

Continuous-Flow System for Separation of Lead(II) from Zinc(II) by Forward- and Back-Extraction Processes

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Abstract

A continuous-flow system for the separation of lead(II) (Pb^{II}) from zinc(II) (Zn^{II}) was developed. The system consists of two extraction coils—one for forward-extraction and the other for back-extraction—connected in series through a phase separator. Firstly, in the forward-extraction process, most Pb^{II} and a small amount of Zn^{II} are extracted into chloroform phase with dithizone (H_2dz). Subsequently, in the back-extraction process, Pb^{II} is back-extracted into the aqueous phase with nitric acid while the Zn^{II} is retained in the organic phase. The experimental conditions were optimized based on the kinetic constants of Zn^{II} and Pb^{II} in forward- and back-extraction. The optimal flow system can quantitatively separate Pb^{II} from Zn^{II} by a single injection of a sample solution. This method is also applicable to a sample solution containing a much higher concentration of Zn^{II} ($4.89 \times 10^{-3} \text{ mol dm}^{-3}$) than that of Pb^{II} ($5.14 \times 10^{-6} \text{ mol dm}^{-3}$).

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

1. Introduction

Apart from their vast range of applications and economic importance, zinc (Zn) and lead (Pb) have been recognized as eco-toxicological hazardous materials [1,2]. The recognition of Zn and Pb has led to increased interest in the development of methods for separating, removing and purifying these and other metals from various sources [3].

As a separation technique, liquid–liquid extraction techniques play an important role in the development of processes for recovering and separating different metal ions [4]. Dithizone (3-mercapto-1,5-diphenylformazan: H_2dz) is a typical extracting agent for separating heavy metals in water or soil samples; it is a S, N binder donor that reacts with soft cations such as Cu, Zn, Pb, or Cd [5]. Although the method of extraction and spectrophotometric determination of metals using H_2dz are sensitive, it has low selectivity for the equilibrium state. For example, a separation of Pb^{II} from Zn^{II} by H_2dz is difficult because of their similar extraction constants (K_{ex}) ($\log K_{\text{ex}} = 3.16$ in Zn^{II} and 1.29×10^{-1} in Pb^{II}) [6–8].

We focused on the difference in the water-exchange rate constants ($k_{\text{H}_2\text{O}}$) of the aqua complex ions between Zn and Pb ($k_{\text{H}_2\text{O}} = 10^{7.7} \text{ s}^{-1}$ in Zn^{II} and $10^{9.6} \text{ s}^{-1}$ in Pb^{II}) [7,8] and carried out fundamental studies using a batch procedure. Firstly, the forward- and back-extraction rates of Zn^{II} and Pb^{II} were measured. Pb^{II} was selectively back-extracted into an acidic aqueous phase from an organic phase with H_2dz . The forward-extraction of Pb^{II} was kinetically achieved from the aqueous phase to the organic phase of H_2dz with DPTA-OH(1,3-diamino-2-hydroxypropan-*N,N,N',N'*-tetraacetic acid) as a masking reagent for Zn^{II} . The kinetic forward- and back-extraction processes were found to be favorable for the quantitative separation of Pb^{II} from Zn^{II} . However, the abovementioned batch procedure required transfer of the solution into another separatory funnel.

Accordingly, we aimed to separate Pb^{II} from Zn^{II} using a flow injection technique, which has widely been used for a variety of analytes and applications [9] and which allows solvent extraction to be carried out continuously. This technique has been applied to determination of various substances including metals [10–17].

This paper describes a continuously extractive flow system that can be used for the separation of Pb^{II} from Zn^{II} by connecting both forward- and back-extraction processes.

2. Experimental

2.1 Reagents

Dithizone and metal salts were purchased from Wako Pure Chemicals and were used without further purification. Stock solutions of $1.0 \times 10^{-1} \text{ mol dm}^{-3}$ DPTA-OH were prepared by water that included the appropriate amount of sodium hydroxide (Dojin Chemicals Co.). Those of MOPS (3-morpholino propane sulfate), sodium perchlorate and sodium acetate (1.0 mol dm^{-3} each) were prepared by dissolving each in water. The water used to prepare the reagents was purified using a Milli-Q water purification system (Millipore Co.). Bis(dithizonato)zinc(II) ($\text{Zn}(\text{Hdz})_2$) and bis(dithizonato)lead(II) ($\text{Pb}(\text{Hdz})_2$) were prepared as described in a previous study [18]. Polytetrafluoroethylene (PTFE) chips (*ca.* $0.4 \text{ mm} \times 0.4 \text{ mm} \times 0.1 \text{ mm}$) were cut from a PTFE tube and used as packing material.

2.2 Apparatus

Two double-plunger pumps (Sanuki Kogyo, DMX-2000) were used for propelling the sample and reagent solutions. A phase separator (Sanuki Kogyo) with a porous PTFE-membrane filter and an air-trapping system (Sanuki Kogyo, AD-2) were used for the separation of the organic and aqueous phases. In the continuous-flow separation system, two PTFE tubes packed with PTFE chips (2 m in length for forward-extraction and 0.2 m in length for back-extraction) were used as the forward- and back-extraction coils. A Hitachi (Model Z-6100) atomic absorption spectrometer (AAS) equipped with a hollow cathode lamp (Hamamatsu Photonics) was used for the identification of metal ions. A Fisher Scientific pH meter (Accumet pH meter 15) was used for the pH measurements.

2.3 Procedure

2.3.1 Measurement of forward- and back-extraction rate constants for Zn^{II} and Pb^{II} using a batch procedure

For measurement of the forward-extraction rate constant, an aqueous solution containing Zn^{II} or Pb^{II} with $1 \times 10^{-1} \text{ mol dm}^{-3}$ acetic acid-sodium acetate buffer or $1 \times 10^{-1} \text{ mol dm}^{-3}$ sodium

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perchlorate were introduced in a glass funnel. A chloroform solution containing $1 \times 10^{-4} \sim 4 \times 10^{-3} \text{ mol dm}^{-3}$ dithizone (Hdz) was also introduced in the glass funnel. After the aqueous phase was separated from the organic phase, the concentration of the metal ions in the aqueous phase was measured with the AAS. The above measurements were conducted using various concentrations of dithizone at various reaction (extraction) times.

For measurement of the back-extraction rate constant, an aqueous solution of $1 \times 10^{-2} \text{ mol dm}^{-3}$ nitric acid, and a chloroform solution containing $\text{Zn}(\text{Hdz})_2$ or $\text{Pb}(\text{Hdz})_2$ were introduced in a glass funnel. The subsequent steps were the same as those in the case of forward-extraction, as described above.

2.3.2 Continuous-flow separation system of Pb^{II} from Zn^{II}

Figure 1 shows a schematic diagram of the proposed system. A sample solution (S) containing Zn^{II} and Pb^{II} ions, $1 \times 10^{-3} \text{ mol dm}^{-3}$ DPTA-OH, and MOPS buffer (pH 7) was propelled by a double-plunger pump (P_1). A chloroform solution containing $1 \times 10^{-2} \text{ mol dm}^{-3}$ dithizone (R_1) was also introduced. The solutions were allowed to mix at a T-connector and were then introduced into the forward-extraction coil packed with PTFE chips (EC_f , $\phi 2 \text{ mm}$, length of 2 m). The phases were separated by the phase separator (PS_1), and the organic phase was pumped further downstream. An aqueous solution with its concentration adjusted to $1 \times 10^{-1} \text{ mol dm}^{-3}$ of nitric acid solution (R_2) was also propelled by the double-plunger pump (P_2) and mixed with the organic phase. The mixture was introduced into the back-extraction coil packed with PTFE chips (EC_b , $\phi 2 \text{ mm}$, length of 0.2 m), and the aqueous phase was separated from the organic phase by the phase separator (PS_2). The concentration of Pb^{II} separated from Zn^{II} in the aqueous phase was measured with the AAS. All experiments were carried out at room temperature (ca. 293 K).

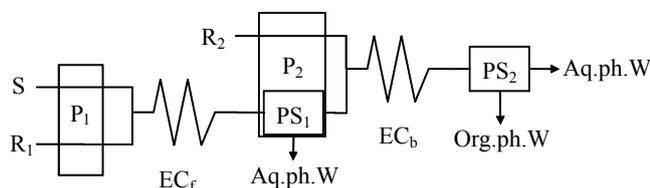


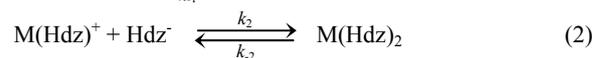
Fig. 1 Continuous-flow system for separating Pb^{II} from Zn^{II}
S: sample solution, R_1 : chloroform solution containing $1 \times 10^{-2} \text{ mol dm}^{-3}$ dithizone, R_2 : nitric acid solution (pH 1), EC_f : forward-extraction coil packed with PTFE chips ($\phi 2 \text{ mm}$, 2 m length), EC_b : back-extraction coil packed with PTFE chips ($\phi 2 \text{ mm}$, 0.2 m in length), P_1 : double plunger pump ($1.18 \text{ cm}^3 \text{ min}^{-1}$), P_2 : double plunger pump ($0.944 \text{ cm}^3 \text{ min}^{-1}$), PS_1 : phase separator with PTFE membrane filter, PS_2 : phase separator with PTFE membrane filter, Aq.ph: subjected to AAS, Aq.ph.W: aqueous phase waste, and Org.ph.W: organic phase waste.

3. Results and Discussion

3.1 Evaluation of forward- and back-extraction rate constants for Zn^{II} and Pb^{II}

As shown in Fig. 1, Pb^{II} is forward-extracted into the organic phase and is quantitatively back-extracted into the aqueous phase. Therefore, the effects of reaction conditions on the kinetic extractions of Zn^{II} and Pb^{II} were investigated.

The forward-extraction rate constant was determined as follows. Complexation of divalent metal ions (M^{2+}) with dithizone in an aqueous phase proceeds according to



The equilibrium constants (K_1 and K_2) are defined using forward reaction constant (k_1 and k_2) and back reaction constant (k_{-1} and k_{-2}) as the following equations:

$$K_1 = k_1 / k_{-1}, \quad K_2 = k_2 / k_{-2} \quad (3, 4)$$

Generally, in a forward-extraction rate, a generation of $\text{M}(\text{Hdz})^+$ is predominant in rate-determining step ($k_1 > k_2$).

By assuming that the extraction rate (v_+) of metal using dithizone is of the first order with respect to the concentration of metal ions in the aqueous phase ($[\text{M}^{2+}]$), we can define the reaction rate according to the following equation:

$$v_+ = -\frac{d[\text{M}^{2+}]}{dt} = k_{\text{obsd}(+)}[\text{M}^{2+}] = k_1[\text{M}^{2+}][\text{Hdz}^-] \quad (5)$$

where t and $k_{\text{obsd}(+)}$ denote the extraction time and the observed rate constant of the forward-extraction, respectively.

$$K_a = \frac{[\text{H}^+][\text{Hdz}^-]}{[\text{H}_2\text{dz}]} \quad (6)$$

$$K_D = \frac{[\text{H}_2\text{dz}]_{\text{org}}}{[\text{H}_2\text{dz}]} \quad (7)$$

where $[\text{H}_2\text{dz}]_{\text{org}}$ is the concentration of an extraction reagent H_2dz in the organic phase. K_a is the dissociation constant of H_2dz in the aqueous phase, and K_D is the distribution coefficient of H_2dz . By substituting Eqs. (6) and (7) in Eq. (5), the following equation gives Eq. (8).

$$-\frac{d[\text{M}^{2+}]}{dt} = \frac{k_1 K_a [\text{H}_2\text{dz}]_{\text{org}}}{K_D [\text{H}^+]} [\text{M}^{2+}] = k_+ \frac{[\text{H}_2\text{dz}]_{\text{org}}}{[\text{H}^+]} [\text{M}^{2+}] \quad (8)$$

On integration, the below equation gives Eq. (9).

$$-\ln[\text{M}^{2+}]_t = -\ln[\text{M}^{2+}]_{t=0} + k_+ \frac{[\text{H}_2\text{dz}]_{\text{org}}}{[\text{H}^+]} t \quad (9)$$

According to Eq.(9), a plot of $-\ln[\text{M}^{2+}]_t$ against t should be a straight line having a slope of k_+ . As an example, a plot of $-\ln[\text{M}^{2+}]_t$ against $[\text{HR}]_{\text{org}}/[\text{H}^+]t$ at pH 4.8 is shown in Fig. 2, where the data points fall on a straight line; this straight line verifies the validity of Eq.(9).

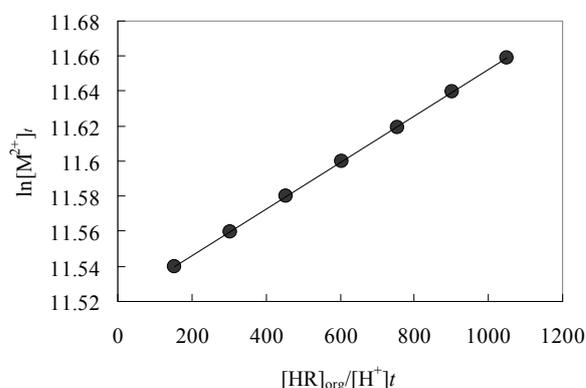


Fig. 2 Plot of $-\ln[\text{M}^{2+}]_t$ as a function of $[\text{HR}]_{\text{org}}/[\text{H}^+]t$. $[\text{M}^{2+}] = [\text{Zn}^{\text{II}}] = 1 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{HR}]_{\text{org}} = [\text{H}_2\text{dz}] = 1 \times 10^{-4} \text{ mol dm}^{-3}$; and pH 4.8.

The back-extraction rate constant was also determined in a similar manner; in this case, a dissociation of $M(\text{Hdz})^+$ is assumed to be predominant in a rate-determining step. The extraction rate (v_-) of metal using dithizone is of the first order with respect to the concentration of the metal complex in the organic phase ($[M(\text{Hdz})_2]_{\text{org}}$). Under this assumption, the back-extraction rate can be expressed by the following equation:

$$v_- = -\frac{d[M(\text{Hdz})_2]_{\text{org}}}{dt} = k_{\text{obsd}(-)}[M(\text{Hdz})_2] = k_{-1}[M(\text{Hdz})^+] \quad (10)$$

where $k_{\text{obsd}(-)}$ denote the observed rate constant of the back-extraction.

$$K_2 = \frac{[M(\text{Hdz})_2]}{[M(\text{Hdz})^+][\text{Hdz}^-]} \quad (11)$$

$$K_{\text{DM}} = \frac{[M(\text{Hdz})_2]_{\text{org}}}{[M(\text{Hdz})_2]} \quad (12)$$

where K_{DM} is distribution coefficient of $M(\text{Hdz})_2$ into organic phase. By substituting Eqs. (11) and (12) in Eq. (10), the following equation gives Eq. (13).

$$\begin{aligned} -\frac{d[M(\text{Hdz})_2]}{dt} &= \frac{k_{-1}K_{\text{D}}}{K_2K_{\text{DM}}K_{\text{a}}}\frac{[\text{H}^+]}{[\text{H}(\text{Hdz})]_{\text{org}}}[M(\text{Hdz})_2]_{\text{org}} \\ &= k_{-}\frac{[\text{H}^+]}{[\text{H}(\text{Hdz})]_{\text{org}}}[M(\text{Hdz})_2]_{\text{org}} \end{aligned} \quad (13)$$

On integration, the below equation gives Eq. (14).

$$-\ln[M(\text{Hdz})_2]_{\text{org},t} = -\ln[M(\text{Hdz})_2]_{\text{org},t=0} + k_{-}\frac{[\text{H}^+]}{[\text{H}_2\text{dz}]_{\text{org}}}t \quad (14)$$

Once the extraction rates k_+ and k_- were determined for forward and back extractions, respectively, the extraction constant (K_{ex}) was calculated from k_+/k_- . The average obtained values are summarized in Table 1. The results show that both the k_+ and k_- values of Pb^{II} were greater compared to those of Zn^{II} . The rate constant of Pb^{II} for back-extraction was higher than that for forward-extraction ones. Moreover, the K_{ex} values determined in this study were in agreement with the literature.

Table 1 Forward- and back-extraction rate constants of Zn^{II} and Pb^{II} and their $\log K_{\text{ex}}$

	k_+ / s^{-1}	k_- / s^{-1}	$\log K_{\text{ex}}$	
			determined	Refs. [7,8]
Zn^{II}	1.34×10^{-4}	2.45×10^{-5}	3.15	3.16
Pb^{II}	2.39×10^{-3}	1.86×10^{-2}	1.28×10^{-1}	1.29×10^{-1}

3.2 Kinetic separation of Pb^{II} from Zn^{II} by forward-extraction in presence of a complex reagent

For the separation of Pb^{II} from Zn^{II} , a masking reagent is required to ensure that $K_{\text{ML}}^{\text{Zn}} > K_{\text{ML}}^{\text{Pb}}$. The stability constants ($\log K_{\text{ML}}$) for some masking reagents are listed in Table 2.

Among these reagents, $K_{\text{ML}}^{\text{Zn}} > K_{\text{ML}}^{\text{Pb}}$ holds only for DPTA-OH. Therefore, it was used as the masking reagent in our flow system. The effect of the concentration of DPTA-OH was studied. As shown in Fig. 3, Pb^{II} was found to be selectively extracted in the presence of DPTA-OH.

Table 2 $\log K_{\text{ML}}$ values of Zn^{II} and Pb^{II} complexes

Masking reagents	$\log K_{\text{ML}}$	
	Zn^{II}	Pb^{II}
DHEG	6.50	7.50
IDA	7.27	7.45
NTA	10.7	11.4
DPTA-OH	13.7	11.4
EDTA-OH	14.5	15.5
GEDTA	14.5	14.7
HIDA	16.2	17.3
EDTA	16.5	18.0
TTHA	16.7	17.1
CyDTA	18.7	19.7
DTPA	18.8	18.8

DHEG: dihydroxyethyl glycine; IDA: iminodiacetic acid; NTA: nitrilotriacetic acid; EDTA-OH: *N*-(2-hydroxyethyl)ethylenediamine-*N,N,N'*-triacetic acid; GEDTA: *O,O'*-bis(2-aminoethyl)ethyleneglycol-*N,N,N',N'*-tetraacetic acid; EDTA: ethylenediamine-*N,N,N',N'*-tetraacetic acid; TTHA: triethylenetetramine-*N,N,N',N'',N'',N''*-hexaacetic acid; CyDTA: *trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid; DTPA: diethylenetriamine-*N,N,N',N'',N''*-pentaacetic acid.

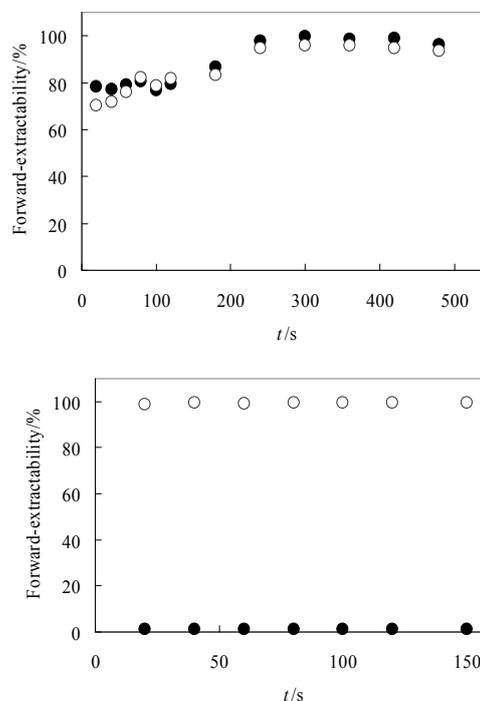


Fig. 3 Forward-extractabilities of Pb^{II} and Zn^{II} as function of extraction times in the absence (upper) and presence (bottom) of DPTA-OH. Organic phase: chloroform containing $1 \times 10^{-2} \text{ mol dm}^{-3} \text{ H}_2\text{dz}$; aqueous phase: $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ containing $1 \times 10^{-4} \text{ mol dm}^{-3} \text{ Zn}^{\text{II}}$ or $1 \times 10^{-5} \text{ mol dm}^{-3} \text{ Pb}^{\text{II}}$; $1 \times 10^{-2} \text{ mol dm}^{-3} \text{ DPTA-OH}$; and pH 7.0. Plots: $\bullet = \text{Zn}^{\text{II}}$, and $\circ = \text{Pb}^{\text{II}}$.

3.3 Kinetic separation of Pb^{II} from Zn^{II} by back-extraction using a continuous flow system

On the basis of the above results, the flow system was evaluated by requiring Pb^{II} to be extracted into the aqueous phase. The effect for length of the back-extraction coil was studied. Figure 4 plots the back-extractabilities to length of PTFE tube as the coil. The solid lines are theoretical values calculated from $k_{\text{obsd}(-)}$ in Eq. (15).

$$k_{\text{obsd}(-)} = k_{-} \frac{[\text{H}^{+}]}{[\text{H}(\text{Hdz})]_{\text{brg}}} \quad (15)$$

As shown in Fig. 4, Pb^{II} was not quantitatively separated from Zn^{II} without regarding to length of the coil. PTFE chips ($0.5 \times 0.5 \text{ mm}^2$) were packed into the coil ($\phi 2.0 \text{ mm}$). This is described by Nord and Karlberg, who suggested that back-extraction was accelerated with hydrophobic adsorption of chloroform to the surface of the chip [19]. By packing PTFE chips, the separation was quantitatively obtained. Although the back-extractability of Zn^{II} slightly increased with the reaction time, the influence for separation of Pb^{II} and Zn^{II} was not significant.

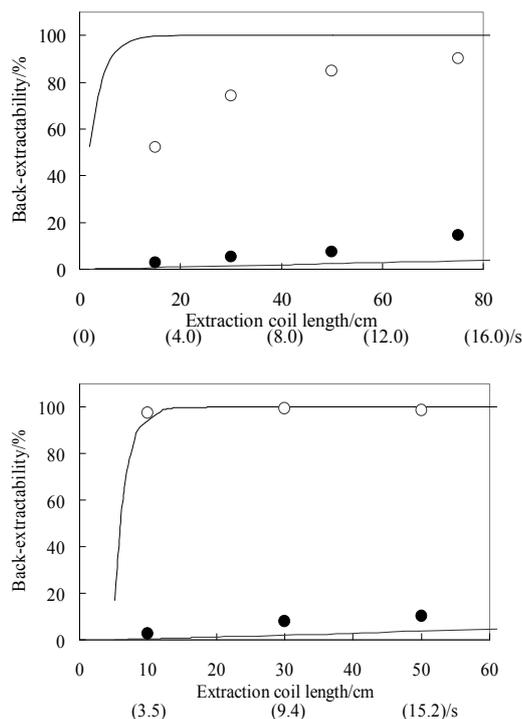


Fig. 4 Back-extractabilities of Pb^{II} and Zn^{II} as a function of the extraction coil length. Coil: (upper) PTFE tube alone; and (bottom) PTFE tube packed with PTFE chips. Organic phase: chloroform containing $1 \times 10^{-3} \text{ mol dm}^{-3} \text{ H}_2\text{dz}$, $5 \times 10^{-5} \text{ mol dm}^{-3} \text{ Zn}^{\text{II}}$ and $5 \times 10^{-5} \text{ mol dm}^{-3} \text{ Pb}^{\text{II}}$; aqueous phase: $1 \times 10^{-3} \text{ mol dm}^{-3} \text{ HNO}_3$; and pH 1.0. Solid lines show theoretical values from $k_{\text{obsd}(-)}$. The numbers under the horizontal axis are reaction times. Plots: ● = Zn^{II} , and ○ = Pb^{II} .

3.4 Kinetic separation of Pb^{II} from Zn^{II} by forward- and back-extraction using a continuous flow system

The abovementioned conditions were introduced to the continuous flow system in Fig. 1, and the kinetic separation of Pb^{II} from Zn^{II} by forward- and back-extraction was examined. The results are summarized in Table 3. Although the concentration of Zn^{II} in tested sample was around 1000 times higher than that of Pb^{II} , the proposed system could effectively and quantitatively separate Pb^{II} from Zn^{II} matrix.

Table 3 Extractability of Pb^{II} in Zn^{II} matrix with the continuous flow system

	Metal concentration / mol dm^{-3}	Extractability / %
$[\text{Zn}^{\text{II}}]$	4.89×10^{-3}	0.23
$[\text{Pb}^{\text{II}}]$	5.14×10^{-6}	95

Flow rate: $P_1 = 1.18 \text{ ml/min}$, $P_2 = 0.944 \text{ ml/min}$; extraction coil length: $\text{EC}_f = 2 \text{ m}$, $\text{EC}_b = 0.2 \text{ m}$

4. Conclusion

A continuous-flow system was developed for the separation of Pb^{II} from Zn^{II} by forward- and back-extraction processes using dithizone-chloroform. The proposed system allowed the quantitative separation of Pb^{II} from Zn^{II} using only two double-plunger pumps. This suggested that the system may be applicable to the separation of labile metal ions from inert ones in general.

We anticipate newer methods of kinetically separating metal ions using this flow system since the desired extraction time is obtained by simply adjusting the extraction coil length.

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