Selective Spectrophotometric Determination of Trace Amounts of Cadmium in Soil and Sediment Samples Using a Green Aqueous Biphasic Extraction

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A green extraction spectrophotometric method was presented for the determination of trace amounts of cadmium in soil and sediment samples. This method is based on the selective extraction of cadmium as its iodide complex by aqueous biphasic extraction composed of polyethylene glycol (PEG) and sodium sulfate, and a subsequent sensitive determination by spectrophotometry using 2-(5-bromo-2-pyridylazo)-5-[N-n-propyl-N-(3-sulfopropyl)amino]phenol. This extraction method is simple and environmentally benign, since the organic solvents used for the traditional liquid-liquid extractions are replaced by the non-toxic polymer and inorganic salt. Cadmium can be selectively extracted from soil and sediment samples into the PEG-rich upper phase by an aqueous biphasic system containing potassium iodide and sulfuric acid. The proposed method was applied to the determination of cadmium in certified reference materials for soil and river sediment. The obtained results were in good agreement with the certified values.

Keywords Simple spectrophotometric method, aqueous biphasic extraction, polyethylene glycol, cadmium, soil, sediment

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Introduction

Cadmium is one of the most toxic metals, and contributes to many illnesses, including lung, kidney and bone diseases.1,2 A comprehensive review of studies on the health effects of cadmium is presented in Regulations (Preambles to Final Rules) of Occupational Safety & Health Administration.3 The contamination of soil with cadmium may cause not only severe ecosystem disturbance, but also hazards to the health of humans through the intake of cadmium-contaminated vegetables and drinking of contaminated ground water, etc. Thus accurate determinations of cadmium at trace levels in soils have been required.4

Determinations of cadmium in soils have been carried out using analytical techniques, such as atomic absorption spectrometry (AAS),4–8 inductively coupled plasma atomic emission spectrometry (ICP-AES)9,10 and inductively coupled plasma mass spectrometry (ICP-MS)10,11 after the extraction of cadmium with acid solutions, such as hydrochloric acid, nitric acid and aqua regia.4–6,9–11,13 Although these methods are highly sensitive, they need expensive instrumentation, and involve time-consuming procedures. Furthermore, these methods cannot be used for on-site measurements. Nowadays, due to environmental concerns, fast on-site analyses of soils are required.12 The UV-visible spectrophotometric method has an advantage in that it is capable of performing fast on-site quantitative analyses with an inexpensive devise and simple procedures.13,14 However, the conventional spectrophotometric methods lack selectivity and suffer from serious interference of foreign metal ions in soils.15 Liquid-liquid extraction is one of the most effective techniques not only for separation, but also for the enrichment of metal ions, and is widely used for analytical applications as a sample pretreatment technique. Metal ions in an aqueous solution are usually extracted into a water-immiscible organic solvent using suitable extracting reagents. However, a number of organic solvents employed for metal extraction are toxic, flammable and volatile. On the other hand, it has been shown that aqueous biphasic systems consisting of water, certain inorganic salts and water-soluble polymers can be efficient for the separation of metal ions.16–20 Among many kinds of water-soluble polymers that have been utilized to form the aqueous biphasic systems, polyethylene glycols (PEGs) are exclusively used in combination with inorganic salts, such as Na2SO4. Because PEGs are nontoxic, nonflammable and nonvolatile, PEG-based aqueous biphasic systems can be regarded as environmentally benign, compared with conventional liquid-liquid extraction systems utilizing water-immiscible organic solvents.

Recently, we developed a simple and highly selective and sensitive method for the determination of trace amounts of zinc in environmental water samples using aqueous biphasic extraction and spectrophotometric measurement.24 This method
is based on the separation and preconcentration of zinc as its thiocyanate complex by PEG/Na$_2$SO$_4$ aqueous biphasic extraction, and subsequent determination by spectrophotometry after the complexation of zinc ion with 2-(5-bromo-2-pyridylazo)-5-[-N-n-propyl-N-(3-sulfopropyl)amino]phenol (5-Br-PAPS). Interferences from most of the foreign metal ions were removed by separation with aqueous biphasic extraction. The proposed method was successfully applied to the determination of zinc at the ppb level in tap-water and river-water samples.

In previous studies, we also demonstrated that cadmium can be selectively extracted with iodide ion from the salt-rich phase into the PEG-rich phase in PEG/Na$_2$SO$_4$ aqueous biphasic systems.$^{25}$ It is thus expected that a simple extraction spectrophotometric method for the determination of cadmium can be developed using iodide ion as the extracting agent by PEG/Na$_2$SO$_4$ aqueous biphasic extraction. In this paper, we present a selective and sensitive extraction spectrophotometric method for the determination of cadmium in soil and sediment samples by a PEG/Na$_2$SO$_4$ aqueous biphasic system with iodide ion. We will show that the proposed method allows for accurate and precise determinations of trace-level cadmium in soils and sediments.

**Experimental**

**Materials**

The polyethylene glycol used in this study was PEG#6000 (mean molecular weight = 7400 – 9000) and PEG#4000 (mean molecular weight = 2700 – 3400), purchased from Kanto Chemicals (Tokyo, Japan). Standard stock solutions of Cd(II), Mn(II), Fe(III), Ni(II), Cu(II), Zn(II), Hg(II) and Pb(II) for atomic absorption use (1000 ppm) were obtained from Wako Pure Chemicals (Osaka, Japan). 5-Br-PAPS was purchased from Dojindo Laboratories (Kumamoto, Japan). All other chemicals used were of analytical reagent grade quality; they were purified with an Elix Advantage (Merck Millipore, Tokyo, Japan) and an Arium 611 DI (Sartorius, Tokyo, Japan). Certified reference materials of soil, JSAC 0402 (Japan Society for Analytical Chemistry, Tokyo, Japan), and of river sediment, ERM-CC020 (BAM, Berlin, Germany), were used to test the accuracy of the results.

**Apparatus**

Absorption spectra of 5-Br-PAPS and metal-5-Br-PAPS complexes were recorded using a Hitachi (Tokyo, Japan) Model U-2000 UV-Vis spectrophotometer with a 1.0-cm quartz cell. A Perkin Elmer (Yokohama, Japan) Model OPTIMA 5300DV ICP-AES instrument was used for the determination of metal ions and a comparison with the proposed spectrophotometric method. The operating conditions for ICP-AES measurements are given in Table S1 (Supporting Information).

**Methods**

**Determination of phase diagrams for PEG#6000/Na$_2$SO$_4$ and PEG#4000/Na$_2$SO$_4$ aqueous biphasic systems.** A binodal curve was constructed visually by turbidimetry in which dropwise additions of 20% (w/w) Na$_2$SO$_4$ were made to a solution of one phase until the detection of a change in the turbidity, indicating the formation of two liquid phases.$^{27,28}$ The temperature of the solutions was kept constant at 25.0 ± 0.1 °C by means of a water bath. The tie-line for the aqueous biphasic system adopted for the extraction of Cd(II) was determined by the lever arm rule from the total composition of the system and the ratio of the weights of the two phases.$^{27}$

**Determination of stoichiometry for Cd(II)-5-Br-PAPS complex.** Equimolar (7 × 10$^{-3}$ M) stock solutions of Cd(II) and 5-Br-PAPS were prepared separately. These solutions were mixed in a 10-mL volumetric flask and diluted after the addition of 2 mL of a 1.0 M NaHCO$_3$–Na$_2$CO$_3$ buffer solution (pH 9.7), so that the total concentration of Cd(II) and 5-Br-PAPS was 1.5 × 10$^{-3}$ M. The absorbance at 556.5 nm was recorded and plotted against the mole fraction of the chelating reagent.

**Standard procedure for aqueous biphasic extraction.** All of the extraction experiments were carried out at room temperature. The aqueous biphasic system was prepared by mixing 1 g of a 50% (w/w) PEG#6000 solution and 7 g of a 20% (w/w) Na$_2$SO$_4$ solution in 15-mL graduated polypropylene centrifuge tubes. To this extraction system, certain volumes of stock solutions of metal ions, 2 M KI solution and 1 or 10% (w/w) of H$_2$SO$_4$ were added. The total volume of the solutions of metal ions, KI and H$_2$SO$_4$ added was adjusted to 2 mL with water. The systems were mechanically shaken for 10 min, and then centrifuged for 10 min at 3000 rpm. The volumes of the two coexisting phases were measured, and then 0.50 g of the upper phase was weighed out and placed in a 10-mL volumetric flask. The weight of the total upper phase was measured by pipetting it out thoroughly to a weighing bottle for a biphasic system similarly prepared, but containing no metal ions. After the solutions of the masking reagents, 1 M NaHCO$_3$–Na$_2$CO$_3$ buffer (pH 9.7) and 0.7 M 5-Br-PAPS were added, the solution was made up to the mark with water. The absorbance was recorded at 556.5 nm.

The concentrations of metal ions, including Cd(II) in the upper and lower phases, were determined by ICP-AES. An aliquot of each phase was weighed out and diluted to 5 mL with water. Several aliquots of 1 mL of this solution were transferred to 10-mL volumetric flasks. To each of the volumetric flasks, 1 mL of 1% (w/w) salicylaldoxime, 1 mL of 0.1 M Na$_2$SO$_3$, 1 mL of 1% (w/w) salicylaldoxime, 1 mL of 1% (w/w) dimethylglyoxime and 2 mL of 1 M NaHCO$_3$–Na$_2$CO$_3$ buffer (pH 9.7). After the solution was allowed to stand for 20 min, 600 µL of 0.7 mM 5-Br-PAPS was added, and the solution was diluted to the mark with water. The absorbance was measured at 556.5 nm against a reagent blank. The cadmium content in a sample was determined using a concurrently prepared calibration graph.
Results and Discussion

Phase diagrams for PEG#6000/Na₂SO₄ and PEG#4000/Na₂SO₄ aqueous biphasic systems

Although we found that Cd(II) is selectively extracted as its iodide complex into the PEG-rich phase, the distribution ratio of Cd(II) obtained for PEG#4000/Na₂SO₄ aqueous biphasic system is not high enough for quantitative extraction. It has been known that phase separation occurs at lower concentrations of the polymer and salt, and that the composition difference between the upper and lower phases becomes larger when the molecular weight of PEG is increased. We have thus used PEG#6000 as a polymer component of the aqueous biphasic system for the extraction of Cd(II), since the extractability of the iodide complex of Cd(II) is expected to be increased, while the distribution ratios of other metal ions are decreased.

Figure 1 compares the phase diagrams for the PEG#6000/Na₂SO₄ and PEG#4000/Na₂SO₄ aqueous biphasic systems. One can clearly observe that the higher molecular mass of PEG causes the binodal line to shift to lower concentrations of PEG and Na₂SO₄.

Effect of the iodide concentration on the extraction of Cd(II)

The effect of the iodide concentration on the extraction of Cd(II) in the PEG#6000/Na₂SO₄ aqueous biphasic system was examined by adding different amounts of KI to the system. To the aqueous biphasic system, prepared by mixing 1 g of 50% (w/w) PEG#6000 solution and 7 g of 20% (w/w) Na₂SO₄ solution, 500 μL of 10 ppm Cd(II) stock solution, 100 μL of 1% (w/w) H₂SO₄ and 0 – 400 μL of 2 M KI solution were added. The total volume of the solutions added to the aqueous biphasic system was adjusted to 2 mL with water. The total composition and the compositions of the upper and lower phases of this extraction system that we adopted are represented by the points T, U, and L in Fig. 1, respectively. A quantitative extraction of Cd(II) (>99%) into the upper PEG-rich phase was attained when 0.6 mmol or more of KI was added (Fig. 2). We thus added 400 μL of 2 M KI to the extraction system in following experiments.

Stoichiometry for Cd(II)-5-Br-PAPS complex

The effect of the pH on the formation of the Cd(II)-5-Br-PAPS complex was examined using a NaHCO₃–Na₂CO₃ buffer. It was observed that the absorbance of the complex increased with an increase in the pH from 7.0 to 9.0 and remained constant between 9.0 and 10.0. Therefore, we adopted pH 9.7 for further studies. The absorption spectrum of Cd(II)-5-Br-PAPS complex is shown in Fig. 3 together with those for the complexes of some other metal ions.

The composition of the complex was studied by the method of continuous variation according to the procedure described in the Experimental section. We measured the absorbance at the maximum absorption wavelength for the Cd(II)-5-Br-PAPS complex, 556.5 nm, although the reagent 5-Br-PAPS also has absorption (ca. 20% of the absorbance of the complex at equimolar concentration). A plot of the absorbance versus mole fraction of 5-Br-PAPS (Fig. S1, Supporting Information) shows a maximum at mole fraction of 0.64, indicating the formation of 1:2 (Cd(II):5-Br-PAPS) complex.

The absorption coefficient for the complex at 556.5 nm is
The concentration. We have thus examine was carried out for 30 min by adding 1.5 mmol of H2SO4 to the aqueous biphasic extraction with iodide ion at a moderate acid. It was completely extracted by the addition of 1.2 mmol of H2SO4, shown in Fig. S2 (Supporting Information). Cd(II) was also examined using 1 M HCl according to the test method in Notification No. 19 of the Ministry of the Environment of Japan based on the Soil Contamination Countermeasures Law. In a 50-mL polypropylene bottle, 1 g of the reference material of soil (JSAC 0402) was shaken with 35 mL of 1 M HCl for 10 min. The upper phase was filtered with a 0.45-μm membrane filter and the concentration of Cd(II) was determined by ICP-AES.

Extraction of Cd(II) in a soil sample

As mentioned above, the extraction of metal ions in soils and sediments is usually performed using concentrated strong acid solutions. It is expected, however, that we can extract Cd(II) by aqueous biphasic extraction with iodide ion at a moderate acid concentration. We have thus examined the effect of the amount of H2SO4 on the extraction of Cd(II) in 0.1 g of the reference material of soil (JSAC 0402) by aqueous biphasic extraction. The aqueous biphasic extraction system was prepared by mixing 1 g of 50% (w/w) PEG#6000 solution, 7 g of 20% (w/w) Na2SO4 solution, 400 μL of 2 M KI solution, 1.2 mL of 10% (w/w) of H2SO4, and 400 μL of water. The mixture was shaken for 5 – 30 min, and then centrifuged at 3000 rpm for 10 min. The upper phase was filtered with a 0.45-μm membrane filter and the concentration of Cd(II) was determined by ICP-AES.

Selectivity enhancement using masking reagents

As shown in Table 1, only Cd(II) is quantitatively extracted into the upper phase in the PEG-Na2SO4-KI aqueous biphasic system. However, other metal ions such as Fe(III) and Cu(II) also slightly distribute into the PEG-rich phase, which may interfere with an accurate determination of Cd(II). We have reported that salicylaldoxime acts as a good masking agent for Cu(II) in the formation of a complex with 5-Br-PAPS. In addition, phosphate ion suppresses the extraction of Fe(III) into the upper phase, and dimethylglyoxime can mask the reaction of Ni(II) with 5-Br-PAPS. Therefore, we added Na2HPO4 to strip Fe(III) from the upper phase after the aqueous biphasic extraction with H2SO4, and salicylaldoxime and dimethylglyoxime to the sample solution before the reaction of Cd(II) with 5-Br-PAPS proceeds, as described above. A solution of Na2SO3 was also added to suppress oxidation of the iodide ion.

Table 1

| Amount of soil/g | Quantification result/μg g⁻¹ a |
|-----------------|-------------------------------|
| 0.05            | 17.2 ± 1.0                    |
| 0.07            | 17.3 ± 0.5                    |
| 0.1             | 17.1 ± 0.6                    |
| 0.2             | 16.6 ± 0.5                    |
| 0.5             | 16.7 ± 0.3                    |

a. Mean ± standard deviation (n = 3).

Table 2

| Amount of soil/g | Quantification result/μg g⁻¹ a |
|-----------------|-------------------------------|
| 0.05            | 17.2 ± 1.0                    |
| 0.07            | 17.3 ± 0.5                    |
| 0.1             | 17.1 ± 0.6                    |
| 0.2             | 16.6 ± 0.5                    |
| 0.5             | 16.7 ± 0.3                    |

a. Mean ± standard deviation (n = 3).

1.5 × 10⁸ L mol⁻¹ cm⁻¹. The calibration curve is linear in the concentration range of 0 – 250 μg L⁻¹, and is given as A (absorbance) = 1.024Cd(Cd μg L⁻¹) + 0.024 with a correlation coefficient (r²) of 0.9997. The determination limit calculated with ten-times the standard deviation of the reagent blank value is 14.3 μg L⁻¹. These results indicate that a sensitive spectrophotometric determination of trace amounts of cadmium can be achieved using 5-Br-PAPS.
Determination of Cd(II) in soil and sediment samples

The accuracy and precision of the method was evaluated by analyzing certified reference materials for soil and river sediment. After extraction for the river sediment sample, the upper phase was colored orange. We thus calculated the absorbance at 556.5 nm by subtracting the absorbance obtained for the upper phase solution containing no chromogenic reagent from that of the final solution prepared by the standard procedure. The determination of metal ions was performed by ICP-AES. The extraction method developed is more environmentally friendly than the usual ones resorting to organic solvents; furthermore, it enables one to selectively extract the target metal ion in soil and sediment samples. The present work describes for the first time the use of an aqueous biphasic extraction system coupled to spectrophotometry to determine a metal ion in soil and sediment samples. This method provides a universal protocol for the extraction spectrophotometric determination of various metal ions in environmental samples, and is expected to be readily applied to other metal ions of interest using the reagents which selectively extract them.

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Supporting Information

An additional table and figures. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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