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Spectrophotometric Determination of Iron(II) after Separation by Collection of Its Ternary Complex of 1,10-Phenanthroline and Tetraphenylborate on Microcrystalline Naphthalene

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A new procedure for the spectrophotometric determination of iron(II) after collection of its ternary complex with 1,10-phenanthroline and tetraphenylborate on microcrystalline naphthalene is described. In the presence of tetraphenylborate, the tris(1,10-phenanthroline)iron(II) ion is quantitatively collected on microcrystalline naphthalene as the ion-association complex. The system conforms to Beer's law over the range 3—50 μg of iron in 10 ml of the solvent. The molar absorptivity was 1.2×10^4 l mol^{-1} cm^{-1} at 514 nm. The effect of various factors, such as wavelength, pH, amounts of reagent and naphthalene, shaking time, and diverse ions, were also studied. The procedure method was satisfactorily applied to the determination of iron in standard aluminium alloy, aluminium, and magnesium metals.

1,10-Phenanthroline is a sensitive and selective reagent for iron(II) and it has been widely employed for the spectrophotometric determination of iron and the method has been applied to the determination of iron[1)] in alloys, metals and water samples.

The water-soluble complex ferroin, $[Fe(phen)_3]^{2+}$ produced with this is insoluble in organic solvents, but some of its ion-association complexes with colorless inorganic anions, such as ClO_4^-, I^-, SCN^-, CN^-, BF_4^-, $PtCl_6^-$, $AuCl_4^-$, $AuBr_4^-$, and with some organic anions such as pentachlorophenolate, trichloroacetate, and 1,2-bis(octyloxycarbonyl)ethanesulfonate, are extractable by suitable organic solvents and may be used for the extractive colorimetric determination of metals[2—4)] or of the associated anions.[5—7)]

Since 1969, we have developed a new method[8—12)] for the spectrophotometric determination of trace metals using naphthalene as an extractant or collector, as well as by solvent extraction in chloroform or benzene. In the present communication, the technique described above was used for the collection of iron ion which forms ion-association complex with complexing reagent at room temperature.

We have observed that the cationic complex $[Fe(phen)_3]^{2+}$ reacts with sodium tetraphenylborate to form a very stable water-insoluble colored ternary complex. This ternary complex is difficult to be dissolved in organic solvents except with nitrobenzene because of low solubility of the complex in solvent. However, this complex can be easily collected on microcrystalline naphthalene even by vigorous shaking for a few seconds and is freely soluble in acetonitrile and *N,N*-dimethylformamide, which are miscible with water. This simple and inexpensive procedure can be successfully applied for analysis of iron in metal alloys.

Experimental

Reagents. Standard iron(III) solution, 1000 ppm. Prepared by dissolving 0.8635 g of ammonium iron(III) sulfate dodecahydrate in 100 ml of 0.5 M (1 M = 1 mol dm^{-3}) H_2SO_4 and by diluting to 500 ml with water.

1,10-Phenanthroline(phen) solution, 0.2%. Prepared by dissolving 0.2 g of the reagent in a small volume of concentrated hydrochloric acid and diluting to 100 ml with water.

Hydroxylammonium chloride solution, 2% in water.

Sodium tetraphenylborate solution, 1% water.

Naphthalene solution, 20% in acetone.

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 were used without further purification.

Apparatus. The absorbance measurements were made with a Bausch and Lomb spectronic-70 spectrophotometer, using 1 cm cells.

All the pH measurements were done with a Beckman Model H-2 pH meter.

Procedure. Transfer a sample solution containing 3—50 μg of iron(III) to a tightly stoppered Erlenmeyer flask (100 ml), add 1.0 ml of 2% hydroxylammonium chloride solution and 5.0 ml of 0.2% 1,10-phenanthroline solution and adjust pH to 4.5 with 2.0 ml of acetate buffer. Mix the solution, add 1.0 ml of 1% sodium tetraphenylborate solution and let stand for 10 min. Add 2.0 ml of 20% naphthalene solution in acetone to this sample solution using a small nozzled pipe attached to a rubber bulb, and shake the mixture vigolously for 30 s. Collect the colored naphthalene mixture on a filter paper placed flat on a Teflon filter plate in a funnel or a sintered glass filter (No. 2) by filtration. Wash it with water and dry at 50—60 °C. Then dissolve the mixture in *N,N*-dimethylformamide and dilute to exactly 10 ml. Measure the absorbance of the solution in a 1-cm glass cell against the reagent blank.

Results and Discussion

Absorption Spectra. Sample solution containing 30 μg of iron(II), 5.0 ml of 0.2% 1,10-phenanthroline solution and 1.0 ml of 1% sodium tetraphenylborate solution was prepared by the procedure. The absorption spectrum of the iron(II)–phen–TPB complex in naphthalene–*N,N*-dimethylformamide solution is shown in Fig. 1, together with that of the reagent blank. The ternary complex has its absorbance maximum at 514 nm. The reagent blank does not absorb at wavelengths longer than 430 nm. Therefore, 514 nm was

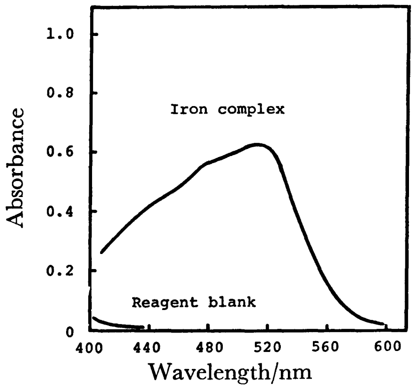

Fig. 1. Absorption spectra of 1,10-phenanthroline and ternary complex with sodium tetraphenylborate in naphthalene-*N*,*N*-dimethylformamide solution.
Iron(II): 30 μg; pH: 4.5; 0.2% 1,10-phenanthroline: 5.0 ml; 1% sodium tetraphenylborate: 1.0 ml; reference: water.

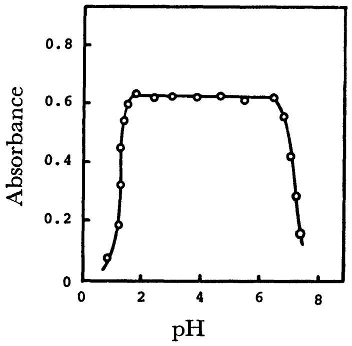

Fig. 2. Effect of pH.
Iron(II): 30 μg; wavelength: 514 nm; 0.2% 1,10-phenanthroline: 5.0 ml; 1% sodium tetraphenylborate: 1.0 ml; naphthalene: 1.5 g; shaking time: 30 s; standing time: 30 min, reference: reagent blank.

chosen as an optimum wavelength.

Effect of pH. The effect of pH on the absorbance of the ternary complex was investigated with a sample containing 30 μg of iron. The pH of the solution after collection was measured at room temperature. The pH for the collection of the ternary complex on microcrystalline naphthalene was varied between 0.5 and 7.7. The optimum pH for quantitative collection was 1.7—6.4, as shown in Fig. 2. Hence pH 4.5 was chosen for convenience.

Effect of Hydroxylammonium Chloride Concentration. Varying amounts of hydroxylammonium chloride as a reducing agent were added to the sample containing 30 μg of iron(III). Iron(III) was completely reduced to iron(II) with 0.2 ml of 2% solution to 5.0 ml of 10% hydroxylammonium chloride solution. In this study, 1.0 ml of 2% solution was used.

Effect of 1,10-Phenanthroline and Sodium Tetraphenylborate Concentration. The effect of 1,10-phenanthroline concentration on the absorbance was examined with a solution containing 30 μg of iron. With other variables held constant, 0.3 ml of 0.2% 1,10-phenanthroline solution was found to be sufficient for full color development for 30 μg of iron. The absorbance remained constant even with 8.0 ml of the reagent (Fig. 3).

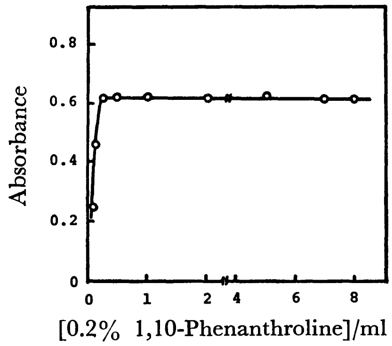

Fig. 3. Effect of 1,10-phenanthroline concentration. Iron(II): 30 μg; wavelength: 514 nm; pH: 4.5; rest of the conditions were the same as above. Reference: reagent blank.

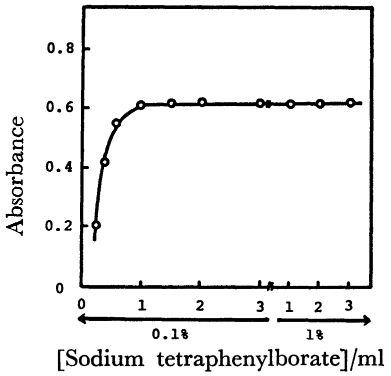

Fig. 4. Effect of sodium tetraphenylborate concentration.
Iron(II): 30 μg; wavelength: 514 nm; rest of the conditions were the same as above. reference: reagent blank.

Similar studies with a sodium tetraphenylborate showed that the absorbance remained unchanged over the range of 1.0 ml of 0.1% TPB solution to 3.0 ml of 1% TPB solution (Fig. 4). In this work, 5.0 ml of 0.2% 1,10-phenanthroline solution and 1.0 ml of 1% sodium tetraphenylborate solution were used.

Effect of Addition of Buffer Solution and Digestion Time. Addition of 0.5—5.0 ml of the acetate buffer did not cause practically variation in the absorbance. Thus 1.5 ml of the buffer was added for collection. A solution containing the iron(II)–phen–TPB complex was digested at room temperature (20—25 °C). The rate of formation of this ion-association complex is very fast at room temperature. The complex was found to be stable even at a temperature of 81 °C. It was scarcely dissociated in aqueous solution.

Effect of Naphthalene Concentration and Shaking Time. The collection of the ternary complex in the solution was carried out with addition of 0.5—4.0 ml of 20% naphthalene solution in acetone by vigorous shaking for 30 s. The collection did not cause any change with increasing amount of naphthalene. Thus, 2.0 ml of 20% naphthalene solution was taken as the suitable amount. Two ml of 20% naphthalene solution was added to the solution containing the ternary complex, and the mixed solution was shaken vigorously for 90 s. The complex was completely collected on naphthalene by vigorous shaking for a few seconds. Shaking for 30 s was found to be satisfactory for complete collection.

Effect of Volume of Aqueous Phase. The volume of aqueous phase was varied between 40 and 2400 ml, and the effect of volume of aqueous phase on the absorbance was examined. The absorbance was almost constant over the range of up to 2200 ml, but decreased gradually with increase in the volume of aqueous phase. For larger volumes of aqueous phase, the collection of the complex on naphthalene was carried out by using a larger volumes of the reagent solutions and shaking and digestion for longer time. In this series of tests, 10 ml of 0.2% 1,10-phenanthroline solution and 2.5 ml of 1% sodium tetraphenylborate solution were taken; the mixed solution was shaken for 2 min and digested for 20 min, 3.0 ml of 20% naphthalene solution being used.

Effect of Standing Time. The collected naphthalene mixture was dissolved in *N,N*-dimethylformamide. The color of the complex thus obtained is very stable, and the absorbance remained constant for a long time.

Calibration Curve. Based on the optimum conditions described above, a calibration curve was constructed according to the procedure. Beer's law was obeyed for 3—50 μg of iron(II) in 10 ml of *N,N*-dimethylformamide, at 514 nm. The molar absorptivity at 514 nm was found to be 1.2×10^4 l mol^{-1} cm^{-1}. The sensitivity was 0.0047 μg/cm^2 in *N,N*-dimethylformamide and 0.0050 μg/cm^2 in aqueous medium for 0.001 absorbance. Ten parallel determinations of 30 μg of iron gave a standard deviation of 0.00421 μg with relative standard deviation of 0.66%.

Choice of Solvent. Tests were made with various organic solvents to dissolve the collected naphthalene mixture. This mixture is easily soluble in *N,N*-dimethylformamide and acetonitrile, but insoluble in dioxane, chloroform, benzene, toluene, xylene, *o*-dichlorobenzene, isopentyl acetate, isobutyl methyl ketone (MIBK), carbon tetrachloride, methanol, ethanol, chlorobenzene, *etc*, at room temperature.

Effect of Diverse Ions. The effect of diverse ions on the iron determination was studied by adding various amounts of diverse ions in question to a solution containing 30 μg of iron and applying the procedure. The tolerance limits (error<5%) for the diverse ions are listed in Table 1. Most of the alkali salts did not interfere, but only 2 and 7 mg of KCN and sodium oxalate respectively could be tolerated. Larger amounts of inorganic anions such as thiocyanate and perchlorate, which form the ion-association complex, did not interfere in the determination. Bi^{3+} (100 μg) and Sn^{2+}(300 μg) also would be tolerated. If the iron content in practical samples is lower and diverse metal ions interfere with iron determination, extraction by organic solvents(MIBK or diethyl ether) is very efficient for the iron determination.

Analysis of Iron in Reference Material and Metal Samples. The proposed method was applied to the determination of iron in the reference material(aluminium alloy), metallic aluminium and magnesium samples, and the results (Table 2) are in reasonably good agreement with those obtained by the standard spectrophotometric procedure employing 2,4,6-tripyridyl-*s*-triazine (TPTZ) method[13—14]. The analytical procedures were as follows: 1.0 g of standard aluminium alloy (NBS, SRM-85b) was accurately taken in a 100-ml beaker to which were added 40—50 ml of hydrochloric acid (1+1) and 3 ml of 30% hydrogen peroxide. This was heated over the boiling water for about 10 min, the mixture dissolved completely and the excess of hydrogen peroxide decomposed. After cooling the volume of sam-

Table 1. Tolerance limits for diverse metal salts and metal ions

Diverse metal salt	Tolerance limit[a]	Diverse ion	Tolerance limit[a]
KSCN	9 g	Al^{3+}	20 mg
NaI	10 g	Bi^{3+}	100 μg
$CH_3COONa\cdot3H_2O$	2 g	Cr^{6+}	11 mg
KNO_3	7 g	Ca^{2+}	500 mg
Na_2SO_4	6 g	Cd^{2+}	1500 μg
KH_2PO_4	0.5 g	Co^{2+}	400 μg
$KClO_4$	0.5 g	Cu^{2+}	500 μg
NaCl	0.1 g	Hg^{2+}	2000 μg
Na$_2$tartrate	1.5 g	Mn^{2+}	70 mg
Na$_3$citrate	20 mg	Mg^{2+}	200 mg
Na$_2$oxalate	7 mg	Ni^{2+}	700 μg
KCN	2 mg	Pb^{2+}	3000 μg
		Sn^{2+}	300 μg
		Zn^{2+}	4000 μg

Iron(II): 30 μg; pH: 4.5; 0.2% 1,10-phenanthroline: 5.0 ml. a) Error <5%.

Table 2. Analysis of samples for ion

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	0.239±0.002	0.238±0.001
Aluminium metal (powder)	—	—	0.136±0.001	0.138±0.001
Magnesium metal (powder)	—	—	0.0024±0.0002	0.0025±0.0001

a) Average of 5 individual samples.

ple was completed to 200 ml with water. An aliquot of this sample was taken in a separatory funnel, followed by 40 ml of hydrochloric acid (1+1). Iron(III) in this sample was extracted by vigorous shaking for 5 min with 20 ml of MIBK.15) It was then back-extracted from the organic phase with 25 ml of water and the proposed method and TPTZ procedure were applied.

Metallic aluminium powder was analyzed in the same way as for the case of the standard aluminium alloy.

Metallic magnesium powder was analyzed in the same way as described above.

In the present work, the collection of the ternary complex on naphthalene is easily achieved merely by contact with microcrystalline naphthalene or by vigorous shaking for a few seconds. A very small amount (0.5 g) of the organic phase (naphthalene) is required for the complete collection which enhances the sensitivity as the whole of the organic phase may be taken for the analysis. Generally diverse metal ions and alkali metal salts (Table 1) even at higher concentrations level have very little influence on the analytical determination compared with the 1,10-phenanthroline procedure in aqueous medium1) or organic solvent extraction.16) Furthermore no remarkable difference was observed in the molar absorptivity, sensitivity and precision of the ternary complex for the above described procedures.

In conclusion, this inexpensive and relatively simple procedure can be successfully employed for the determination of iron in standard aluminium alloy and metal samples.

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