Spectrophotometric Determination of Iron (III) after Separation by Adsorption of its N-Benzoyl-N-Phenyl-Hydroxylamine Complex on Naphthalene

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Abstract. A novel method for the spectrophotometric determination of trace amount of iron (III) after separation of its BPA complex by adsorption on microcrystalline naphthalene is described. The ε_{max} of the DMF solution of the adsorbate containing iron (III)-BPA complex at λ_{max} 437 nm has been found to be 4.47×10^3. The effect of variables and interfering ions on the efficacy of the method has been studied. Sensitivity (in Sandell's notation) is 1.25×10^{-2} μg of iron (III)/cm^2 and at a mean absorbance of 0.4000 is 1.25%. The method is useful for the analysis of standard reference materials and environmental samples. The results are comparable with those obtained using ortho phenanthroline.

1. Introduction

Spectrophotometric determination of metals after extraction of metal complexes with organic solvents is widely used for trace determination of metal ions; but this method is not applicable when the complex has a low partition coefficient in the organic/aqueous phase. Both, the partition coefficient as well as the rate of formation of the complex, increase with increase in temperature. This fact has been profitably exploited by the author (M. S.) for extraction of metal complexes into molten naphthalene. A new method has now been developed for the separation and determination of the desired complex by adsorption on microcrystalline naphthalene, which is subsequently dissolved in a suitable solvent for photometric measurements[1-4]. In this communication, the determination of iron(III) as a red coloured complex with N-benzoly-N-phenyl hydroxylamine (BPA) has been reported.

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2. Experimental

Standard iron (III) solution was prepared by diluting iron (III) chloride solution (1000 ppm) obtained from Wako Pure chemical Ltd., Japan. In case of alloys, the sample is dissolved in 1:1 HCl and then treated with 30 per cent H_2O_2. Excess H_2O_2 is decomposed by heating and iron extracted into MIBK. Iron (III) is then back extracted from the organic phase into the aqueous phase. Lake water samples have been used as such. A 0.2 per cent solution of BPA (AR grade) in ethanol and 20 per cent naphthalene solution in acetone was used for complexation and adsorption studies respectively. Unimolar solutions each of acetic acid and ammonium acetate for *pH* 3–6 and ammonia and ammonium acetate for *pH* 8–11, mixed in recommended proportions, were used as buffers to control the *pH* of the solution. Hitachi model 200–20 double beam spectrophotometer and Toa-Dempa HM–5A *pH*-meter were employed for absorption and *pH* measurements respectively.

A series of sample solutions was prepared containing 1–12 ml of 10 ppm standard iron (III) solution, 2.0 ml of the buffer (*pH* 5.0) and 2.0 ml of 0.2 per cent ethanolic BPA solution. The mixture was diluted to 50 ml with distilled water and allowed to stand for about 30 minutes at room temperature.

3.0 ml of 20 per cent naphthalene solution in acetone was then added rapidly and the whole mixture vigorously shook on a shaking machine for one minute. Microcrystalline naphthalene that got separated contained the entire iron (III)–BPA complex adsorbed on it. It was filtered under suction through either filter papar 5C (Toyo Rosai Co., Japan) supported on a filter disc or a sintered glass crucible No. 2. The residue was washed several times with water and dried at 50–60°C in oven. Dried microcrystalline naphthalene was then dissolved carefully in dimethyl formamide and the final volume made upto 10 ml. The absorbance of this solution was measured against reagent as blank prepared similarly.

3. Results and Discussion

The absorption spectra of the reagent and iron (III)—BPA complex in naphthalene-dimethylformamide solution is shown in Fig. 1. The complex has only one absorption
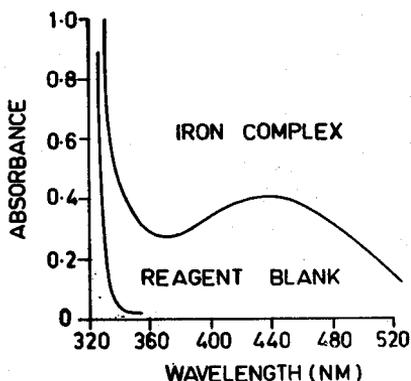
Figure 1. Absorption spectra of reagent (BPA) and iron complex in naphthalene—DMF solution.

maxima at 437 nm at which all absorption measurements have been made. It is observed that the amount of complex adsorbed on naphthalene is dependent on the *pH* of the solution. The adsorption starts at *pH* 1.8 and increases sharply with *pH*, being maximum and almost constant in the range 3.2–8.3. Above this *pH*, the adsorption of the complex on naphthalene was found to decrease rapidly. Consequently, minor variations in the amount of buffer, show no measurable change. Subsequent studies were carried out at *pH* 5.0. Although 80-and 100-fold excess of BPA and naphthalene, have been found to be adequate for complexatio n and adsorption, a 100- and 600-fold excess of the complexone and the adsorbent respectively have been used in all studies. Experiments have also been carried out to evaluate the effect of digestion time, shaking time, standing time and the volume of aqueous phase on the amount of complex adsorbed on naphthalene. These parameters do not exercise any significant effect on the adsorption of the complex. However, of various solvents viz. acetonitrile, benzene, chlorobenzene, chloroform, acetone, dioxane, toluene, xylene, ethyl acetate, petroleum ether, solvent ether and dimethyl formamide that dissolve the complex adsorbed on naphthalene, dimethylformamide has been found to be most suitable in the present case.

Interference caused in the estimation of iron (III), using BPA, due to the presence of diverse ions has also been studied. The tolerance limits for various cations

Table 1. Analysis of iron in standard reference materials (alloys).

Sample	Composition (%)		Iron certified value (%)	Present* method (%)	1,10–phenanthroline* method (%)
N. B. S.	*Cu* : 3.99,	*Mg* : 1.49		0.237	0.218
SRM–85B	*Mn* : 0.61,	*Cr* : 0.21		0.237	0.216
Al alloy	*Si* : 0.18,	*Ni* : 0.089	0.240	0.238	0.214
	Zn : 0.03,	*Ti* : 0.022		0.239	0.222
	Pb : 0.021,	*Ga* : 0.019		0.238	0.233
	V : 0.006,				
N. B. S.	*Al* : 2.98,	*Zn* : 1.05		0.00198	0.00185
SRM–171	*Mn* : 0.45,	*Si* : 0.0118		0.00196	0.00185
Mg alloy	*Cu* : 0.0112,	*Pb* : 0.0033	0.0018	0.00196	0.00186
	Ni : 0.0009,			0.00194	0.00186
Metallic	—		—	0.139	0.141
aluminium				0.140	0.141
(powder)				0.141	0.144
				0.147	0.142
				0.149	0.142
Metallic	—		—	0.154	0.148
aluminium				0.154	0.145
(shot)				0.159	0.147
				0.154	0.147
				0.151	0.149

*Each value represents on independent set.

and anions per $50\mu g$ of iron (III) are : HPO_4^{2-}(3 mg), $H_2PO_4^{2-}$(15 mg), NO_3^- (150 mg), SO_4^{2-}(480 mg), CO_3^{2-}(10 mg) CN^-(15 mg), acetate (50 mg), tartrate (15 mg), citrate (2 mg), Mg^{3+}(80 μg), Ni^{2+}(70 μg), Cd^{2+}(80 μg), Cu^{2+}(300 μg), Cr^{6+}(100 μg) Ca^{2+} (3 μg), Zn^{2+}(20 μg), Hg^{2+}(40 μg), Bi^{3+}(20 μg), Pd^{2+}(50 μg). EDTA interferred seriously and in contrast to other cations, copper caused a positive interference.

Under the optimum conditions the Beer's law is obeyed at λ_{max} 437 nm between the iron (III) concentration limits of 0.1-2.5 ppm in the aqueous phase. The molar absorptivity of the complex is 4.47×10^3, the sensitivity being $1.25 \times 10^{-2}\mu g$ of iron (III) for 0.001 absorbance. Ten replicate determinations of the samples containing 50 μg of iron (III) gave a mean absorbance of 0.400 with a relative standard deviation of 1.25 per cent.

This method has been successfully applied to the analysis of iron in alloys and lake water samples. The results obtained have been compared with those obtained using 1,10-phenanthroline (Table 1).

References

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