



Simple and high-sensitivity colorimetric analysis of cadmium using homogeneous liquid–liquid extraction

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Abstract

Colorimetric determination with dithizone (diphenylthiocarbazone) is a simple method that has been applied to analyze cadmium (Cd) ions in water. However, determining concentrations close to the environmental standard value ($3 \mu\text{g L}^{-1}$) using this method is difficult because of its low sensitivity. Herein, we exploited the phase separation phenomenon to generate a small amount of the extraction phase by adding a mixture of 2-propanol and a small amount of chloroform to a water sample, as a pre-concentration method for the Cd(II) ions. The obtained Cd(II)-dithizone complex was successfully extracted into this phase. We then constructed a simple and highly sensitive colorimetric analysis method for the ppb level of Cd(II) using this phase separation technique.

Keywords Cadmium ion · Homogeneous liquid–liquid extraction · Phase separation · Dithizone

Introduction

Cadmium ions (Cd(II)) are essential in several industrial applications, such as alloys, pigments, batteries, and reactor control rods [1]. However, water pollution caused by Cd(II) is a severe environmental issue in some regions of the world [2–4] because Cd(II) causes serious health problems, such as Itai-Itai disease. Therefore, the World Health Organization (WHO) and Japanese environmental standards define the standard value of the Cd(II) concentration in water environments to be $3.0 \mu\text{g L}^{-1}$ or less, and monitoring the concentration of cadmium in water resources was made mandatory by WHO [5].

Instrumental analyses, such as inductively coupled plasma optical emission spectrometry (ICP-OES), are frequently used analytical methods for the determination of

Cd(II), having a high level of sensitivity [6]. However, these techniques require expensive instruments and involve complex operations. On the contrary, colorimetric determination with dithizone has been widely used as a simple analytical method for the determination of Cd(II) [7–9]. This method exploits a color reaction (colorless to red) to quantify the Cd (II) concentration of sample solutions under basic conditions. However, determining Cd(II) concentrations close to the environmental standard value ($3.0 \mu\text{g L}^{-1}$) via this method is difficult because of its low sensitivity.

To improve the sensitivity of colorimetric analysis with dithizone, we herein focused on the phase separation phenomenon. Specifically, we explored homogeneous liquid–liquid extraction, whereby a small amount of the extraction phase is generated [10–12]. Through homogeneous liquid–liquid extraction, the analyte can be concentrated from a milliliter-scale sample to a microliter-scale extraction phase in a short period of time. This fact indicates that this method is a simple preconcentration method yielding a high concentration rate. Therefore, it has been applied to increase the sensitivity of several instrumental analysis techniques, [10–14] such as gas chromatography-mass spectrometry (GC–MS) [10]. Recently, it was found that a mixture of water, 2-propanol, and chloroform generates a similar microscale water-insoluble extraction phase, and a Cd(II)–dithizone complex can be concentrated. Therefore, the purpose of

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this study was to develop a highly sensitive colorimetric analysis technique for Cd(II) using phase separation with water, 2-propanol, and chloroform, and to evaluate the proposed method for environmental analysis.

Experimental

Reagents and apparatus

A standard Cd(II) solution, Dithizone, chloroform, 2-propanol, and sodium carbonate was obtained from Fuji Film Wako Pure Chemical Industries Ltd., Japan. Standard river water was obtained from the National Institute of Advanced Industrial Science and Technology (AIST); this standard contained 1.0 ppb of Cd. An AV-630 spectrophotometer (JASCO Corp.) was used to measure the absorbance. An MCF-1350 centrifugal separator (LMS, Co., Ltd.) was used to promote phase separation.

Procedure

First, 2 mL of 1.0 mol L⁻¹ sodium hydroxide and 7.8 × 10⁻⁶ mol L⁻¹ of dithizone solution were dissolved in 1.5 mL of 2-propanol. Then, 0.50 mL of chloroform was mixed with 10 mL of the sample solution. The obtained sample was centrifuged for 3 min at 3000 rpm. Subsequently, 0.40 mL of the sedimented organic liquid phase was diluted fivefold with chloroform. The absorption spectra of the organic and aqueous phases

Fig. 1 Principle of the proposed phase separation phenomenon. [dithizone] = 2.0 ppm, [NaOH] = 0.10 mol L⁻¹, 2-propanol: 1.5 mL, chloroform: 0.50 mL

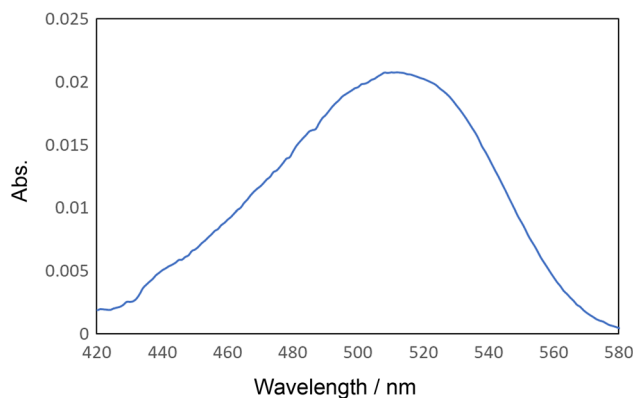
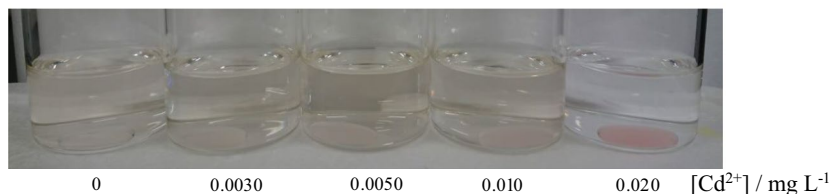
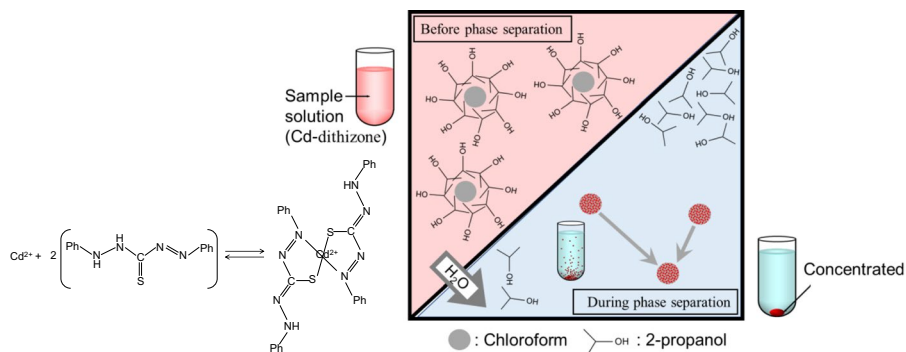


Fig. 2 UV-vis spectrum of Cd(II)-dithizone. [Cd²⁺] = 0.020 mg L⁻¹

were measured at 516 nm using an ultraviolet-visible (UV-Vis) spectrophotometer.

Results and discussion

When a sample solution containing Cd(II) was added to a 2-propanol solution containing a small amount of chloroform, phase separation occurred rapidly, and a small amount of the extraction phase was generated. Figure 1 shows the principle of this phase separation phenomenon. After extracting a sample with a concentration of 3.0 μg L⁻¹, the measurement results of the concentration of cadmium in the concentrated phase (0.40 mL) and the aqueous phase (10 mL) were 0.16 mg L⁻¹, 0.80 μg L⁻¹. From these results, the extraction rate of this method was 88%.

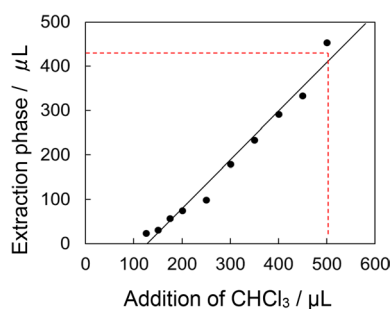


Fig. 3 Influence of the amount of reagent used on the volume of the extraction phase. CHCl_3 : 2-propanol=1: 3, $[\text{Cd}^{2+}] = 0.010 \text{ mg L}^{-1}$, $[\text{NaOH}] = 1.0 \text{ mol L}^{-1}$, $[\text{dithizone}] = 2.0 \text{ ppm}$.—: optimum condition (Addition, 500 μL ; extraction phase, 410 μL)

Chloroform and 2-propanol were rendered homogeneously miscible by solvating chloroform with 2-propanol. However, 2-propanol was diluted by adding a water-based sample to the mixed solution. Therefore, chloroform could not be dissolved, meaning that it eventually sedimented, as 2-propanol lost its function as a solvated molecule by dilution. Similar phase separations have been reported with water/polar organic solvent/non-polar organic solvent systems [13–15]. Figure 2 shows the absorption spectrum of the concentrated Cd (II)-dithizone complex by this method. A spectrum with a maximum absorption wavelength at a wavelength of 516 nm was observed.

Figure 3 shows the influence of the amount of chloroform used on the volume of the extraction phase. This result shows that the amount of chloroform used can control the volume of the extraction phase. In this study, when the volume of the concentrated phase was reduced, the concentration ratio increased, but the time required for phase separation increased. Therefore, 0.50 mL of chloroform was set as the optimum condition which has a sufficient concentration ratio and is easy to operate. Under these optimized conditions, an extraction percentage of 88% was achieved, and the concentration factor was improved 34-fold (from 14 to 0.41 mL).

Using the spectrophotometer, the detection limit (3σ) of 1.6 ppb was determined. The relative standard deviation (RSD) at 10 ppb was 4.8% ($n = 5$). The detection limit of cadmium in the conventional dithizone method was 100 $\mu\text{g L}^{-1}$. This result indicated that this proposed method is better than the conventional method. In addition, using this method, it has become possible to measure the environmental standard value of 3.0 $\mu\text{g L}^{-1}$.

As dithizone forms colored complexes with most metal ions, it is also used for the colorimetric analysis of heavy metal ions other than Cd. This indicates that the dithizone method lacks selectivity. However, under strongly basic conditions, most metal ions form hydroxide precipitates, meaning that the method's selectivity for Cd increases [16].

Therefore, in this study, Cd was determined under basic conditions. The influence of coexisting ions were examined. Almost none of the cations and anions, except for Mg(II) and Ni(II) ions, affected the efficacy of the proposed method. The ions that did affect the proposed method resembled those that are also known to influence the conventional dithizone colorimetric method [17]. However, this influence was reduced by the addition of Na_2CO_3 in the case of Mg(II). Although magnesium ions form a precipitate with carbonate ions, Cd ions do not, because they exist as anions in a basic state. Therefore, the addition of sodium carbonate appears to have reduced the interference of magnesium ions. To verify the validity of the proposed method for determining Cd(II), we determined the Cd(II) concentration in standard river water for a known amount of added Cd(II). A reasonable recovery rate was obtained for all samples (Table 1), establishing the method's applicability to real environmental samples.

Conclusions

In this study, the Cd(II)–dithizone complex was extracted into a small amount of the extracted phase using phase separation with water, 2-propanol, and chloroform. Using this method, trace levels of Cd(II) can be successfully quantified. Furthermore, this method was employed for the determination of the Cd(II) concentration in standard river water. Although there exists scope for improvement in terms of interference from coexisting substances, the proposed method was successfully adapted for samples with low concentrations of coexisting substances via the use of a masking agent.

Table 1 Analytical results for Cd(II) in standard river water

Sample	$[\text{Cd}^{2+}]/\text{mg L}^{-1}$			Recovery (%)	R.S.D. (%)
	Content	Added	Found		
No.1	0.0010	0.010	0.011	98	2.4
No.2	0.0010	0.020	0.021	100	0.50

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