The Spectrophotometric Determination of Anions by Solvent Extraction with Metal Chelate Cations. VIII.* A New Method for the Determination of Cadmium

By Keiya KOTSUJI

(Received November 7, 1964)

In a previous paper of this series, it has been shown that cadmium iodide complex, as well as mercuric iodide complex, can be extracted into 1, 2-dichloroethane with 2, 2′-dipyridyl iron(II) chelate.(1) Consequently, a method for the determination of cadmium has been investigated, in which the metal ion in aqueous solution is extracted into dichloroethane with dipyridyl iron(II) chelate in the presence of excess iodide and the absorbance of the resulting chelate in the organic phase is measured.

Many reagents have been used for the

---

* Presented at the 12th Annual Meeting of the Japan Society for Analytical Chemistry, Kanazawa, October, 1963.

1) Y. Yamamoto and K. Kotsuji, This Bulletin, 37, 594 (1964).

colorimetric determination of cadmium, the most favored being dithizone.[2,3] Other reagents which have been suggested include di-β-naphthylthiocarbazone,[4] 4-hydroxy-3-nitrobenzenearsonic acid,[5] 1-(6-bromobenzothiazol-2-ylazo)-2-naphthol,[6] "Cadion," a triazine dye,[7] glyoxal bis(2-hydroxy-anil),[8] and diethyldithiocarbamate.[9,10] Although a differential ultraviolet spectrophotometric method using 1,10-phenanthroline has also been devised, numerous interference have been found.[11] However, the proposed method is different from the known methods described above in the mechanism of color reaction.

Experimental

Apparatus and Reagents. — Unless otherwise stated, apparatus and reagents were the same as those described in a previous paper.[12]

Standard Cadmium Solution.—Guaranteed cadmium sulfate ($3CdSO_4 \cdot 8H_2O$) was dissolved in distilled water, containing sufficient sulfuric acid to prevent hydrolysis, and diluted with distilled water to a concentration of 1000 p. p. m. of cadmium. The cadmium content was determined by an EDTA titration. This standard solution was diluted to the concentration required for the experiments.

All other reagents of analytical grade were used without further purification.

Procedure. — Mix 2,2'-dipyridyl (8×10^{-3} M), ferrous ammonium sulfate (2×10^{-3} M), sodium acetate (3 M), potassium iodide (0.3 M), and standard cadmium solution in the proper concentration. Adjust the pH of the solution to the required value with dilute sulfuric acid or dilute sodium hydroxide solution and then dilute it to 25 ml. with distilled water. To this, add 10.0 ml. of dichloroethane and shake the solution for 4 min. After standing the solution for 20 min., transfer the organic layer into a flask containing 1 g. of anhydrous sodium sulfate and shake it vigorously to make the solution transparent. Then transfer it into a 10 mm. cell. Measure the absorbance of the solution at 526 mμ using a reagent blank solution or dichloroethane as a reference. Measure the pH of the aqueous layer after the separation.

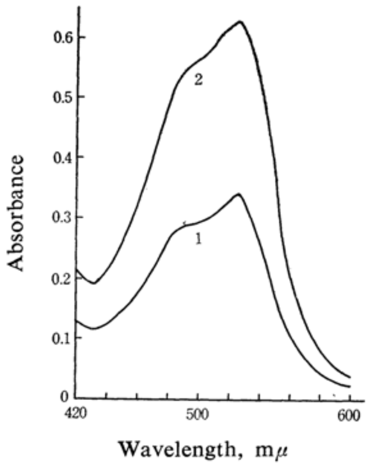

Fig. 1. Absorption spectra.
Reference: Dichloroethane, pH: 6.5
Curve 1: Spectrum of organic phase extracted from the aqueous solution (25 ml.) contained Dip. 6.4×10^{-4} M, Fe(II) 1.6×10^{-4} M, NaAc 0.24 M, KI 8.4×10^{-2} M but Cd is absent.
Curve 2: Spectrum of organic phase extracted from the aqueous solution (25 ml.) containing 1.6 p. p. m. of Cd in addition to the same component as that of curve 1.

Results and Discussion

Absorption Spectrum. — The spectral absorbance curves using dichloroethane as a reference are shown in Fig. 1. Curve 1 is a spectrum of the extract when cadmium ions are absent, while curve 2 is that of the extract with cadmium ions. It is observed that the presence of cadmium ions leads to a considerable increase in the absorbance and that both curves have a maximum absorbance at 526 mμ. The maximum absorbance is shifted from 522 mμ, the value in aqueous solution,[13] to 526 mμ in dichloroethane solution. This slight red shift in the organic layer may be attributed to the effect of the association between the chelate cation and the complex anion in dichloroethane. Feigl[14] has shown that 2,2'-dipyridyl iron(II) chelate can be precipitated as red crystals with a divalent complex anion such as tetra-iodocadmium. From these facts, the chemical formula of the extracted species is assumed to be $Fe(Dip.)_3 \cdot CdI_4$.

The maximum difference in absorbance for curve 1 and curve 2 is found at 526 mμ. Therefore, the absorbance was measured at this wavelength.

Effect of Reagents.—*Effect of 2,2'-Dipyridyl*

---

[2] E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York (1950), p. 228.

[3] B. E. Saltzman, *Anal. Chem.*, **25**, 493 (1953).

[4] J. Cholak and D. M. Hubbard, *Ind. Eng. Chem., Anal. Ed.*, **16**, 333 (1944).

[5] W. Nielsh and G. Boltz, *Chem. Z.*, **79**, 364 (1955).

[6] V. G. Brudz, D. A. Drapkina, K. A. Smirnova, N. I. Doroshina, Z. S. Sidenko and G. S. Chizhova, U. S. S. R. 146088, April 6, 1962; *Chem. Abstr.*, **57**, 9219 (1962).

[7] P. Chavanne and C. Geronimi, *Anal. Chim. Acta*, **19**, 377 (1958).

[8] S. Ôi, *Japan Analyst* (*Bunseki Kagaku*), **9**, 770 (1960).

[9] E. Sudo, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **73**, 693 (1952).

[10] D. F. Boltz and E. J. Havlena, *Anal. Chim. Acta*, **30**, 565 (1964).

[11] C. Wadelin and M. G. Mellon, *Anal. Chem.*, **24**, 894 (1952).

[12] K. Kotsuji, This Bulletin, **83**, 402 (1965).

[13] M. L. Moss and M. C. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **14**, 826 (1942).

[14] F. Feigl, "Spot Test, Part I, Inorganic Application," Elsevier Publishing Company, New York (1954), p. 90.

Iron(II) Chelate and Potassium Iodide Concentration.—The formation of extractable species may be mainly governed by the concentration of the 2, 2′-dipyridyl iron(II) chelate cation as well as the tetraiodo-cadmium complex anion. Moreover, a large excess of potassium iodide is necessary to obtain a quantitative formation of tetraiodo-cadmium complex. The effect of such variables on the extraction was investigated.

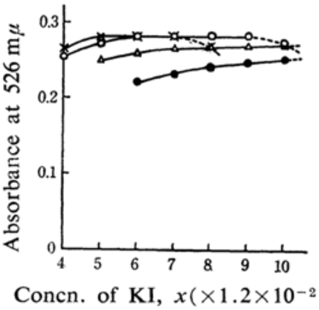

Fig. 2. Effect of 2,2′-dipyridyl iron(II) chelate and potassium iodide concentrations.
The concentration of acetate in the final solutions was 0.24 M.
Concn. of cadmium, 1.6 p. p. m.
pH of aqueous layer, 6.5
Shaking time., 4 mm.
Reference, Reagent blank

	Concn. of Dip. M	Concn of Fe(II) M
-×-	9.6×10^{-4}	2.4×10^{-4}
-○-	6.4×10^{-4}	1.6×10^{-4}
-△-	3.2×10^{-4}	0.8×10^{-4}
-●-	1.6×10^{-4}	0.4×10^{-4}

To a solution containing a constant amount of cadmium, were added varying amounts of potassium iodide, ferrous ammonium sulfate, and 2, 2′-dipyridyl, the mole ratio of dipyridyl to ferrous iron being kept at 4 to 1. In this case, it seems reasonable to assume that the concentration of ferrous iron is approximately equal to that of 2, 2′-dipyridyl iron(II) chelate because of the high stability of the chelate.[15] The pH of the solutions was kept at 6.5 and the extraction procedure was carried out for such solutions. The results are shown in Fig. 2. When the final concentration of the ferrous ammonium sulfate was lower than 8×10^{-5} M, rather low recovery was observed although the recovery increased with rise of potassium iodide concentration. When the concentration of ferrous ammonium sulfate was kept in the range of 1.6×10^{-4}—2.4×10^{-4} M, the recovery reached a maximum provided the iodide concentration was higher than 7.2×10^{-2} M. However, a large excess of iodide or of chelate caused a decrease in the absorbance. Therefore, the concentrations of ferrous ammonium sulfate and potassium iodide were kept at 1.6×10^{-4} M and 8.4×10^{-2} M, respectively, in this work.

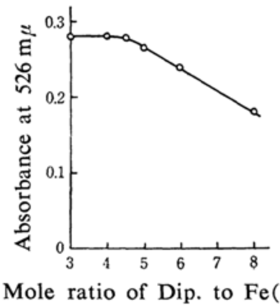

Fig. 3. Effect of mole ratio of Dip. to iron(II).
The concentrations of iron(II), iodide, and acetate in the final solutions were 1.6×10^{-4} M, 8.4×10^{-2} M, and 0.24 M respectively.
Concn. of cadmium, 1.6 p. p. m.
pH of aqueous layer, 6.5
Shaking time, 4 min.
Reference, Reagent blank

Effect of 2,2′-Dipyridyl Concentration.—While keeping other variables constant, differing amounts of dipyridyl were added, and the extraction was carried out according to the procedure described above. The results are shown in Fig. 3. When the mole ratio of dipyridyl to iron(II) was higher than 4.5, a decrease in the absorbance was observed. This may be caused by the formation of colorless 2, 2′-dipyridyl cadmium chelate, which is more stable than tetraiodo-cadmium complex,[15,16] by the reaction of excess amounts of dipyridyl with tetraiodo-cadmium complex in the presence of excess iodide. On the other hand, a slight excess of dipyridyl is necessary for the stoichiometric formation of the dipyridyl iron(II) chelate cation. Therefore, this mole ratio was kept at 4 in this work.

Effect of Sodium Acetate Concentration.—Sodium acetate was effective in keeping the pH of the solution constant. When the acetate concentration was maintained at 0.2 to 0.3 M in the solution to be extracted, no effect on the recovery was observed. The concentration of the acetate was kept at 0.24 M in this work.

Effect of Shaking Time.—The shaking time during the extraction was varied from 2 to 20 min., while the other variables were kept constant. Variation in the shaking time did not produce any measurable change in the

---

[15] K. B. Yatsimirskii and V. P. Vasil'ev, "Instability Constants of Complex Compounds," Pergamon Press, Oxford (1960), p. 139.

[16] J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants, Part II, Inorganic Ligands," The Chemical Society, London (1958), p. 120.

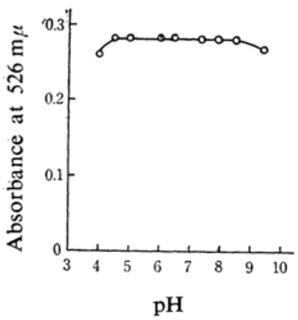

Fig. 4. Effect of pH.
The concentrations of dipyridyl, iron(II), iodide, and acetate in the final solutions were 6.4 $\times 10^{-4}$ M, 1.6×10^{-4} M, 8.4×10^{-2} M, and 0.24 M respectively.
Concn. of cadmium, 1.6 p. p. m.
Shaking time, 4 min.
Reference, Reagent blank

absorbance of the extracts. The shaking time was thus chosen to be 4 min. in this work.

Effect of pH.—The effect of the pH of the aqueous layer on the extraction is shown in Fig. 4. Low recoveries were obtained in the pH ranges below 4.5 and above 8.5. The pH of the solution was adjusted to 6.5 in this work.

Stability of Color. — Color developed immediately at room temperature and the intensity was not influenced by a temperature at 15—20°C. The color of the extract in the stoppered transmission cell was stable for more than 6 hr.

Choice of Organic Solvent. — Besides 1, 2-dichloroethane, various other solvents were tested for the extraction. They were chloroform, carbon tetrachloride, isoamyl alcohol, methylisobutyl ketone, cyclohexanone, benzene, and nitrobenzene. Only 1, 2-dichloroethane proved satisfactory. Although nitrobenzene behaved similarly to dichloroethane in this system, the reagent blank was too high to obtain a satisfactory net absorbance value.

Percentage of Extraction. — The degree of extraction of cadmium was checked by stripping cadmium from an aliquot of the dichloroethane extract with 1 N sulfuric acid. The amount of stripped cadmium was determined as follows. The aqueous layer was heated with nitric acid and sulfuric acid until strong fumes were observed. After cooling, the solution was neutralized with sodium hydroxide and diluted to a standard volume. Then an aliquot containing less than 20 μg. of cadmium was taken. The cadmium was determined by the photometric dithizone method, as described by Saltzman.[3]

The degree of the extraction using 10.0 ml. of dichloroethane was about 99%.

Calibration Curve. — Two milliliters of the 2, 2′-dipyridyl solution, 2 ml. of the ferrous ammonium sulfate solution, 2 ml. of the sodium acetate solution, 7 ml. of the potassium iodide solution, and varying amounts (1—7 ml.) of the standard cadmium solution (10 p. p. m.) were mixed and diluted to 25 ml. with distilled water. Then 10.0 ml. of dichloroethane was added, and the mixture was treated according

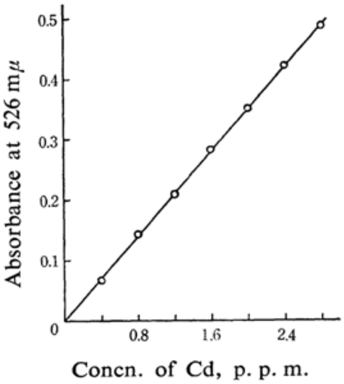

Fig. 5. Calibration curve at 526 mμ.
The concentrations of dipyridyl, iron(II), iodide, and acetate in the final solutions were 6.4×10^{-4} M, 1.6×10^{-4} M, 8.4×10^{-2} M, and 0.24 M respectively.
pH of aqueous layer, 6.5
Shaking time, 4 min.
Reference, Reagent blank

TABLE I. EFFECT OF DIVERSE IONS ON EXTRACTION AND DETERMINATION OF CADMIUM

(0.8 p. p. m. of cadmium taken in each case)

Ion	Ion concn. p. p. m.	Absorbance at 526 mμ	Relative error %
None	—	0.141*	
Zn^{2+}	40	0.141	±0.0
Pb^{2+}	0.4	0.142	+0.7
Pb^{2+}	0.8	0.144	+2.1
Hg^{2+}	0.4	0.183	+29.8
Hg^{2+}	0.8	0.221	+56.0
Bi^{3+}	0.4	0.160	+12.9
Bi^{3+}	0.8	0.174	+23.4
Cu^{2+}	0.4	0.131	−7.1
Cu^{2+}	0.8	0.124	−12.1
SO_4^{2-}	1650	0.142	+0.7
NO_3^-	1500	0.141	±0.0
Cl^-	1700	0.140	−0.7
Cl^-	3400	0.128	−9.1
Br^-	1000	0.139	−1.5
Br^-	2000	0.126	−10.6
Citrate	400	0.138	−2.1
Tartrate	1400	0.141	±0.0

pH of aqueous layer: 6.5, other variables were the same as that of the calibration curve.
* The absorbance of 0.8 p. p. m. of cadmium without diverse ions.

to the procedure described above. The absorbance of each of the standard extracts was measured at 526 mμ against the reagent blank. As shown in Fig. 5, Beer's law is followed in the 0.4—2.8 p. p. m. range of cadmium ions.

Effect of Diverse Ions.—A study was made on the effects of several cations and anions. Absorbance measurements were made on the dichloroethane extracts obtained from the solutions containing various amounts of diverse ions with 0.8 p. p. m. of cadmium. The results are given in Table I. Nitrate, chloride and sulfate do not interfere even when the concentration is as high as 1500 p. p. m. Zinc ion may be present in the concentration of 40 p. p. m. without interference. Interferences by lead(II), mercury(II), and bismuth(III) ions may be due to the behavior of their iodo-complexes being similar to that of the tetraiodo-cadmium complex anion. Ethylenediaminetetraacetate causes serious interference, even when only a small amount is present, because the cadmium chelate of ethylenediaminetetraacetate[17] is more stable than the tetraiodocadmium complex.

Summary

A new method for the determination of cadmium has been proposed. The method is based upon solvent extraction of the associated complex formed between 2, 2'-dipyridyl iron(II) chelate cation and tetraiodo-cadmium complex anion and upon estimation of the absorbance due to the chelate cation in the organic phase.

The author wishes to express his sincere thanks to Professor Yuroku Yamamoto of Hiroshima University for his kind guidance and encouragement throughout this work. He is also grateful to Professor Shigehiko Hayashi for his kind advice and to Mr. Toshiyuki Sakurai for his assistance in this work.

Faculty of Liberal Arts
Fukui University
Makinoshima, Fukui

---

[17] J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants, Part I, Organic Ligands," The Chemical Society, London (1957), p. 76.