

Continuous Flow System for Separation of Cadmium(II) from Zinc(II) Based on Forward- and Back-Extraction Processes

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Abstract

A continuous flow system for the separation of cadmium(II) from zinc(II) was developed based on dithizone extraction. The proposed flow system has two extraction coils, a forward-extraction coil and a back-extraction coil, connected in series through a phase separator. In the forward-extraction coil, cadmium(II) is extracted into the organic phase while zinc(II) is hardly extracted. In the back-extraction coil, cadmium(II) is back-extracted into the aqueous phase while zinc(II) remains in the organic phase. Consequently, only passing the sample solution through the flow system, we can separate cadmium(II) from zinc(II) quantitatively. To obtain a suitable condition, forward- and back-extraction rate constants of cadmium(II) were measured. Although the change in the flow rate of the pumps in the proposed system slightly affected the extraction rates, the use of PTFE chips as packing materials in the extraction coils gave large extraction rate constants. The effect of the length of the extraction coils on the separation efficiency was also examined. The result suggested that the flow system equipped with the extraction coils packed with PTFE chips (9 m in length for forward-extraction and 25 cm in length for back-extraction) allowed the quantitative separation of cadmium(II) from zinc(II).

Keywords Solvent extraction, kinetic separation, cadmium(II), zinc(II), dithizone, continuous flow system

1. Introduction

Separation of cadmium(II) from zinc(II) is very important from industrial and environmental view points because cadmium(II) has considerably high toxicity compared with zinc(II). Dithizone (3-mercapto-1,5-diphenylformazan) extraction has been widely used for separation of cadmium(II) and zinc(II) from water samples [1]. However, since the extraction constants (K_{ex}) for cadmium(II) and zinc(II) with dithizone are almost the same ($\log K_{ex} = 2.14$ for cadmium(II), 2.3 for zinc(II)) [2], their mutual separation with dithizone in the equilibrium state is a difficult task. Further, the kinetic separation of cadmium(II) from zinc(II) using only dithizone seems to be difficult, because the extraction rate for cadmium(II) with dithizone ($1.6 \times 10^7 \text{ mol}^{-1} \text{ s}^{-1}$) is close to that for zinc(II) ($6.9 \times 10^6 \text{ mol}^{-1} \text{ s}^{-1}$) [3].

In the previous work, the back-extraction rates of bis(dithizonato)zinc(II) and bis(dithizonato)cadmium(II) were measured, and the possibility of the mutual separation of cadmium(II) from zinc(II) using the back-extraction process has been considered [4,5]. In addition, in the presence of nitrilotriacetic acid (NTA), the kinetically controlled separation of cadmium(II) from zinc(II) using forward-extraction process was studied, and the feasibility of the method for the mutual separation of cadmium(II) from zinc(II) was demonstrated [6]. From the above results, combination of the forward- and back-extraction processes based on kinetic aspects will enable the quantitative separation of cadmium(II) from zinc(II). However, in this case, the procedure will be somewhat tedious because it is necessary to transfer the solution into another separatory funnel. Moreover, the kinetic separation by batch procedure will be a laborious technique because the regulation of the extraction time including a separation procedure seems to be difficult.

On the other hand, a flow injection technique has been widely used for analytical purposes [7]. A flow injection technique makes it possible to develop not only automatic systems but also precision methods. Solvent extraction using a flow injection technique has been also developed and it has been used to the determination of some extractable species such as surfactants [8-13]. However, the extractive flow technique has hardly been used for the mutual separation of metal ions. The extractive flow system seems to be useful for the mutual separation of metal ions, because it would easily be possible to construct the system with both forward- and back-extraction processes. Further, kinetic separation would be easily performed by the extractive flow system, because desired extraction time is obtained by only adjusting the extraction coil length. From the point of view, the extractive flow system for the mutual separation of metal ions was developed. This paper describes the feasibility of the proposed system for the separation of cadmium(II) from zinc(II).

2. Experimental

2.1. Reagents

Dithizone and metal salts were obtained from Wako Pure Chemicals, and were used without further purification. A stock solution of NTA was prepared by dissolving appropriate amounts of nitrilotriacetic acid disodium salt (Aldrich Chemical Co.) in water. The water used to prepare the reagent was obtained from a Milli-Q water-purification system (Millipore Co.). Bis(dithizonato)cadmium(II) ($\text{Cd}(\text{Hdz})_2$) and zinc(II) ($\text{Zn}(\text{Hdz})_2$) were prepared as described previously [5]. PTFE chips (*ca.* $0.4 \times 0.4 \times 0.1$ mm) used as packing materials were made by cutting a PTFE tube. Flusin T (trifluoro resin, particle diameter: 0.25 – 0.5 mm, GL Sciences Inc.) and glass beads (particle diameter: 0.6 mm) were also used as packing materials.

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2.2. Apparatus

Two double-plunger pumps (Sanuki Kogyo, DMX-2000) were used for propelling sample and reagent solutions. A phase separator (Sanuki Kogyo) with porous PTFE membrane filter and an air-trapping system (Sanuki Kogyo, AD-2) were used for the separation of organic and aqueous phases. In the continuous flow separation system, two PTFE tubes packed with PTFE chips (9 m in length for forward-extraction and 25 cm in length for back-extraction) were used as forward- and back-extraction coils. A Hitachi (Model Z-6100) atomic absorption spectrophotometer (AAS) equipped with a hollow cathode lamp (Hamamatsu Photonics) was used for the determination of metal ions. A Fisher Scientific pH meter (Accumet pH meter 15) was used for pH measurements.

2.3. Procedure

2.3.1. Measurement of observed rate constants of forward- and back-extraction of cadmium(II)

For the measurement of the forward-extraction rate constant, an aqueous solution containing 1×10^{-5} mol dm⁻³ cadmium(II), 1×10^{-2} mol dm⁻³ NTA and 1×10^{-2} mol dm⁻³ 3-morpholinopropanesulfonic acid (MOPS) buffer (pH = 7.0) was propelled by a double-plunger pump. A chloroform solution containing 1×10^{-3} mol dm⁻³ dithizone (H₂dz) was also propelled by the double-plunger pump. The solutions were merged through a T-connector and then introduced into an extraction coil. After the aqueous phase was separated from the organic phase by a phase separator, the cadmium(II) concentration in the aqueous phase was measured by AAS. The above procedures were conducted at various extraction coil length and various flow rate. The reaction (extraction) time was defined as the residence time of the solution within the extraction coil.

For the measurement of the back-extraction rate constant, an aqueous solution adjusted the pH to 1.8 with nitric acid was propelled by a double-plunger pump. A chloroform solution containing 1×10^{-5} mol dm⁻³ Cd(Hdz)₂ was also propelled by the double-plunger pump. Other procedures were same to the forward-extraction ones mentioned above.

2.3.2. Continuous flow separation of cadmium(II) from zinc(II)

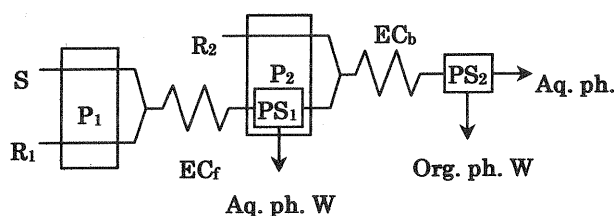


Fig. 1 Continuous flow system for separation of cadmium(II) from zinc(II).

S: sample solution, R₁: chloroform solution containing 1×10^{-3} mol dm⁻³ dithizone, R₂: nitric acid solution (pH 1.8), EC_f: forward-extraction coil packed with PTFE chips (ϕ 2mm, 9m in length), EC_b: back-extraction coil packed with PTFE chips (ϕ 2mm, 25cm in length), P₁: double plunger pump ($1.2 \text{ cm}^3 \text{ min}^{-1}$), P₂: double plunger pump ($1.0 \text{ cm}^3 \text{ min}^{-1}$), PS₁: phase separator used air-trap system, PS₂: phase separator used PTFE membrane filter, Aq. ph.: aqueous phase applying to AAS, Aq. ph. W: Aqueous phase waste, Org. ph. W: Organic phase waste.

Schematic diagram of the proposed system is shown in Fig. 1. A sample solution containing cadmium(II), zinc(II), 1×10^{-2} mol dm⁻³ NTA and 1×10^{-2} mol dm⁻³ MOPS buffer (pH = 7.0) was propelled by the double-plunger pump (P₁). A chloroform solution containing 1×10^{-3} mol dm⁻³ dithizone (H₂dz) was also propelled. The solutions were merged through a T-connector and then introduced into the forward-extraction coil packed with PTFE chips (EC_f, ϕ 2 mm, 9 m in length). The phases were separated with the air-trapping system (PS₁) and the organic phase was pumped into the flow line. An aqueous solution, of which the pH was adjusted to 1.8 with nitric acid, was also propelled by the double plunger pump (P₂) and merged with the organic phase. The mixture was introduced into the back-extraction coil packed with PTFE chips (EC_b, ϕ 2 mm, 25 cm in length) and then the aqueous phase was separated from the organic phase with the phase separator (PS₂). The cadmium(II) and zinc(II) concentrations in the aqueous phase were measured with an atomic absorption spectrophotometer. All experiments were carried out at room temperature (*ca.* 293 K).

3. Results and Discussion

3.1. Evaluation of the extraction rate of cadmium(II)

In the proposed system shown in Fig. 1, cadmium(II) has to be extracted quantitatively into the organic phase and then back-extracted into the aqueous phase. Therefore, evaluation of the effect of the reaction conditions on the extraction rates of cadmium(II) is extremely important. The reagent concentrations (NTA = 1×10^{-2} mol dm⁻³, H₂dz = 1×10^{-3} mol dm⁻³) and the pHs (pH 7.0 for forward-extraction, pH 1.8 for back-extraction) were adopted based on the previous studies [5,6]. In this paper, the effects of packing materials in the extraction coil and of the flow rate of the pump on the extraction rates were investigated.

The forward-extraction rate constant was determined as follows. Assuming that the extraction rate of cadmium(II) with dithizone is first order with respect to the concentration of cadmium(II) in the aqueous phase ($[\text{Cd}^{\text{II}}]$), the reaction rate is defined as

$$-\frac{d[\text{Cd}^{\text{II}}]}{dt} = k_{\text{obsd}(f)}[\text{Cd}^{\text{II}}], \quad (1)$$

where t and $k_{\text{obsd}(f)}$ denote the extraction time and the observed rate constant for forward-extraction, respectively. Integration results in

$$-\ln[\text{Cd}^{\text{II}}]_t = -\ln[\text{Cd}^{\text{II}}]_{t=0} + k_{\text{obsd}(f)}t. \quad (2)$$

According to Eq. (2), a plot of $-\ln[\text{Cd}^{\text{II}}]_t$ against t should give a straight line having a slope of $k_{\text{obsd}(f)}$. On the other hand, the back-extraction rate constant was also determined by the similar manner, where it was assumed that the back-extraction rate of Cd(Hdz)₂ is first order with respect to the concentration of Cd(Hdz)₂ in the organic phase. This manner gives the following equation.

$$-\ln[\text{Cd}(\text{Hdz})_2]_{\text{org},t} = -\ln[\text{Cd}(\text{Hdz})_2]_{\text{org},t=0} + k_{\text{obsd}(b)}t, \quad (3)$$

where org and $k_{\text{obsd}(b)}$ denote the organic phase and the observed rate constant for back-extraction, respectively. According to Eq. (3), a plot of $-\ln[\text{Cd}(\text{Hdz})_2]_{\text{org},t}$ against t

should give a straight line having a slope of $k_{\text{obsd}(t)}$. As an example, plots of $-\ln[\text{Cd}^{\text{II}}]$, against t are shown in Fig. 2, where each plot falls on a straight line, showing that Eq. (2) is valid. Plots of $-\ln[\text{Cd}(\text{Hdz})_2]_{\text{org},t}$ against t also gave straight lines.

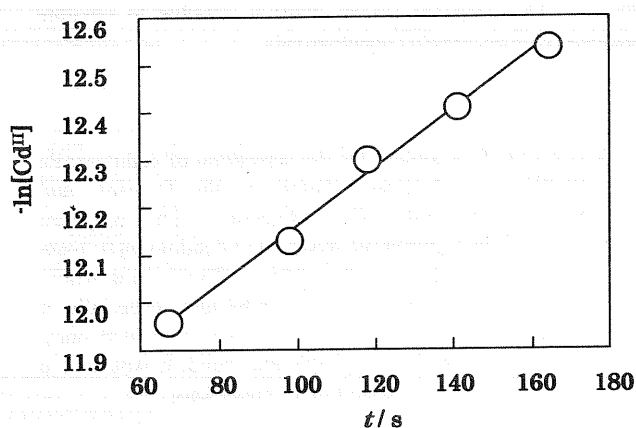


Fig. 2 A plot of $-\ln[\text{Cd}^{\text{II}}]$, against t . $[\text{Cd}^{\text{II}}]: 1 \times 10^{-5} \text{ mol dm}^{-3}$, extraction coil: PTFE tube packed with PTFE chips (ϕ 2mm), flow rate: $2.5 \text{ cm}^3 \text{ min}^{-1}$.

Table 1 Forward- and back-extraction rate constants obtained by use of extraction coils packed with packing materials

Packing materials	$k_{\text{obsd}(t)} / \text{s}^*$	$k_{\text{obsd}(b)} / \text{s}^*$
none	2.2×10^{-3}	1.2×10^{-2}
glass beads	3.2×10^{-3}	4.8×10^{-2}
Flushin T	5.0×10^{-3}	3.1×10^{-2}
PTFE chips	6.8×10^{-3}	5.8×10^{-2}

*Flow rate: $2.5 \text{ cm}^3 \text{ min}^{-1}$

To evaluate the effect of the packing materials on the extraction rates, $k_{\text{obsd}(t)}$ and $k_{\text{obsd}(b)}$ were measured. The obtained values are summarized in Table 1. The results show that the forward- and back-extraction rate constants increase by packing the materials into the extraction coil, and that the rate constants depend on the kind of the materials. Among them, PTFE chips gave the largest value. In the case of the extractive flow system using a PTFE tube as an extraction coil, it is known that extraction takes place at the surface on the PTFE tube [14]. Therefore, the extraction coil packed with PTFE chips, which has large surface area on PTFE, would provide a large extraction rate. In the proposed flow system, the extraction coil packed with PTFE chips was used as forward- and back-extraction coils.

The effect of flow rate on the extraction rate was examined, and the results are shown in Figs. 3 and 4. The extraction rate constants slightly increased with increasing the flow rate, but significant effects were not observed. In this case, the flow rates of $1.2 \text{ cm}^3 \text{ min}^{-1}$ for forward-extraction (pump P_1) and $1.0 \text{ cm}^3 \text{ min}^{-1}$ for back-extraction (pump P_2), which gave good phase-separation efficiency, were adopted.

3.2. Effect of extraction coil length on the separation of cadmium(II) from zinc(II)

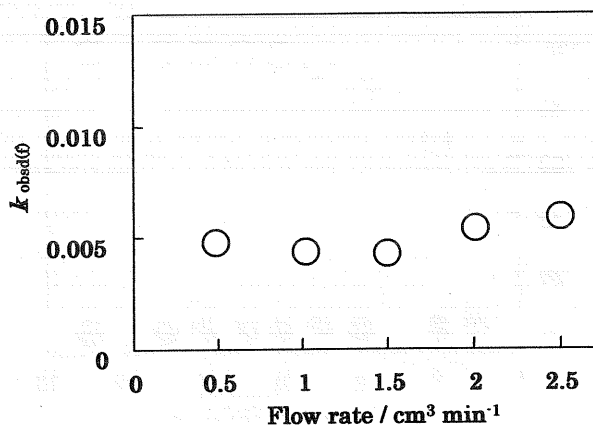


Fig. 3 Effect of flow rate on the forward-extraction rate constant ($k_{\text{obsd}(t)}$). $[\text{Cd}^{\text{II}}]: 1 \times 10^{-5} \text{ mol dm}^{-3}$, extraction coil: PTFE tube packed with PTFE chips (ϕ 2mm, 9m in length).

The effect of extraction coil length was examined, and the

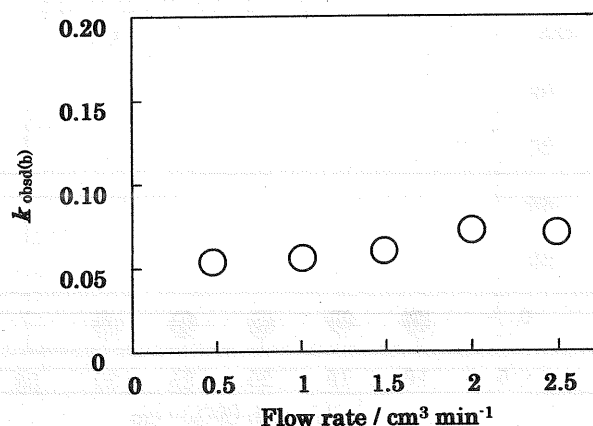


Fig. 4 Effect of flow rate on the back-extraction rate constant ($k_{\text{obsd}(b)}$). $[\text{Cd}^{\text{II}}]: 1 \times 10^{-5} \text{ mol dm}^{-3}$, extraction coil: PTFE tube packed with PTFE chips (ϕ 2mm, 25 cm in length).

results are shown in Figs. 5 and 6. For the forward-extraction, the extractability of cadmium(II) gradually increased with increasing in the extraction coil length and attained the maximum value at the extraction coil length in more than 8 m. In contrast, the extraction rate of zinc(II) was extremely slow, zinc(II) was hardly extracted into the organic phase under the experimental conditions. Therefore, the 9 m of PTFE tube packed with PTFE chips was selected as the forward-extraction coil. On the other hand, for the back-extraction, the extraction rate of cadmium(II) was considerably large, cadmium(II) was quantitatively back-extracted into the aqueous phase by use of the coil longer than 25 cm. Since zinc(II) was hardly back-extracted under the experimental conditions, the 25 cm of PTFE tube packed with PTFE chips was used as the back-extraction coil.

3.3. Separation of cadmium(II) from zinc(II) by continuous flow system

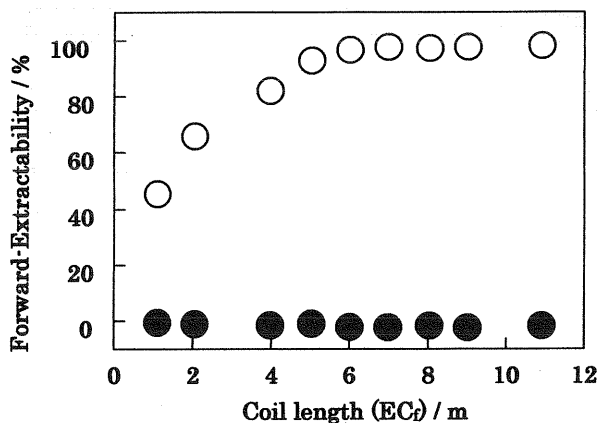


Fig. 5 Forward-extractability of cadmium(II) (○) and zinc(II) (●). [Cd^{II}]: 5×10^{-6} mol dm⁻³, [Zn^{II}]: 1×10^{-5} mol dm⁻³, extraction coil: PTFE tube packed with PTFE chips (ϕ 2mm, 9m in length), flow rate: 1.2 cm³ min⁻¹.

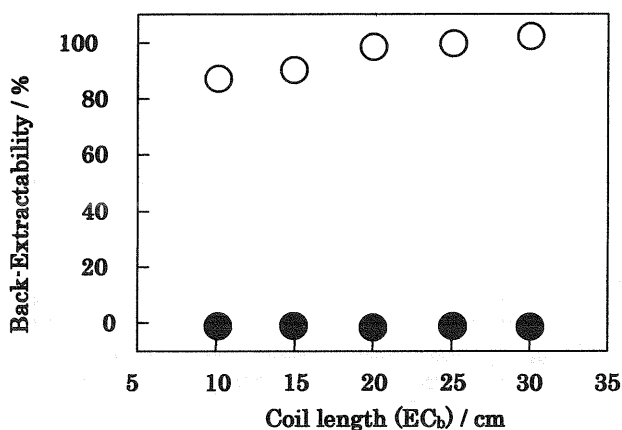


Fig. 6 Back-extractability of cadmium(II) (○) and zinc(II) (●). [Cd^{II}]: 5×10^{-6} mol dm⁻³, [Zn^{II}]: 1×10^{-5} mol dm⁻³, extraction coil: PTFE tube packed with PTFE chips (ϕ 2mm, 25 cm in length), flow rate: 1.0 cm³ min⁻¹.

On the basis of the above conditions, the continuous flow system for the separation of cadmium(II) from zinc(II) was constructed as shown in Fig. 1. To confirm the feasibility of the proposed system, a composite sample solution containing 5×10^{-6} mol dm⁻³ of cadmium(II), 5×10^{-3} mol dm⁻³ of zinc(II),

1×10^{-2} mol dm⁻³ of NTA and 1×10^{-2} mol dm⁻³ of MOPS buffer (pH 7.0) was prepared and introduced into the system. Consequently, the recoveries, defined as (concentrations in the aqueous phase back-extracted) / (concentrations in the sample solution) \times 100, were 97 % for cadmium(II) and 0.04% for zinc(II). The proposed system made it possible to separate cadmium(II) from zinc(II) quantitatively.

4. Conclusion

A continuous flow system for the separation of cadmium(II) from zinc(II) was developed based on the forward- and back-extraction processes with dithizone. The proposed system allowed the quantitative separation of cadmium(II) from zinc(II) only by switching on the pumps. The method would be applied to the separation of other metal ions; especially, it will be possible to separate labile metal ions from inert ones. Since the proposed method is simple and rapid, it would be a useful tool for the mutual separation of metal ions.

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