Spectrophotometric Determination of Cadmium(II) with Dithizone and 1,10-Phenanthroline

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Cadmium(II) has been quantitatively separated from zinc(II) by an ion-pair extraction system. An ion-pair consisting of cadmium(II) and 1,10-phenanthroline (phen) was found to be preferentially extracted into chloroform from an aqueous chloride solution containing zinc(II). The extracted species in chloroform reacted with dithizone (H_2Dz) to give the reddish mixed complex $Cd(HDz)_2(phen)$ having an absorption maximum at approximately 505 nm. The resulting calibration curve obeys Beer's law, the Sandell sensitivity being 0.0013 μg cm^{-2}. The effect of diverse ions has been examined, and a new highly selective method for the spectrophotometric determination of trace amounts of cadmium in metallic zinc established.

The spectrophotometric determination of cadmium(II) with dithiozone (H_2Dz) is well known as a highly sensitive method.[1] The separation of cadmium(II) from zinc(II) however remains a difficult problem. During the studies on the mutual separation of zinc(II) and cadmium(II) employing the synergistic extraction systems,[2–4] 1,10-phenanthroline (phen) was found to be the most suitable among several synergists. A new method of separation and determination of cadmium(II) was briefly reported.[5] In the preceding paper, it was stated that the species extracted with a mixture of dithizone and 1,10-phenanthroline at a pH of *ca.* 2 was a green complex. The reported procedure for the separation and determination of cadmium(II) is still feasible, however the previous observation concerning the extracted complex was found to be erroneous by additional detailed studies. Cadmium(II) is not extracted as a green complex but as a colorless ion-pair. This conclusion leads to the preferential and quantitative extraction of cadmium(II) using 1,10-phenanthroline alone, and in this case, zinc(II) was shown to remain in the aqueous phase. As a result, a highly selective method for the spectrophotometric determination of trace amounts of cadmium(II) with a mixture of dithizone and 1,10-phenanthroline has been established.

Experimental

Materials and Apparatus. ^{65}Zn and ^{115m}Cd were obtained from Nippon Isotope Kyokai. Dithizone and 1,10-phenanthroline were purchased from Wako Pure Chemicals and all organic solvents were of guaranteed grade.

The γ-ray activities of ^{65}Zn and ^{115m}Cd were measured with a γ-ray spectrometer consisting of a NaI(Tl) well crystal and a Hitachi RAH 403 type 400 channel pulse height analyser. The percent extraction (*E*) was obtained as a function of pH. The measurements of pH were conducted using a Hitachi-Horiba F-5 type pH meter. The absorbance of the organic phase was measured with a Hitachi 200-10 type spectrophotometer.

Extraction Procedure (A): The aqueous phase containing 0.01 mol dm^{-3} 1,10-phenanthroline, 0.1 mol dm^{-3} sodium chloride, 1.0×10^{-6} mol dm^{-3} metal ions, ^{65}Zn and ^{115m}Cd tracers was vigorously shaken for 10 min in a separatory funnel with an equal volume of the organic phase containing 0.002% dithizone. After the phases were allowed to separate, the γ-ray activity of each phase and the pH of the aqueous phase were measured.

Spectrophotometric Determination of Cadmium(II) (B): An aliquot of the sample solution containing less than 20 μg of cadmium(II) was taken in a separatory funnel, and 0.04 mol dm^{-3} 1,10-phenanthroline in water (5 cm^3) and 5 mol dm^{-3} sodium chloride (2 cm^3) added. The pH of the aqueous solution was adjusted to *ca.* 3 by the addition of hydrochloric acid or ammonia with Methyl Orange as the indicator. After the volume of the aqueous phase was adjusted to *ca.* 20 cm^3 with water, chloroform (10.0 cm^3) was added and the mixture shaken for 10 min. Each 5.00 cm^3 of the resulting organic phase and 0.002% dithizone in chloroform was transferred to another separatory funnel containing 5 mol dm^{-3} ammoniacal solution (20 cm^3), and the mixture shaken for 3 min. After the phases were allowed to separate, the absorbance of the organic phase was measured at 505 nm against the reagent blank.

Results and Discussion

Separation of Cadmium(II) from Zinc(II). Extraction curves for cadmium(II) and zinc(II) obtained according to procedure (A) are shown in Fig. 1, in which the selectivity for the separation of both elements

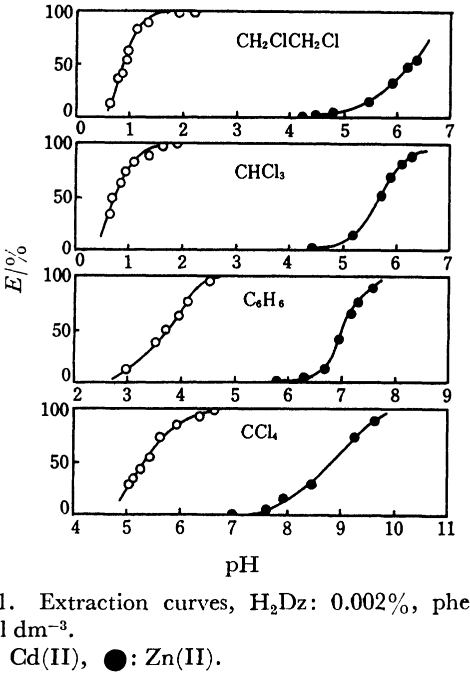

Fig. 1. Extraction curves, H_2Dz: 0.002%, phen: 0.1 mol dm^{-3}.
○: Cd(II), ●: Zn(II).

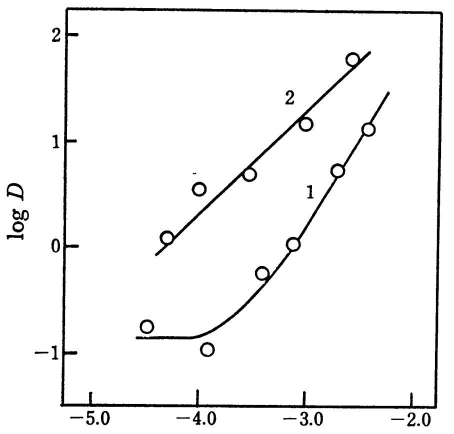

Fig. 2. Effects of dithizone and 1,10-phenanthroline concentrations on the extraction of cadmium(II).
1: log D *vs.* log[H_2O_2], phen: 1.0×10^{-3} mol dm^{-3}, pH: 2.1. 2: log D *vs.* log[phen], H_2Dz: 0.1%, pH: 2.1.

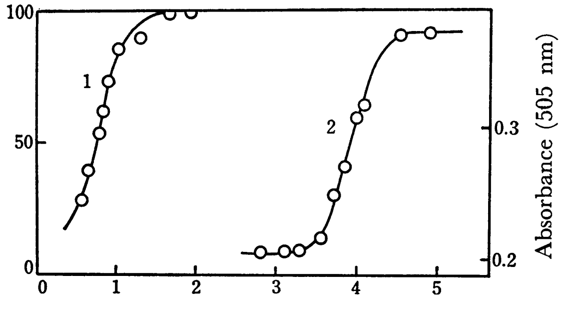

Fig. 3. Effect of pH on the extraction of cadmium(II).
1: E *vs.* pH, H_2Dz: 0.002%, phen: 0.1 mol dm^{-3}.
2: Absorbance *vs.* pH, H_2Dz: 0.001%, phen: 0.01 mol dm^{-3}.

is affected by the nature of the organic solvent. Chloroform and 1,2-dichloroethane both having relatively high polarities were the most suitable solvents for separation, based on the difference in the half extraction pH between cadmium(II) and zinc(II). By employing *e.g.* chloroform as a diluent, the quantitative separation of cadmium(II) from zinc(II) could be attained in the pH range of 2.0 to 4.0.

The Extracted Species of Cadmium(II). In order to examined the composition of cadmium(II) in chloroform, the logarithmic plots are given in Fig. 2, where D denotes the distribution ratio of cadmium(II). The slope analysis of the plots shows that $Cd(HDz)_2(phen)$ may be extracted at high concentration of dithizone. However, the extraction curve of ^{115m}Cd did not agree with that obtained by the spectrophotometric method, as is seen in Fig. 3. It is thought that a colorless species, *i.e.*, $Cd(phen)_3Cl_2$ is extracted at a pH of *ca.* 2.0, while the reddish $Cd(HDz)_2(phen)$ observed above pH 3.5. 1,10-Phenanthroline itself extracts cadmium(II), leaving zinc(II) quantitatively in the aqueous phase. In addition, the optimum concentrations of sodium chloride and 1,10-phenanthroline for the determination of cadmium(II) according to procedure (B) were found to be greater than 0.4 mol dm^{-3} and 5.0×10^{-3} mol dm^{-3}, respectively.

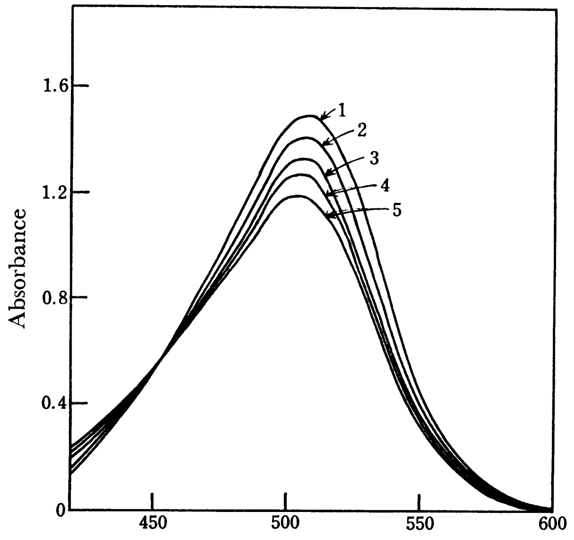

Fig. 4. Absorption spectra of the chloroform phase after shaking with 5 mol dm^{-3} ammoniacal solution. Cd(II): 50 μg, H_2Dz: 0.001%.
[phen]/mol dm^{-3} 1: none, 2: 1.0×10^{-5}, 3: 2.5×10^{-5}, 4: 7.5×10^{-5}, 5: 5.0×10^{-4}.

The Absorption Spectra of the Extracts. The effect of the 1,10-phenanthroline concentration on the absorption spectrum of cadmium(II) dithizonate is shown in Fig. 4. An increase in the 1,10-phenanthroline concentration leads to a decrease in the absorbance at approximately 505 nm, and the isosbestic point appears at 455 nm, indicating that two colored species, namely $Cd(HDz)_2$ and $Cd(HDz)_2(phen)$ may exist in chloroform. Thus;

$$Cd(HDz)_{2,org} + phen_{org} \rightleftharpoons Cd(HDz)_2(phen)_{org} \quad (1)$$

and

$$\log \frac{A_i - A}{A - A_a} = \log K + \log\,[phen]_{org} \quad (2)$$

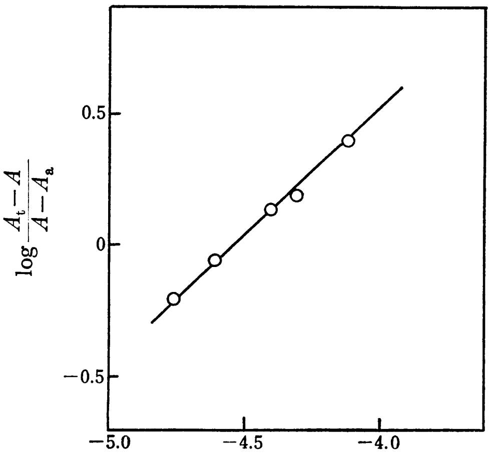

Fig. 5. Composition of the extracted species.

TABLE 1. EFFECTS OF DIVERSE IONS

Metal ions	Added as	Diverse ions added (μg)	Cd(II) found (μg)	Error (μg)
Co^{2+}	Acetate	100	12.7	+0.7
Fe^{3+}	Chloride	100	12.0	0
Fe^{2+}	Sulfate	100	12.3	+0.3
Pb^{2+}	Nitrate	100	11.9	−0.1
Mn^{2+}	Sulfate	100	12.0	0
Ni^{2+}	Chloride	100	12.3	+0.3
Sn^{2+}	Chloride	100	12.6	+0.6
Ag^{+}	Acetate	100	25.0	+13.0
Ag^{+}	Acetate	10	16.1	+4.1
Hg^{2+}	Nitrate	100	33.5	+21.5
Hg^{2+}	Nitrate	10	17.9	+5.9
Hg^{2+}	Nitrate	100[a)]	12.0	0
Cu^{2+}	Sulfate	100	13.9	+1.9
Cu^{2+}	Sulfate	25	12.9	+0.9
Cu^{2+}	Sulfate	100[b)]	13.1	+1.1
Cu^{2+}	Sulfate	100[c)]	12.0	0
Zn^{2+}	Chloride	100	12.1	+0.1
Zn^{2+}	Chloride	1000	13.2	+1.2
Zn^{2+}	Chloride	10mg[d)]	12.0	0
Zn^{2+}	Chloride	100mg[e)]	12.1	+0.1

12.0 μg of cadmium(II) was taken. a) 2 cm^3 of 1 mol dm^{-3} thiosulfate soln was added. b) 1 cm^3 of 1 mol dm^{-3} thiourea soln was added. c) 2 cm^3 of 1 mol dm^{-3} thiourea soln was added. d) The initial extraction of Cd(II) was performed in the presence of 0.1 mol dm^{-3} phen. soln. e) The initial extraction of Cd(II) was performed in the presence of 0.25 mol dm^{-3} phen. soln.

where the subscript org refers to the organic phase, K denotes the equilibrium constant for Eq. 1, A is the absorbance at 505 nm, and A_i and A_a represent the absorbances of $Cd(HDz)_2$ and $Cd(HDz)_2(phen)$ respectively. According to Eq. 2, a plot of the value of the left-hand side against log $[phen]_{org}$ should give a straight line having a slope of unity. As shown in Fig. 5, the above assumption is confirmed and the value of K has been calculated to be $10^{-4.54\pm0.02}$. Since no change in the spectrum of $Cd(HDz)_2(phen)$ was observed within one hour, $Cd(HDz)_2(phen)$ is considered to be useful for analytical purposes.

Calibration Curve. The calibration curve prepared according to procedure (B) was linear in the range of zero to 20 μg of cadmium(II), and passed through the origin. The molar absorptivity at 505 nm was shown to be 65000 $dm^3\ mol^{-1}\ cm^{-1}$, the Sandell sensitivity being 0.0013 μg cm^{-2}. The reproducibility test taking 12.0 μg of cadmium(II) gave an average absorbance of 0.361 from 7 determinations, the relative standard deviation being 0.0050.

Effect of Diverse Ions. The experimental results are summarized in Table 1. Each 100 μg of cobalt(II), iron(II, III), lead(II), manganese(II), nickel(II), and tin(II) did not interfere with the determination. Interferences caused by the presence of mercury(II) and copper(II) could be eliminated by the addition of thiosulfate and thiourea, respectively.

Analytical Result. The above procedure (B) was applied to the analysis of cadmium in a metallic zinc, which was found to contain 221±6 ppm as the average value of 5 determinations. The result agrees with the value obtained by the atomic absorption spectrometry (223 ppm).

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References

1) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, New York (1959), p. 350.

2) H. Akaiwa, H. Kawamoto, and Y. Tsutsumi, *Bunseki Kagaku*, **26**, 202 (1977).

3) H. Akaiwa, H. Kawamoto, and Y. Tsutsumi, *Bunseki Kagaku*, **27**, 447 (1978).

4) H. Akaiwa, H. Kawamoto, K. Ogura, and M. Konishi, *Bunseki Kagaku*, **27**, 329 (1978).

5) H. Akaiwa, H. Kawamoto, and E. Yoshimatsu, *Chem. Lett.*, **1978**, 421.