorption flow rate. Acetone and ethanol as organic solvent, 1 M KCN as ligand, 4 M HNO₃ and 4 M HCl as acid and 4 M HNO₃ heated to 50 °C were used to desorb quantitatively Cd(II) or Cu(II) adsorbed on XAD-4-BI. Among these reagents, 4 M HNO₃ heated to 50 °C was the most effective for desorption, as shown in Figure 7. The use of 10 mL of 4 M HNO₃ heated to 50 °C at the flow rate of 0.5 mL min^{-1} for desorption of Cd(II) or Cu(II) was the most effective. Therefore, the desorption flow rate of 4 M HNO₃ heated to 50 °C was optimized to 0.5 mL min^{-1} . Unfortunately, XAD-4-BI could be used only once when employing 4 M HNO₃ heated to 50 °C. However, it is an insignificant problem because XAD-4 resin could be reused

Table 2. Tolerance limit^a for various species in 15 ng mL^{-1} Cd(II) solution and 30 ng mL^{-1} Cu(II) solution at pH 6.0

Concentration of species ($\mu\text{g mL}^{-1}$)	Interfering species on Cd(II)	Interfering species on Cu(II)
200	Na ⁺ , NH ₄ ⁺ , CH ₃ COO ⁻ , Cl ⁻	Na ⁺ , NH ₄ ⁺ , Ca ²⁺ , CH ₃ COO ⁻
100	Ca ²⁺ , Mg ²⁺ , Br ⁻	Mg ²⁺ , Cl ⁻
50	I ⁻	Br ⁻ , I ⁻
30	Co(II), Ni(II)	Co(II), Ni(II), SCN ⁻
10	SCN ⁻ , C ₂ O ₄ ²⁻	C ₂ O ₄ ²⁻
5.0	PO ₄ ³⁻	Al ³⁺ , CN ⁻
1.0	Pb(II), Al ³⁺ , CN ⁻	Pb(II), Fe(III), Cd(II), PO ₄ ³⁻
0.5	Fe(III), Cu(II)	Sn(II)
0.3	Sn(II)	
0.1	Bi(III)	Bi(III)

^aTolerance limit is the maximum concentration in which there is less than 5% effect on absorbance.

several times and bismuthiol I can be well and simply adsorbed on XAD-4- resin.

Effect of coexisting species. Preconcentration procedures for trace metal ions could be strongly affected by the matrix constituents of the samples, because we assumed that they prevent the Cu(II)-bismuthiol I complex from forming. Various ions were used to investigate their interference effects on 15 ng mL^{-1} Cd(II) or 20 ng mL^{-1} Cu(II) solution under the optimum conditions given above. The results of interference studies are summarized in Table 2. Bi(III), Sn(II), and Fe(III) showed more interference than any other ion. However, the interference by these ions could be overcome sufficiently by adjusting the amount of XAD-4-BI to 0.70 g, although elution time increased.

Calibration curve and detection limit. Calibration curves for Cd and Cu were constructed at optimum conditions. The linear range of Cd(II) was $0.5\text{--}40 \text{ ng mL}^{-1}$ that of Cu(II) was $2.0\text{--}120 \text{ ng mL}^{-1}$. The regression equation, the correlation coefficient (R^2) and the detection limit obtained by this proposed technique were $y = 0.026(\pm 0.008)x + 0.004(\pm 0.003)$ (x unit: ng mL^{-1}), and 0.3 ng mL^{-1} for Cd(II), and $y = 0.0093(\pm 0.0010)x + 0.026 (\pm 0.008)$ (x unit: ng mL^{-1}), and 1.02 ng mL^{-1} for Cu(II).

Aqueous samples. Cd(II) and Cu(II) in the stream water, the reservoir water, the tap water and the untreated wastewater sample were determined by this proposed method, and the results are shown in Table 3. In this determination, the relative standard deviations were less than 7.0%, except for tap water. Cd(II) and Cu(II) in real samples were also determined by ICP-MS. No difference between results from the proposed method and the ICP-MS had been established at 95% confidence level. The recovery yields of Cd(II) in the real samples, spiked with 10 and 20 ng mL^{-1} Cd(II), were investigated and found to be more than 90%. And for Cu(II), recovery yields were more than 94%. Therefore, we have concluded that this proposed technique could be applied to the determination of Cd(II) and Cu(II) in real aqueous samples.

Table 3. Determination and recovery yields of Cd(II) and Cu(II) in several aqueous samples

Real sample	Cd(II)				Cu(II)			
	Spiked (ng mL ⁻¹)	Measured (ng mL ⁻¹)*		Recovery yield (%)	Spiked (ng mL ⁻¹)	Measured (ng mL ⁻¹) ^a		Recovery yield (%)
		This method	ICP-MS			This method	ICP-MS	
Stream water	0	7.2(±0.4)	7.0(±0.5)		0	28.6(±1.4)	28.1(±1.1)	
	10	16.6(±0.9)		94	20	48.2(±2.3)		98
	20	25.7(±1.1)		93	40	66.1(±3.8)		94
Reservoir water	0	8.6(±0.6)	8.2(±0.5)		0	23.5(±1.4)	24.1(±1.2)	
	10	18.0(±0.9)		94	20	43.8(±2.1)		102
	20	27.8(±1.3)		96	40	62.3(±2.9)		97
Tap water	0	3.2(±0.5)	3.8(±0.5)		0	10.6(±0.7)	10.2(±0.6)	
	10	12.5(±0.7)		93	20	29.8(±1.5)		96
	20	22.0(±1.2)		94	40	49.8(±2.6)		98
Wastewater	0	21.6(±1.1)	20.8(±0.5)		0	42.3(±2.1)	41.8(±2.0)	
	10	30.7(±1.6)		91	20	62.8(±2.9)		103
	20	40.2(±2.0)		93	40	83.2(±3.8)		102

^aThe mean values in this method were obtained from 7 samples and those in ICP-MS were obtained from 5 samples.

Table 4. Determination and recovery yields of Cd(II) and Cu(II) in the plastic sample and the diluted brass sample

Real sample	Cd(II)				Cu(II)			
	Spiked (ng mL ⁻¹)	Measured (ng mL ⁻¹)*		Recovery yield (%)	Spiked (ng mL ⁻¹)	Measured (ng mL ⁻¹) ^a		Recovery yield (%)
		This method	ICP-MS			This method	ICP-MS	
Plastic	0	0(±0.5)	0(±0.4)		0	0(±0.4)	0(±0.4)	
	10	9.5(±0.9)		95	20	19.4(±0.7)		97
	20	20.4(±1.4)		102	40	38.3(±1.5)		96
Diluted brass sample	0	0(±0.6)	0(±0.7)		0	32.0(±2.0)	32.8(±2.6)	
	10	9.6(±0.7)		96	20	51.2(±2.6)		96
	20	18.6(±1.0)		93	40	72.1(±3.5)		100

^aThe mean values in this method were obtained from 7 samples and those in ICP-MS were obtained from 5 samples.

Table 5. Determination of Cd(II) and Cu(II) in certified rice flour samples (KRISS CRM)

CRM	Cd(II)		Cu(II)	
	Certified value (mg kg ⁻¹)	Measured value (mg kg ⁻¹)	Certified value (mg kg ⁻¹)	Measured value (mg kg ⁻¹)
CRM 108-01-001(normal)	0.031(±0.002)	No detection	3.22(±0.09)	3.14(±0.18)
CRM 108-01-002(fortified)	1.32(±0.24)	1.28(±0.16)	4.59(±0.74)	4.46(±0.32)

Brass and plastic samples. Cd(II) and Cu(II) in the brass sample and plastic sample were determined by this proposed method and ICP-MS, and the results are shown in Table 4. Cd(II) in diluted brass sample and plastic sample was not detected, but its recovery yields obtained from the spiked Cd(II) standard solution were more than 93%. And the concentration of Cu(II) in diluted brass sample was 32.0 ng mL⁻¹ (64.0% in original sample). Its recovery yields obtained from the spiked Cu(II) standard solution was more than 96%. No Cu(II) was found in the plastic sample, but its recovery yields in the plastics solution spiked with Cu(II) standard solution were about 96-97%.

Rice flour CRM sample. Cd(II) and Cu(II) in two rice flour CRM samples was determined by this proposed method. The results are shown in Table 5. One sample was a

normal rice flour CRM sample, the other was a fortified rice flour CRM sample. They were not different for the CRM value and measured an average value at a 95% confidence level. However, Cd(II) in a normal rice flour CRM sample could not be measured because of a very low concentration of Cd(II) in the prepared solution. Therefore, we concluded that this proposed technique could be applied to the determination of Cd(II) and Cu(II) in rice flour samples.

Conclusions

A new XAD-4 resin loaded with bismuthiol I has been prepared. The XAD-4-BI resin was an effective material for the separation and preconcentration of Cd(II) and Cu(II) in aqueous solutions, plastics, diluted brass, and rice flour

CRM samples. The preconcentration factor of this method on Cd(II) and Cu(II) was about 100. The recovery yields obtained with the spiked real samples were about 91-103%. The results obtained in the determination of Cd(II) and Cu(II) with this method and ICP-MS were not different at a 95% confidence level.

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