Spectrophotometric Determination of Trace Amounts of Iron(III) with 2-(5-Chloro-2-pyridylazo)-5-diethylaminophenol

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2-(5-Chloro-2-pyridylazo)-5-diethylaminophenol (5-Cl-PADAP) has been used as a chromogenic reagent for spectrophotometric determination of lead[1] and cobalt[2] with satisfactory results because of its high sensitivity and selectivity. During the studies on the spectrophotometric determination of cobalt, we noticed that 5-Cl-PADAP gave a bright blue - purple colour with iron(III) at pH 3–6. On the basis of this new colour reaction, a method has been developed for the determination of iron(III).

The coloured complex exhibits two absorption peaks, at 545 nm and 605 nm. Beer's law is obeyed in the range 0–20 μg of iron(III) per 25 ml of final solution. The colour system is stable for 24 h and is unaffected even by the presence of a large number of foreign ions. The proposed method is highly sensitive, rapid and accurate. It has been applied to the determination of iron in aluminium and magnesium metals and their alloys as well as some products of the chemical industry used for the manufacture of electronic optical glass.

Experimental

Apparatus

Absorption spectra were obtained with a Zeiss Specord ultraviolet - visible double-beam, recording spectrophotometer. For measurements at a single wavelength, a Model 721 spectro-

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photometer was employed. pH measurements were made with a Lei-ci, Model 25, direct-reading pH meter with a glass - calomel electrode assembly.

Reagents

All chemicals were of analytical-reagent grade.

Standard iron solution. Dissolve 0.4317 g of ammonium iron(III) sulphate in distilled water, add 15 ml of hydrochloric acid (1 + 1) and dilute to 500 ml with distilled water. This solution contains 0.1 mg ml^{-1} of iron. Prepare a 10.0 μg ml^{-1} solution by dilution with distilled water.

5-Cl-PADAP solution, 0.02% m/V in ethanol. 5-Cl-PADAP, supplied by the Institute of Environmental Chemistry, Academica Sinica, Beijing (Peking), China, can be prepared[3,4] by coupling 3-diethylaminophenol (0.082 mol) with 5-chloro-2-pyridyldiazoate (0.15 mol) and recrystallising the product from ethanol.

Sodium acetate buffer, pH 3.6. Dissolve 8 g of sodium acetate ($NaC_2H_3O_2.3H_2O$) in distilled water, add 134 ml of 6 M acetic acid and dilute to 500 ml with water.

Recommended Procedures

Into a 25-ml calibrated flask, pipette an aliquot of the sample containing not more than 20 μg of iron and add with swirling 2 ml of sodium acetate buffer (pH 3.6), 5 ml of ethanol and 2 ml of 5-Cl-PADAP solution. Dilute to volume with distilled water and mix well. Measure the absorbance at 605 nm in a 1-cm cell against a reagent blank after 30 min.

Procedure for determination of iron in aluminium and magnesium metals and their alloys

Weigh 0.5 g of the sample, prepare the sample solution by the appropriate method[5] and dilute to 100 ml with distilled water in a calibrated flask. An aliquot of 1–5 ml of this solution is taken for analysis as described above.

Procedure for determination of iron in products of the chemical industry

For nitrate and carbonate salts and boric acid samples, weigh 2–5 g of the sample, dissolve it in 5 ml of hydrochloric acid (1 + 1) and dilute with distilled water to 50 ml in a calibrated flask. An aliquot of 1–5 ml of this solution is taken for analysis as described above.

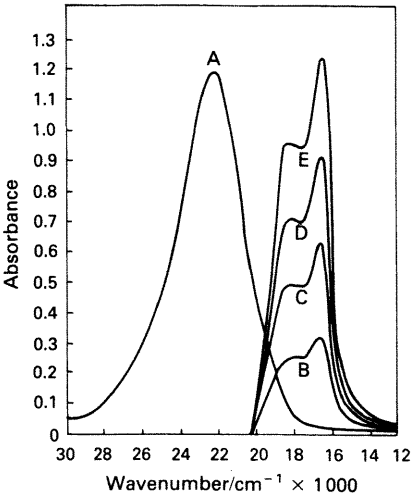

Fig. 1. Absorption spectra of 5-Cl-PADAP (R represents 5-Cl-PADAP in ethanol) and its iron complex, pH 3.6, 1-cm cell. A, 0.02% R against water; B, 5 μg of Fe(III) against R; C, 10 μg of Fe(III) against R; D, 15 μg of Fe(III) against R; and E, 20 μg of Fe(III) against R.

For lead tetroxide (red lead, Pb_3O_4) and quartz, weigh 2–5 g of the sample, prepare the sample solution in the usual way[6] and dilute it to 50 ml with distilled water in a calibrated flask. An aliquot of 1–5 ml of this solution is taken for analysis as described above.

Results and Discussion

Absorption Spectra

The absorption spectra of 5-Cl-PADAP and its iron(III) complex at pH 3.6 in water - ethanol medium are shown in Fig. 1. The iron(III) complex exhibits two absorption peaks, at 545 nm and 605 nm, whereas that of the reagent is at 450 nm. At 605 nm the reagent shows no absorption, and all measurements are therefore made at this wavelength.

Effect of Variables

Effect of pH

The pH of the reaction mixture was varied from 1.0 to 7.0, and the absorbance was found to be maximum in the range 3.0–6.0. Hence, all studies were carried out at pH 3.6 with sodium acetate buffer. The effect of pH on colour development is shown in Fig. 2.

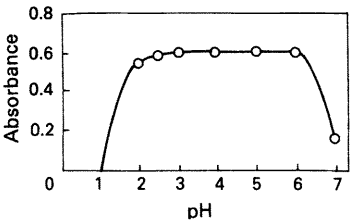

Fig. 2. Effect of pH on absorbance.

Effect of reagent concentration

The absorbance values at pH 3.6 of a water - ethanol solution containing 10 μg of iron and increasing amounts of 5-Cl-PADAP showed that the absorbance remained constant after addition of 1.5 ml of the reagent. Therefore, 2.0 ml of the reagent solution were used in all studies.

Role of ethanol

Because some precipitate was observed after the complex formation, ethanol was added to increase the solubilities both of the reagent and the complex and also the stability of the complex. The addition of ethanol in amounts from 2 to 10 ml gave identical absorbance values. Hence, 5 ml of ethanol was preferred.

Time for the formation of the complex and stability of the complex

The formation of the coloured complex of iron(III) with 5-Cl-PADAP is instantaneous. However, a 20-min standing period was allowed for equilibration. Measurement of the absorbance was therefore carried out 30 min after the addition of 5-Cl-PADAP and thereafter the colour of the complex remained virtually constant for 24 h.

Adherence to Beer's Law and Sensitivity

A series of standard iron solutions were prepared and the absorbance of each was measured and plotted against concentration. From 0 to 20 μg of iron(III) there is a linear relationship between absorbance and concentration. From this straight line, the average molar absorptivity (ϵ) of the iron complex was calculated as 8.82×10^4 l mol^{-1} cm^{-1} and Sandell's sensitivity (based on an absorbance of 0.001 unit) of the colour reaction was 0.00063 μg cm^{-2}. Hence it is evident that the method reported here is more sensitive than that involving pyridylazonaphthol (PAN) ($\epsilon = 1.6 \times 10^4$ l mol^{-1} cm^{-1}) or pyridylazoresorcinol (PAR) ($\epsilon = 4.2 \times 10^4$ l mol^{-1} cm^{-1}).[7]

TABLE I

TOLERANCE LIMITS IN THE DETERMINATION OF 10 μg PER 25 ml OF IRON(III) WITH 5-Cl-PADAP

Ions tolerated	Tolerance limit/ μg per 25 ml
K^+, Na^+, NH_4^+, NO_3^-, Cl^-	5×10^4
Cd^{2+}	3×10^4
Mn^{2+}, SO_4^{2-}	1×10^4
Li^+, Be^{2+}, Mg^{2+}, Al^{3+}, SiO_3^{3-}, Br^-	1×10^3
PO_4^{3-}	500
Ag^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Hg^{2+}, Y^{3+}, La^{3+}, Pb^{2+}, Cr^{3+}, Mo^{6+}	100
Cr^{6+}	85
Cu^{2+}, Co^{2+}, Ni^{2+}	2

TABLE II

RECOVERY OF ADDED IRON FROM PRODUCTS OF THE CHEMICAL INDUSTRY

Sample	Original iron content, %	Iron added, %	Iron found, %	Recovery of added iron, %
Potassium nitrate	0.002 3	0.000 5	0.002 84	108
	0.002 3	0.001	0.003 5	105
Barium carbonate	0.001 3	0.000 5	0.001 81	102
	0.001 3	0.001	0.002 33	102.5
Red lead	0.003 4	0.000 5	0.003 89	97
	0.003 4	0.001	0.004 36	96

TABLE III

RESULTS OF REPLICATE ANALYSES

Sample	Mean iron content (eight determinations), %	Standard deviation, %	Coefficient of variation, %
Boric acid	0.002 0	0.000 15	0.075
Red lead	0.001 3	0.000 13	0.10
Quartz	0.003 4	0.000 13	0.038

TABLE IV

COMPARISON OF RESULTS BETWEEN 1,10-PHENANTHROLINE AND 5-Cl-PADAP METHODS OF DETERMINING IRON IN MISCELLANEOUS SAMPLES

Sample	Iron content, %	
	By 1,10-phenanthroline method	By 5-Cl-PADAP method
Aluminium metal	0.060	0.062
Magnesium metal	0.060	0.061
Magnesium metal	0.031	0.030
Aluminium alloy	0.044	0.050
Magnesium alloy	0.014	0.013
Potassium carbonate	0.007 0	0.006 8
Sodium carbonate	0.004 4	0.004 1
Barium carbonate	0.003 7	0.003 4
Potassium nitrate	0.002 4	0.002 3
Barium nitrate	0.001 4	0.001 3
Boric acid	0.002 2	0.002 0
Red lead	0.001 5	0.001 3
Quartz	0.003 5	0.003 4

Effect of Foreign Ions

The effect of various amounts of 30 foreign ions on the determination of 10 μg of iron(III) per 25 ml of solution was examined under the experimental conditions used. The tolerance limits showed that iron(III) could be determined in the presence of a large number of ions (Table I). Hence, the selectivity of the present method is good.

Composition of the Complex

The composition of the complex was determined by the continuous variation method[8] (Fig. 3) and the molar-ratio method[9] (Fig. 4). A ratio of iron(III) to 5-Cl-PADAP of 1:2 in the complex molecule was obtained by both methods.

Precision and Accuracy

Some typical results obtained for the recovery of known amounts of iron added to three samples and 8-fold replicate determinations on each of the three samples are shown in Tables II and III, indicating that the method is reproducible and accurate. The results of analysis in comparison with the 1,10-phenanthroline method[10] are given in Table IV, showing the satisfactory nature of the procedure.

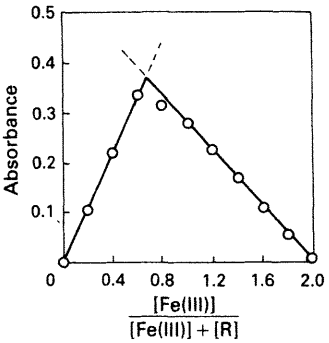

Fig. 3. Determination of the composition of Fe(III) - 5-Cl-PADAP (R) complex by continuous variation method. [Fe(III)] + [R] = 8.0×10^{-6} M.

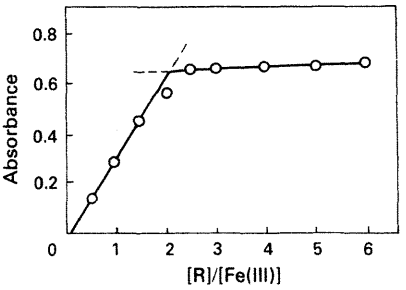

Fig. 4. Determination of the composition of Fe(III) - 5-Cl-PADAP (R) complex by molar ratio method.

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