The Spectrophotometric Determination of Anions by Solvent Extraction with Metal Chelate Cations. VI. A New Method for the Determination of Mercury(II)

By Keiya KOTSUJI

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Margerum and Banks[1] have reported that the 1,10-phenanthroline iron(II) chelate cation is extracted as the perchlorate complex into nitrobenzene. Diamond and Tuck[2] and Kuznetsov[3] have recently described how a large anion, such as ClO_4^-, I^- or NCS^-, can be extracted into nitrobenzene with a large cation of the phenanthroline iron(II) chelate. In a similar fashion, Tribalat and Beydon[4-7] have shown that a large anion, such as ReO_4^- or TcO_4^-, can be extracted into a polar solvent with a large cation of an onium compound, such as Ph_4As^+ or Ph_4P^+.

On the other hand, in the first paper[8] of this series, it has been shown how the 2,2′-dipyridyl iron(II) chelate cation is extracted into nitrobenzene from an aqueous solution containing perchlorate ion. Moreover, as has previously been reported,[9] mercury(II) can be extracted into 1,2-dichloroethane with the dipyridyl iron(II) chelate if the aqueous solution contains a large excess of iodide ions; the intensity of the red color of this extract is proportional to the amount of mercury(II). A consideration of these findings led to the present study, which is concerned with the optimum conditions for the determination of mercury(II).

This paper will report on a new spectrophotometric method for the determination of mercury(II) with the 2,2′-dipyridyl iron(II) chelate, based upon a solvent extraction of the associated complex formed between the colored dipyridyl iron(II) chelate cation and the colorless tetra-iodo-mercury(II) complex anion, and upon the estimation of the chelate absorbance in the organic phase.

For the colorimetric determination of mercury, the dithizone method[10] is most familiar, but other methods are known in the literature, using diethyldithiocarbamate[11] and diphenylcarbazone[12]. Karas and Pinter[13] have shown that the intensity of the red color of the dipyridyl iron(II) chelate is inversely proportional to the amount of mercury(II), since

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[1] D. W. Margerum and C. V. Banks, *Anal. Chem.*, **26**, 200 (1954).

[2] R. M. Diamond and D. G. Tuck, "Progress in Inorganic Chemistry," Vol. II, Interscience Publishers, New York (1960), pp. 139—150.

[3] B. I. Kuznetsov, "The Chemical Basis for the Photometric Method by Solvent Extraction in Analytical Chemistry," State Printing Office of USSR, Moscow (1963), p. 11.

[4] S. Tribalat, *Anal. Chim. Acta*, **3**, 113 (1949).

[5] S. Tribalat, ibid., **4**, 228 (1950).

[6] S. Tribalat, ibid., **5**, 115 (1951).

[7] S. Tribalat and J. Beydon, ibid., **6**, 96 (1952).

[8] Y. Yamamoto and K. Kotsuji, This Bulletin, **37**, 785 (1964).

[9] Y. Yamamoto and K. Kotsuji, ibid., **37**, 594 (1964).

[10] E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, New York (1950), p. 441.

[11] E. A. Hakkila and G. R. Waterbury, *Anal. Chem.*, **32**, 1340 (1960).

[12] H. Seno and Y. Kakita, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 452 (1961).

[13] V. Karas and T. Pinter, *Crat. Chem. Acta*, **30**, 141 (1958); *Anal. Abstr.*, 1650 (1959).

mercury replaces iron as the dipyridyl mercury chelate. Goto and Suzuki[14] have determined mercury by extracting the tetra-iodo-complex of mercury(II) with isoamylalcohol and by then measuring the absorbance at 305 mμ. Jackwerth and Spekker[15] have also investigated the extraction of this complex with cyclohexanone.

Therefore, the proposed method is different from the previously known methods in the mechanism of the color reaction.

Experimental

Apparatus and Reagents. — Unless otherwise stated, the apparatus and reagents were the same as those described in the preceding paper.[8]

Standard Mercury Solution.—Guaranteed mercuric chloride was dissolved in hydrochloric acid and diluted with distilled water to a concentration of 1000 p. p. m. of mercury. Ths standard solution was then diluted to the concentration required for the experiments.

1, 2-Dichloroethane was purified according to the method described in the literature.[16]

All the other reagents of an 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 a standard mercury solution in the proper concentration. Adjust the pH of the solution to the required value with a dilute sulfuric acid or a dilute sodium hydroxide solution, and dilute it to 25 ml. with distilled water. To this, add 10.0 ml. of dichloroethane and shake the solution for 6 min. After the solution has stood for 20 min., transfer the organic layer into a flask containing 1 g. of anhydrous sodium sulfate and shake it vigorously in order 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.

Results and Discussion

Absorption Spectrum.—The spectral absorbance curves using dichloroethane as a reference are shown in Fig. 1. They were measured for a dichloroethane solution obtained by extraction from one aqueous solution which contained mercury(II) and one which did not. It was observed that the presence of mercury(II) ions leads to a considerable increase in the absorbance and that both curves have a maximum absorbance at 526 mμ. The absorbance maximum of the chelate cation in the aqueous solution was at 522 mμ, a value which coincides with that found in the literature.[17] 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[18] has shown that the 2, 2′-dipyridyl iron(II) chelate can be precipitated as red crystals with a divalent complex anion, such as tetraiodo-mercury(II) or cadmium. On the basis of these facts, the chemical formula of the extracted species is assumed to be $Fe(Dip.)_3\cdot HgI_4$.

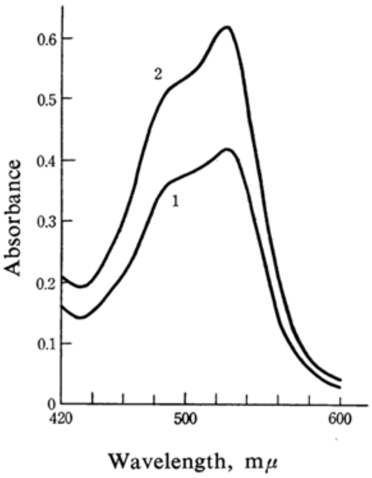

Fig. 1. Absorption spectra.
Reference: Dichloroethane, pH: 6.3
Curve 1: Spectrum of organic phase extracted from the aqueous solution (25 ml.) contained Dip. 9.6×10^{-4} M, Fe(II) 2.4×10^{-4} M, NaAc 0.24 M, KI 8.4×10^{-2} M but Hg is absent.
Curve 2: Spectrum of organic phase extracted from the aqueous solution (25 ml.) containing 2 p. p. m. of Hg in addition to the same component as that of curve 1.

The maximum difference in the absorbance between curve 1 and curve 2 is found at 526 mμ. Therefore, the measurement of the absorbance was carried out at this wavelength.

The Effect of Reagents.—*A) The Effect of the Ferrous Ammonium Sulfate and Potassium Iodide Concentrations.* — The formation of extractable species is governed mainly by the concentration of the 2, 2′-dipyridyl iron(II) chelate cation as well as of the tetra-iodo-mercury(II) complex anion. Moreover, the solution must contain a large excess of potassium iodide for the quantitative formation of the tetra-iodo-mercury(II) complex. The effect

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[14] H. Goto and S. Suzuki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **74**, 142 (1953).

[15] E. Jackwerth and H. Spekker, *Z. anal. Chem.*, **167**, 269 (1959).

[16] L. F. Fieser, "Experiments in Organic Chemistry," Heath and Co., Boston (1957), p. 288.

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

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

of such variables on the extraction was investigated.

To a solution containing a constant amount of mercury(II), various amounts of potassium iodide, ferrous ammonium sulfate, and 2, 2′-dipyridyl, in which the mole ratio of dipyridyl to ferrous iron was kept constant, were added. The mole ratio was kept at 4 to 1 because a slight excess of the dipyridyl seemed to be necessary for the stoichiometric formation of the chelate cation. The pH of the solutions was kept at 6.3, and the extraction procedure was carried out for such solutions. The results are shown in Fig. 2. If the final concentration of the ferrous ammonium sulfate is lower than 1.6×10^{-4} M,* a rather low recovery is observed, although the recovery is improved with increasing concentration of potassium iodide. When the concentration of ferrous ammonium sulfate is kept in the range of 2.4×10^{-4}—4.0×10^{-4} M, the recovery reaches a maximum when the iodide concentration is higher than 7.2×10^{-2} M. However, large excess of iodide or the chelate causes a decrease in the absorbance. Therefore, the concentrations of the ferrous ammonium sulfate and the potassium iodide were kept at 2.4×10^{-4} M and 8.4×10^{-2} M respectively in this work.

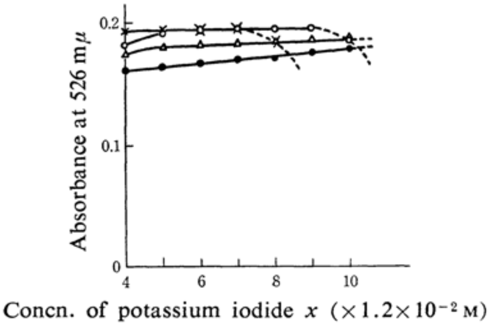

Fig. 2. Effect of ferrous ammonium sulfate and potassium iodide concentrations.
The concentration of acetate in the final solutions was 0.24 M.
Concentration of mercury, 2 p. p. m.
pH of aqueous layer, 6.3
Shaking time, 6 min.
Reference, Reagent blank

	Concn. of Dip., M	Concn. of Fe(II), M
—×—	1.6×10^{-3}	4.0×10^{-4}
—○—	9.6×10^{-4}	2.4×10^{-4}
—△—	6.4×10^{-4}	1.6×10^{-4}
—●—	3.2×10^{-4}	8.0×10^{-5}

B) The Effect of the 2, 2′-Dipyridyl Concentration.—While keeping other variables constant, a different amount of the dipyridyl was added, and the extraction was carried out according to the procedure described above. Figure 3 shows that the mole ratio of the dipyridyl to iron(II) has to be kept higher than 3. This mole ratio was therefore kept at 4 in this work.

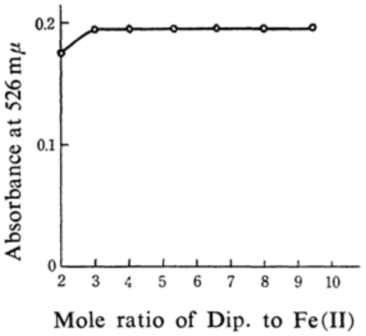

Fig. 3. Effect of mole ratio of Dip. to Fe(II).
The concentrations of iron(II), iodide, and acetate in the final solutions were 2.4×10^{-4} M, 8.4×10^{-2} M, and 0.24 M respectively.
Concentration of mercury, 2 p. p. m.
pH of aqueous layer, 6.3
Shaking time, 6 min.
Reference, Reagent blank

C) The Effect of the Sodium Acetate Concentration. — Sodium acetate was effective in keeping the solution at a constant pH. 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

The Effect of the Shaking Time.—The shaking time for the extraction was varied from 2 to 20 min., while the other variables were kept

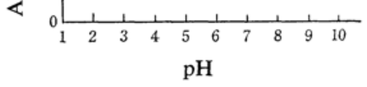

Fig. 4. Effect of pH.
The concentrations of dipyridyl, iron(II), iodide, and acetate in the final solutions were 9.6×10^{-4} M, 2.4×10^{-4} M, 8.4×10^{-2} M, and 0.24 M respectively.
Concentration of mercury, 2 p. p. m.
Shaking time, 6 min.
Reference, Reagent blank

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* The concentration of ferrous iron is approximately equal to that of the 2,2′-dipyridyl iron(II) chelate because of the high stability of the chelate.

constant. When the shaking time was shortened to less than 4 min., a lower recovery was noticed. The shaking time of 6 min. was thus chosen in this work.

The Effect of pH.—The effect of the pH of the aqueous layer on the extraction is shown in Fig. 4. Low recoveries are obtained in the pH ranges below 3 and above 8.5. The pH of the solution was adjusted to 6.3 in this work.

The Stability of the Color.—Color developed immediately at room temperature and was not influenced by the temperature at 10—17°C. The effect of the time of standing on the dichloroethane extract in a transmission cell with a stopper was investigated. The results are shown in Fig. 5. The absorbance remains constant for 60 min. After that the absorbance begins to decrease slightly.

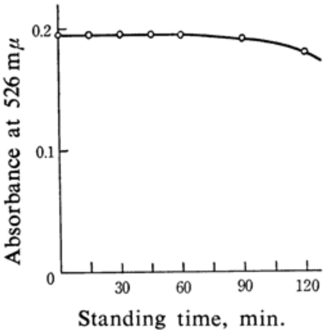

Fig. 5. Stability of color.
The concentrations of dipyridyl, iron(II), iodide, and acetate in the final solutions were 9.6×10^{-4} M, 2.4×10^{-4} M, 8.4×10^{-2} M, and 0.24 M respectively.
Concentration of mercury, 2 p. p. m.
pH of aqueous layer, 6.3
Shaking time, 6 min.
Reference, Reagent blank

The Choice of Organic Solvent.—As has been pointed out by Diamond and Tuck[2)], not only the size of the cation and the anion, but also the dielectric nature of the solvent, govern the extractivity of the associated complex. Various water-immiscible solvents were tested as extraction solvents. 1, 2-dichloroethane, chloroform, carbon tetrachloride, isoamylalcohol, methylisobutylketone, cyclohexanone, benzene, and nitrobenzene. Among them the most favorable degree of separation occured in 1, 2-dichloroethane. As has previously been reported,[8,19)] nitrobenzene is the most available solvent in these systems and behaves similarly to 1, 2-dichloroethane in this case. Unfortunately, the reagent blank was too high to obtain a satisfactory net absorbance value.

The Percentage of Extraction.—The degree of the extraction of mercury(II) was calculated from a measurement of the mercury(II) concentration in the aqueous layer after the extraction. The amount of residual mercury(II) was determined as follows. To the aqueous layer, 20 ml. of a 30% sodium hypophosphite solution and 4 ml. of concentrated hydrochloric acid were added. The mixture was then diluted with distilled water to 50 ml. and was extracted with 10 ml. of isoamylalcohol. The absorbance of the isoamylalcohol extract was measured at 305 mμ, as has been described by Goto and Suzuki.[14)] The degree of the extraction using 10.0 ml. of dichloroethane was about 98%.

Calibration Curve.—Three milliliters of the 2, 2′-dipyridyl solution, 3 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—6 ml.) of the standard mercury 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 to the procedure previously described. The absorbance for each set of the extract was measured at 526 mμ against the reagent blank. As Fig. 6 shows, Beer's law is followed in the 0.4—2.4 p. p. m. range of mercury(II) ions.

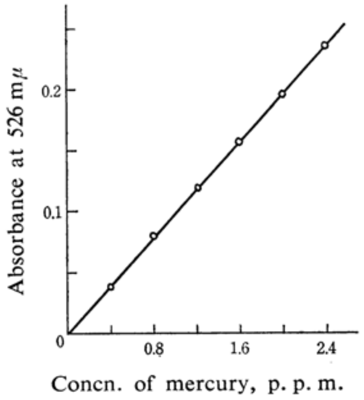

Fig. 6. Calibration curve at 526 mμ.
The concentrations of dipyridyl, iron(II), iodide, and acetate in the final solutions were 9.6×10^{-4} M, 2.4×10^{-4} M, 8.4×10^{-2} M and 0.24 M, respectively.
pH of aqueous layer, 6.3
Shaking time, 6 min.
Reference, Reagent blank

The Effect of Diverse Ions. — A study was made of the effects of several cations and anions. Absorbance measurements were made for the dichloroethane extracts from solutions containing various amount of diverse ions with 2 p. p. m. of mercury(II). The results are given

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19) Y. Yamamoto and S. Kinuwaki, This Bulletin, 37, 434 (1964).

TABLE I. EFFECT OF DIVERSE IONS ON EXTRACTION AND DETERMINATION OF MERCURY(II)
(2 p. p. m. of mercury taken in each case)

Ion	Ion concn., p. p. m.	Absorbance at 526 mμ	Relative error, %
None	—	0.196*	
Zn^{2+}	40	0.197	+ 0.5
Zn^{2+}	80	0.212	+ 8.2
Pb^{2+}	0.4	0.197	+ 0.5
Pb^{2+}	0.8	0.203	+ 3.6
Cd^{2+}	0.4	0.266	+35.8
Cd^{2+}	0.8	0.339	+73.0
Bi^{3+}	0.4	0.227	+15.8
Bi^{3+}	0.8	0.255	+30.0
Cu^{2+}	0.4	0.178	− 9.2
Cu^{2+}	0.8	0.160	−18.4
SO_4^{2-}	1150	0.197	+ 0.5
SO_4^{2-}	2300	0.210	+ 7.2
NO_3^-	1200	0.196	± 0.0
NO_3^-	2400	0.201	+ 2.6
Cl^-	170	0.196	± 0.0
Cl^-	425	0.192	− 2.0
Br^-	150	0.195	− 0.5
Br^-	200	0.193	− 1.5

pH of aqueous layer: 6.3, other variables were the same as that of the calibration curve.

* The absorbance of 2 p. p. m. of mercury(II) without diverse ions.

in Table I. Nitrate and sulfate do not interfere when the concentration is as high as 1000 p. p. m. but at a very large concentration higher results are obtained. The positive errors for zinc(II), cadmium(II), lead(II), and bismuth(III) may be due to the behavior of the iodo complex of these ions being similar to that of the tetra-iodo-mercury(II) complex anion. In order to eliminate the interferences of the diverse ions, the use of ethylenediaminetetraacetate is suggested, because the tetra-iodo-mercury(II) complex[20] is more stable than the mercury(II) chelate of ethylenediaminetetraacetate.[21] Favorable results were obtained when 1 ml. of a 0.05 M disodium ethylenediaminetetraacetate solution was added as a masking agent to the solution to be extracted, as is shown in Table II.

TABLE II. EFFECT OF DIVERSE IONS ON EXTRACTION AND DETERMINATION OF MERCURY(II) IN THE PRESENCE OF EDTA
(2 p. p. m. of mercury taken in each case)

Ion	Ion concn., p. p. m.	Absorbance at 526 mμ	Relative error, %
None	—	0.196*	±0.0
Zn^{2+}	80	0.196	±0.0
Pb^{2+}	40	0.196	±0.0
Pb^{2+}	80	0.206	+5.1
Cd^{2+}	40	0.196	±0.0
Cd^{2+}	80	0.212	+8.2
Bi^{3+}	8	0.197	+0.5
Bi^{3+}	20	0.205	+4.6
Cu^{2+}	8	0.195	−0.5
Cu^{2+}	12	0.186	−5.1

pH of aqueous layer: 6.3, concn. of EDTA: 2×10^{-3} M, other variables were the same as that of the calibration curve.

* The absorbance of 2 p. p. m. of mercury(II) without diverse ions.

Summary

A new method for the determination of mercury(II) has been proposed. The method is based upon the solvent extraction of the associated complex formed between the 2, 2′-dipyridyl iron(II) chelate cation and the tetra-iodo-mercury(II) complex anion and upon the estimation of the absorbance belonging to the chelate cation in the organic phase. The interference of diverse ions is eliminated by using ethylenediaminetetraacetate as a masking agent.

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Faculty of Liberal Arts
Fukui University
Makinoshima, Fukui

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[21] T. Goffart, G. Michel and G. Dnychaerts, *Anal. Chim. Acta*, 9, 184 (1953).