The Spectrophotometric Determination of Anions by Solvent Extraction with Metal Chelate Cations. I. A New Method for the Determinetion of Perchlorate Ions*

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Although there have been no experimental investigations of the extraction for tris-2, 2′-dipyridyl-iron(II)-perchlorate, theoretically the same behavior of the compound as the phenanthroline chelate may be expected.[1,2] In our investigation, it is confirmed that the perchlorate of the dipyridyl-iron(II) chelate can be extracted into nitrobenzene. However, the following differences exist between the dipyridyl and the phenanthroline chelate. If the perchlorate ion is absent in the 0.2 M acetate buffer solution, the dipyridyl chelate can not be extracted into nitrobenzene (this can be confirmed by the colorlessness of the organic layer) ; on the other hand, the phenanthroline chelate can be extracted moderately well. The behavior of iodide ions is more complicated. In the acetate buffer solution (0.2 M), iodide ions can be extracted with the phenenthroline chelate, but not with the dipyridyl chelate. However, the iodide ions are also extracted with the dipyridyl chelate if a small amount of perchlorate is present. Moreover, an anionic complex such as tetra-iodo-cadmium(II) or mercury(II) can be extracted into 1, 2-dichloroethane with the dipyridyl chelate, but not into nitrobenzene. In the case of the phenanthroline chelate, the extraction of the anionic complex is hindered by a large amount of iodide. For other cationic chelates such as cuproine,[*1] Kuznetsov[2] has pointed out that chloride ions are extractable into alcohols with cuproine.[*1] It is also confirmed by radioactive tracer in this work that a trace amount of chloride ions is extracted into hexylalcohol when bathocuproine[*2] is in the organic phase and when copper(I) ions are in the aqueous phase.

These facts suggest that it may be possible to establish a selective and sensitive method for the determination of simple anions or oxygenated anions, and or the anionic complex ions of some metals. The method is thus based upon the estimation of the absorbance belonging to the chelate cations in the organic phase.

The present work is the first of a series of papers on the photometric determination of anions by solvent extraction with a metal chelate. This paper is concerned with the determination of perchlorate with tris-2, 2′-dipyridyl-iron(II) chelate. In that part of the

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[1] R. M. Diamond and D. G. Tuck, "Progress in Inorganic Chemistry," 2, (1960), 139-150.

[2] B. I. Kuznetsov, "The Chemical Basis for Photometric Method by Solvent Extraction in Analytical Chemistry," Moscow (1963), pp. 11-12.

[*1] Biquinolyl.

[*2] 4, 7-Diphenyl-2, 9-dimethyl-1, 10-phenanthroline.

second paper which has been published as a short communication,[3] a colorimetric determination of iodide is treated in the similar way. The third paper[4] is concerned with mercury(II) and cadmium(II).

Experimental

Apparatus. — The spectrophotometric measurements were made with a Hitachi Model EPU-2 spectrophotometer with 10.0 mm. cells.

The shaking was done with a Iwaki Model KM shaker.

The pH measurements were made with a Horiba M-3 pH meter.

The separation of the organic layer from the aqueous layer was carried out with a separatory funnel of about 120 ml.

Materials.—*Ferrous Ammonium Sulfate Solution.* Guaranteed ferrous ammonium sulfate hexahydrate was dissolved in a small volume of water containing 5 ml. of 1 N sulfuric acid; then the mixture was diluted to 500 ml. with water to make a 3.0×10^{-3} M solution. It was standardized with a standard potassium permanganate solution.

2, 2′-Dipyridyl Solution.—Guaranteed 2, 2′-dipyridyl was dissolved in distilled water containing 1 ml. of 1 M hydrochloric acid, and then the mixture was diluted to 300 ml. with water to make a 1.2×10^{-2} M solution.

Standard Perchlorate Solution.—A standard solution containing 1 mg. of perchlorate ions per millilter was prepared by dissolving guaranteed potassium perchlorate (dried at 100°C) in distilled water. This standard solution was diluted to the concentration required for the experiments.

Nitrobenzene was purified by vacuum distillation at 23~25 mmHg.

Anhydrous sodium sulfate, guaranteed reagent. All other reagents used were of analytical grade without further purification.

Procedure.—Mix 2, 2′-dipyridyl, ferrous ammonium sulfate, 3 M sodium acetate, and the standard perchlorate solution in the proper concentration. Adjust the pH of the solution to the required value with dilute sulfuric acid or a dilute sodium hydroxide solution and dilute to 25 ml. with distilled water, Add 10.0 ml. of nitrobenzene. Shake for 20 min. After the solution has stood for 30 min., transfer the organic layer into a glass flask containing 1 g. of anhydrous sodium sulfate and shake vigorously to make the solution transparent. Then transfer it through a folded filter paper into a 10.0 mm. cell. Measure the absorbance of the solution at 524 mμ using a reagent blank solution or nitrobenzene as a reference. Measure the pH of the aqueous layer after the separation.

Results and Discussion

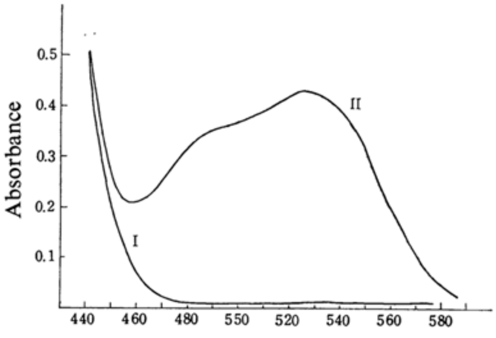
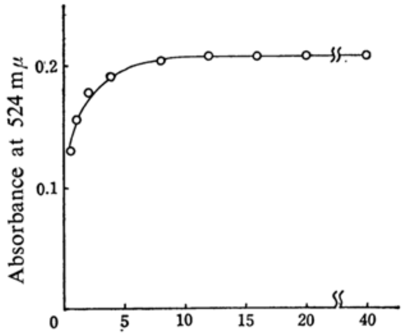


Fig. 1. Absorption spectra.

Curve I Spectrum of nitrobenzen solution extracted from aqueous solution containing Fe(II) 4.8×10^{-4} M, Dip. 2×10^{-3} M, NaAcO 0.24 M, pH 6.5, but ClO_4 absent, reference: water

Curve II Spectrum of nitrobenzene solutions extracted from aqueous solution containing Fe(II) 4.8×10^{-4} M; dip. 2×10^{-3} M, NaAcO 0.24 M, and ClO_4 4×10^{-5} M, pH 6.5; reference: water



Mole ratio of iron(II) to perchlorate

Fig. 2. Effect of concentration of iron(II).

Concn. of Perchlorate: 2.0×10^{-5} M
Mole ratio of dip. to iron: 4
pH: 6.5 Time of shaking: 20 min.
Reference: Reagent blank.

Absorption Spectrum.—The spectral absorbance curves are shown in Fig. 1. They were measured for a nitrobenzene solution obtained by extraction from an aqueous solution which contained perchlorate and one which did not. The absorbance maximum is at 524 mμ in the organic layer. The absorbance maximum of the chelate cation in the aqueous solution was at 522 mμ, a value which coincides with that found in literature.[5] This slight red shift in the organic layer may be attributed to the effect of the association between cations and anions in such a polar solvent as nitrobenzene. Therefore, the chemical formula of the extracted species may be $[Fe(II)(dip.)_3]\cdot(ClO_4)_2$.

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[3] Y. Yamamoto and S. Kinuwaki, This Bulletin 37, 434 (1964).

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

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

The Effect of the Reagent.—The extraction of perchlorate ions into nitrobenzene may be governed by the concentration of ferrous ammonium sulfate, 2, 2′-dipyridyl, and sodium acetate. The effect of changing the amounts of their reagents has to be considered.

A) Thc Effect of the Ferrouso Ammonium Sulfate Concentration.—To a constant amount of perchlorate ions (2.0 p.p.m.), various amounts of 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 may be needed for the stoichiometric formation of the chelate cation. The pH of the solutions was kept at 6.5, and the procedure was carried out for the solution. Figure 2 shows the effect of the concentration of ferrous ions on the extraction of perchlorate ions. It is found that the mole ratio of iron(II) to perchlorate ions has to be held at more than 10 to 1. This mole ratio, therefore, was made 12 to 1 in this work.

B) The Effect of the 2, 2′-Dipyridyl Concentration.—The amount of perchlorate ions and the mole ratio of iron(II) to perchlorate ions were kept at the constants of 2.0 p.p.m. and 12 to 1 respectively. 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 held at more than 3 to 1. This mole ratio was kept at 4 to 1 in this work.

C) The Effect of the Sodium Acetate Concentration. — If the concentration of sodium acetate is low in the aqueous phase, it is time-consuming to separate the two phases because of the formation of an emulsion. It was found that the formation of an emulsion could be prevented by the presence of sodium acetate in a concentration of 0.2∼0.3 M. The salt was also useful as a buffering agent. The concentration of the acetate was kept at 0.24 M in this work.

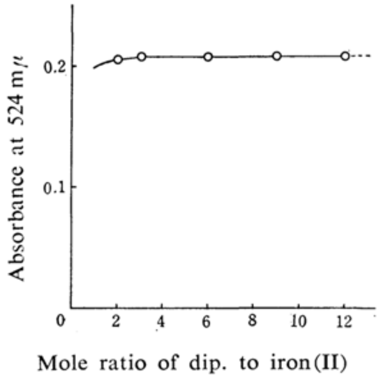

Fig. 3. Effect of mole ratio of dip. to iron(II)
Perchlorate: 2.0×10^{-5} M
Mole ratio of iron(II) to perchlorate: 12
NaAcO: 0.24 M
pH: 6.5
Shaking time: 20 min.

The Effect of the Shaking Time.—The shaking time in the extraction was varied from 5 to 30 min., while the other variables were kept constant. The shaking time had a slight effect on the extraction, and it was enough to shake it for more than 20 min.

The Effect of the pH Value.—It has been stated in the literature,3) and also confirmed in this work, that the optimum pH for the formation of tris-dipyridyl iron chelate ions is in the range of 3∼9 in an aqueous phase. In order to study the effect of pH on the extraction, a series of solutions adjusted to various pH values was preparaed and treated as in the procedure described above. It was found that there is a maximum and constant absorbance in the organic phase over the pH range from 3.5 to 8.5. Therefore, the solution was adjusted at pH 6.5 in this work.

The Stability of the Color.—Color developed immediately at room temperature and was independent of the temperature at 10∼20°C. The color of the organic phase was stable, even after 24 hr.

The Choice of an Organic Solvent.—Besides nitrobenzene, various other solvents were tested for the extraction. They are chloroform, 1, 2-dichloroethane, isoamylalcohol, isopropyl ether, butyl acetate, cyclohexanone, chlorobenzene, and benzene. It was found that the perchlorate of the chelate cation was completely non-extractable into these solvents. Moreover, when a mixed solvent, such as nitrobenzene and benzene (1 : 1) or chloroform (1 : 1) was used, the absorbance of the organic layer was remarkably reduced. The reason may be the reducing of the dielectric nature in the mixed solvent. Therefore, benzene-free nitrobenzene has to be used.

The Effect of the Times of Extraction and of the Percentages of Extraction.—The effect of the times of extraction are shown in Fig. 4. The extraction yield using one 10 ml. portion of nitrobenzene is about 90%. The determination of the percentage of extraction was then attempted as follows. By shaking an aliquot of the extract with 1 N sulfuric acid, the perchlorate was transferred again into an aqueous phase. For this aqueous solution, after the reagents had been added and the pH, adjusted the extraction was performed once more. The absorbance value was about 90% of the first extract. It is, therefore, presumed that the percentage of extraction may be about 90%,

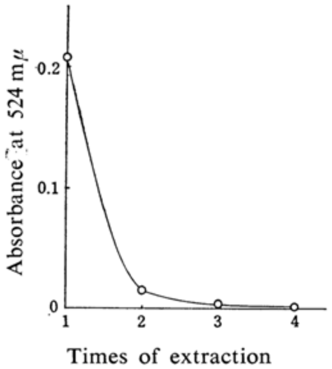

Fig. 4. Effect of times of extraction.
Perchlorate : 2 p.p.m.
(Other valiables were the same as the standard procedure, and the absorbance was measured for the nitrobenzene solution obtained by the extraction)

because Beer's law is followed for the perchlorate, as will be described below.

Calibration Curve.—Four milliliters of the 2, 2′-dipyridyl solution, 4 ml. of the ferrous ammonium sulfate solution, 2 ml. of a 3 M sodium acetate solution, and varying amounts of the standard solution (1∼10 ml.) containing 10 μg. per ml. of perchlorate ions were mixed and diluted to 25 ml. with distilled water. Then 10.0 ml. of nitrobenzene was added, and the mixture was treated according to the procedure. The absorbance for each set was measured at 524 mμ against the reagent blank solution. As is shown in Fig. 5, Beer's law is followed in the 0.4∼4 p. p. m. range of perchlorate ions.

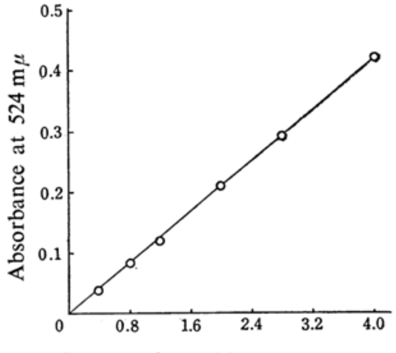

Fig. 5. Calibration curve.
Dip. : 2.0×10^{-3} M
Fe(II) : 4.8×10^{-4} M
NaAc : 0.24 M
pH : 6.5
Reference : Reagent blank

The Effect of Diverse Ions.—Table I shows the absorbances of a series of extracts which have been treated according to the procedure. Measurement was done at 524 mμ using a reagent blank. Each solution contains 2.0 p. p. m. of perchlorate and various amounts of diverse ions. The absorbance of 2.0 p. p. m. of perchlorate is 0.209. It is shown that the determination of perchlorate is not interferred with, or is given a positive error of a few percentage points, by the presence of a considerable amount of halogen or oxygenated halogen ions other than iodide and periodate. The reason for the positive error of a small amount of iodide is not clear, because the iodide in a considerable concentration could not be extracted when the perchlorate is absent. This behavior of iodide is very interesting in a system of these extractions, as has been described above. A small amount of periodate give a negative error, presumably because of the oxidizing action with regard to ferrous iron. The proposed method may be useful for the determination of a small amount of perchlorate contained in such a salt as chloride, bromide, chlorate, bromate, iodate, and sulfate.

TABLE I. EFFECT OF DIVERSE IONS ADDED TO 2 p.p.m. OF ClO^-_4 (Abs. 0.209)

Ion	Added as	Concn. p. p. m.	Absorbance at 524 mμ
None	—	—	0.209
ClO_3^-	$NaClO_3$	8	0.209
ClO_3^-	$NaClO_3$	42	0.243
BrO_3^-	$KBrO_3$	60	0.209
BrO_3^-	$KBrO_3$	120	0.211
IO_3^-	KIO_3	1700	0.209
Cl^-	NaCl	350	0.209
Cl^-	NaCl	3500	0.214
Br^-	KBr	60	0.207
Br^-	KBr	2000	0.214
I^-	KI	0.5	0.209
I^-	KI	1	0.213
IO_4^-	KIO_4	4	0.206
SO_4^{2-}	Na_2SO_4	4000	0.209
NO_3^-	$NaNO_3$	6	0.208
NO_3^-	$NaNO_3$	30	0.223

pH of aqueous layer : 6.5, other variables were the same as that of the calibration curve.

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