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Spectrophotometric Determination of Iron(II) after Extraction of Its 4′-(*p*-Methoxyphenyl)-2,2′ : 6′,2″-terpyridine Complex with Tetraphenylborate Anion into Molten Naphthalene

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A new method is described for the extraction of ion-associated complex of iron(II) 4′-(*p*-methoxyphenyl)-2,2′ : 6′,2″-terpyridine (abbreviated as MPTP) cation with tetraphenylborate (TPB) anion into molten naphthalene. The solid mixture containing the colored complex is dissolved in *N*,*N*-dimethylformamide (DMF) and the absorbance was measured at 576 nm. The other factors such as pH, amounts of reagents and naphthalene, shaking time and diverse ions are studied. The method has been applied for the determination of iron in reference materials and practical samples and the results was compared with the conventional 2,4,6-tri(2-pyridyl)-1,3,5-triazine (TPTZ) procedure.

Extractive spectrophotometry has been widely employed for the analysis of trace amounts of metal ions. However, this method is not applicable when the solubility of metal complexes in solvents is small. By the aid of the extraction with molten naphthalene, such complexes have successfully been applied to the separation and concentration of metal ions.[1–4)]

In the present paper, 4′-(*p*-methoxyphenyl)-2,2′:6′,2″-terpyridine (MPTP) was recommended as a new extraction reagent for the spectrophotometric determination of iron(II) with naphthalene. MPTP reacts with iron(II) to form a water-soluble red complex cation.[5–7)] In the presence of tetraphenylborate(TPB) anion, iron(II)–MPTP cation forms a water-insoluble, thermally stable ion-associated complex. This complex can hardly be extracted into nonaqueous organic solvents because of the poor solubility of the complex in solvents and the incomplete phase separation, but easily extracted into molten naphthalene at temperatures above 81 °C. Compared with the ordinary solvent extraction method, the method is characterized by the greater extraction rate and the higher solubility of the complex into molten naphthalene.

Experimental

Reagents. Standard iron(III) solution, 100 ppm. Prepared by dissolving 0.8635 g of ammonium iron(III) sulfate dodecahydrate in 100 cm^3 of 0.5 M (1 M=1 mol dm^{-3}) H_2SO_4 and by diluting to 500 cm^3 with water.

4′-(*p*-Methoxyphenyl)-2,2′:6′,2″-terpyridine solution, 0.02%. Prepared by dissolving 0.02 g of this reagent in a few drops of concentrated hydrochloric acid and by diluting to 100 cm^3 with water.

Hydroxylammonium chloride solution, 2% in water.

Sodium tetraphenylborate solution, 1% in water.

Buffer solutions were prepared by mixing 1 M acetic acid and 1 M ammonium acetate solution for pH 3—6, and 1 M aqueous ammonia and 1 M ammonium acetate solution for pH 8—11.

Naphthalene, acetone, *N*,*N*-dimethylformamide and all other reagents were of analytical-reagent grade, and used without further purification.

Apparatus. The absorbance measurements were made with a Hitachi Model 200-20 double beam spectrophotometer with 10-mm glass cells.

All the pH measurements were done with a Toa-Dempa HM-5A pH meter.

General Procedure. To about 25 cm^3 of sample solution containing 1—19 μg of iron(III) in a 80-cm^3 tightly stoppered Erlenmeyer flask, add 1.0 cm^3 of 2% hydroxylammonium chloride solution, 2.0 cm^3 of buffer solution (pH 5.0) and 3.0 cm^3 of 0.02% MPTP solution. Mix the solution well and add 1.5 cm^3 of 1% TPB solution. After warming on a water bath (50—60 °C) for 15 min, add 1.5 g of naphthalene and warm the mixture on a water bath at 90 °C to melt naphthalene completely. Shake it vigorously until the naphthalene solidifies forming many fine crystals. Filter the naphthalene mixture on a filter paper (No. 5A). Wash with water, blot the excess water with a dry filter paper and dry in an oven at 50—60 °C. Dissolve the naphthalene in *N*,*N*-dimethylformamide, dilute to 10 cm^3, and measure the absorbance at 576 nm against a reagent blank prepared similarly.

Results and discussion

Absorption Spectra. Absorption spectrum of the ternary complex iron(II)–MPTP–TPB in naphthalene–*N*,*N*-dimethylformamide solution is shown in Fig. 1, together with that of the reagent blank. The complex has an absorption maximum at 576 nm, while the reagent blank showed no significant absorption at this wavelength.

Effect of pH. The effect of pH on the absorbance of the ternary complex was studied at 576 nm (Fig. 2). The pH of aqueous solution after extraction was measured at room temperature. The pH range 4.0—6.8 seems to be suitable for the extraction of the complex.

Effect of Hydroxylammonium Chloride Concentration. Varying volumes of 2% hydroxylammonium chloride solution were added to the sample containing 10 μg of iron(III). Iron(III) was completely reduced to iron (II) by the addition of 0.1—8 cm^3 of 2% solution. Thus 1.0 cm^3 of 2% solution was taken for the further work.

Effect of MPTP and TPB Concentration. Different amounts of MPTP were added to the sample containing 10 μg of iron(III). It was observed that the extraction was quantitative for 0.8—8.0 cm^3 of 0.02% MPTP solution (Fig. 3). Thus 3.0 cm^3 of 0.02% solution was added. Similar studies with sodium tetraphenylborate showed that the absorbance remained

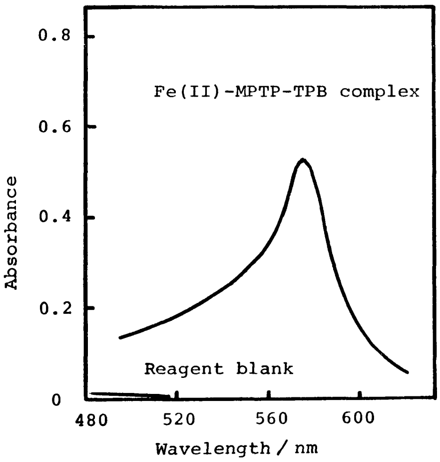

Fig. 1. Absorption spectra of MPTP-TPB and iron(II)-MPTP-TPB complex in naphthalene-*N*,*N*-dimethylformamide solution.
Iron(III): 10 μg; pH: 5.0; 2% $NH_2OH\cdot HCl$: 1.0 cm^3; 0.02% MPTP: 3.0 cm^3; 1% TPB: 1.5 cm^3. Naphthalene: 1.5 g. Reference: water.

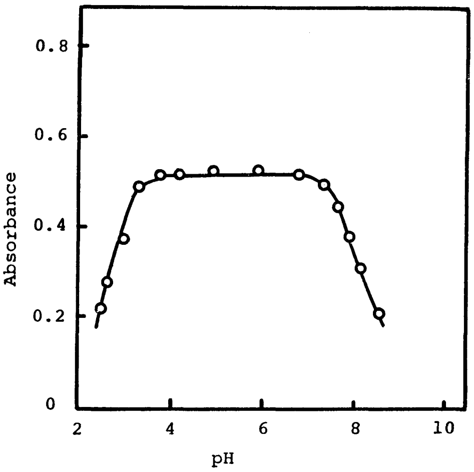

Fig. 2. Effect of pH.
Iron(III): 10 μg; Wavelength: 576 nm; pH: 5.0. Conditions were the same as in Fig. 1. Reference: reagent blank.

constant over the range of 0.1—4.0 cm^3 of 1% TPB solution. Therefore, 1.5 cm^3 of 1% TPB solution was used.

Effect of Buffer Solution and Digestion Time. Varying volumes of buffer solution were added to the sample containing 10 μg of iron(III), other variables being kept constant. When the volumes between 1.0 and 4.0 cm^3 were added, the absorbance did not show any change. The solution containing iron(II)–MPTP–TPB complex at pH 5.0 was digested at 50—60 °C. The digestion time is not critical and only one minute was sufficient for the completion of the complex formation.

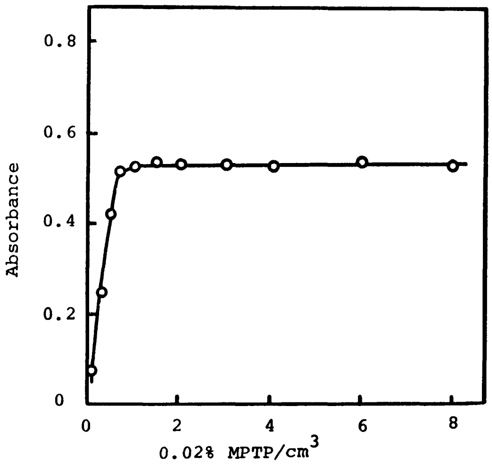

Fig. 3. Effect of reagent concentration.
Iron(III): 10 μg; Wavelength: 576 nm. Conditions were the same as in Fig. 2.

TABLE 1. EFFECT OF DIVERSE IONS

Diverse ion	Tolerance limit	Diverse ion	Tolerance limit
I^-	17 g	Ca^{2+}	200 mg
NO_3^-	6 g	Mn^{2+}	150 mg
SO_4^-	4 g	Cr^{6+}	10 mg
CH_3COO^-	2.2 g	Hg^{2+}	8 mg
Cl^-	2.4 g	Pb^{2+}	4000 μg
SCN^-	1.8 g	Pt^{4+}	1000 μg
Cit^{3-}	0.5 g	Ni^{2+}	500 μg
$Tart^{2-}$	0.3 g	Cd^{2+}	200 μg
ClO_4^-	0.2 g	Sn^{2+}	100 μg
$H_2PO_4^-$	36 mg	Al^{3+}	70 μg
$C_2O_4^{2-}$	20 mg	Zn^{2+}	50 μg
CN^-	1.2 mg	Cu^{2+}	50 μg
H_2edta^{2-}	6.2 μg	Co^{2+}	15 μg
		Bi^{3+}	2 μg

Iron(III): 10 μg; pH: 5.0; 0.02% MPTP: 3.0 cm^3

Effect of Addition of Naphthalene and of Shaking Time. The extraction of the complex into molten naphthalene was carried out by varying amounts of naphthalene from 0.5 to 3.0 g. In all cases the amount of naphthalene had no influence on the absorbance of the system. Thus 1.5 g of naphthalene was used as a suitable amount. Naphthalene(1.5 g) was added to the solution containing the complex and the mixture was shaken vigorously for periods ranging 3 to 90 s. The experimental results showed that the complex is extracted quantitatively into molten naphthalene by vigorous shaking for about a few seconds. Consequently, 30 s of shaking time was selected for convenience.

Effect of Aqueous Phase Volume. Since the organic/aqueous phase ratio is important factor in such procedures, the effect of aqueous phase volume on the extraction of the complex was studied. The extraction was quantitative when the volume of aqueous phase did not exceed 70 cm^3. Above this volume of aqueous phase the extractability decreased gradually.

Effect of Standing Time. The mixture of the ternary complex and naphthalene was dissolved in *N*,*N*-dimethylformamide, and the effect of standing time on the absorbance was examined between 1 and 20 h. It was observed that the absorbance remained constant for these periods. Consequently, 20 min of standing time was selected for all absorbance measurements.

Calibration Curve. The absorbances for varying concentration of iron(III) were measured at 576 nm against a reagent blank under the optimum conditions

Table 2. Analysis of iron in metals

Sample	Composition of alloy (%)	Iron, certified value/%	Iron content[a]/%	
			Present method	TPTZ method
N.B.S. SRM-85b Al alloy	Cu: 3.99, Cr: 0.21 Mn: 0.61, Ni: 0.089 Si: 0.18, Ti: 0.022 Zn: 0.03, Ga: 0.019 V: 0.006, Pb: 0.021	0.24	0.242±0.003	0.253±0.002
N.B.S. SRM-158a Silicon-Bronze alloy	Cu: 90.93, Si: 3.03 Zn: 2.08, Mn: 1.11 Ti: 0.96, Al: 0.46 Pb: 0.097, Ni: 0.001 P: 0.026	1.23	1.21±0.02	1.24±0.02
Metallic magnesium (powder)	—	—	0.0021±0.0001	0.0023±0.0001
Metallic aluminum (powder)	—	—	0.149±0.002	0.151±0.002

a) Average of five determinations.

described above. The results followed Beer's law over the concentration range of 1—19 μg of iron(III) in 10 cm^3 of *N*,*N*-dimethylformamide. The molar absorptivity of the complex was calculated to be 2.9×10^4 dm^3 mol^{-1} cm^{-1}, and the sensitivity was 0.00192 μg of iron(III) per cm^3 for 0.001 absorbance. Ten determinations of a sample containing 10 μg of iron(III) gave a mean absorbance of 0.522 with relative standard deviation of 1.34%.

Choice of Solvent. Various organic solvents were tested to dissolve the extracted mixture of the complex and naphthalene. The mixture is soluble in *N*,*N*-dimethylformamide, dimethyl sulfoxide, propylene carbonate and acetonitrile. *N*,*N*-dimethylformamide is sensitive and cheaper than other solvents mentioned above.

Effect of Diverse Ions. Various amounts of diverse ions were added to the sample containing 10 μg of iron(III). The tolerance limit (Table 1) was listed at the amounts required to cause 5% error. Among anions examined, only Na_2H_2 edta interfered even at the concentration equivalent to that of iron(III). The cations Bi^+ and Co^{2+} interfered seriously.

Iron Analysis in Reference Materials and Metallic Samples. This method has been successfully employed for the analysis of iron in reference materials and other metallic samples. The results are in reasonably good agreement with those obtained by the conventional spectrophotometric method employing 2,4,6-tri(2-pyridyl)-1,3,5-triazine(TPTZ)[8—10], as shown in Table 2. The analytical procedures were as follows: a 1 g portion of reference aluminum alloy(N.B.S., SRM-85b) was gently dissolved in 40 cm^3 of hydrochloric acid(1+1) and 2 cm^3 of 30% hydrogen peroxide. The excess of hydrogen peroxide was decomposed by heating the mixture gently on a boiling-water bath. After cooling, the volume of the sample was adjusted to 500 cm^3 with water. A 2 cm^3 aliquot was transferred to a 100 cm^3 separatory funnel, and 40 cm^3 of hydrochloric acid (1+1) was added. The iron(III) in this sample was extracted by vigorous shaking for 5 min with 20 cm^3 of isobutyl methyl ketone(MIBK).[11] The iron(III) was then back-extracted from the organic phase with 25 cm^3 of water, and the proposed method and TPTZ procedure were applied.

A 100 mg portion of reference silicon bronze alloy (N.B.S., SRM-158a) was dissolved in the mixed solution of 10 cm^3 of hydrochloric acid(1+1), 1 cm^3 of concentrated nitric acid and 3 cm^3 of concentrated sulfuric acid. The mixture was gently heated on a boiling-water bath. The excess of the acids was evaporated and then the solution was diluted to 1000 cm^3 with water. This solution was used for both methods.

Metallic magnesium powder (10 g) and aluminum powder(2 g) were analyzed in the same way as in the case of the aluminum alloy.

In the present study, the extraction of the ternary complex into molten naphthalene is easily attained merely by contact with molten naphthalene or by vigorous shaking for a few seconds. Since a small amount (1.5 g) of organic phase (naphthalene) is required for the complete extraction of the complex, the method is useful for the concentration of trace iron ion from a large volume of aqueous solution, and proved to be more excellent in the sensitivity snd precision than the MPTP procedure[5—7] in aqueous medium.

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