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Note

Extractive Spectrophotometric Determination of Iron(III) with *N*-Hydroxy-*N*-*p*-chlorophenyl-*N*'-(2-methyl)-phenyl-*p*--Toluamidine Hydrochloride in the Presence of Thiocyanate

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A new method is proposed for the extraction and spectrophotometric determination of microgram amounts of iron(III) at ppm level using *N*-hydroxy-*N*-*p*-chlorophenyl-*N*'-2-methylphenyl-*p*-toluamidine hydrochloride (hereafter indicated as HCPMPTH) and potassium thiocyanate as a mixed complex. Iron(III) in 0.10—1.2 mol/dm^3 hydrochloric acid medium forms a benzene extractable orange-red complex with HCPMPTH in presence of thiocyanate. The 1 : 1 : 2 (metal : reagent : thiocyanate) ternary complex shows a sharp absorption maximum at 460 nm. The effective molar absorptivity of the complex is 12565 dm^3 mol^{-1} cm^{-1} with Sandell's sensitivity for iron of 0.0044 μg cm^{-2}. The method is simple, rapid and highly selective and most of the common ions including Fe^{2+}, Mo^{6+}, W^{6+}, Ni^{2+}, Al^{3+}, Zn^{2+}, Cr^{3+} did not interfere.

INTRODUCTION

N-hydroxy-*N*-*N*'-diaryl benzamidines, monobasic and bidentate chelating agents have been used for gravimetric and spectrophotometric determination of various transitional metal ions[1–6]. In the present work, we report the solvent extraction of iron(III) and its subsequent determination in the organic phase as a Fe (HCPMPTH) $(SCN)_2$ complex. Several methods[7–13] have been suggested for colorimetric determination of iron of these, the iron thiocyanate method[7] is commonly used for routine work and has a number of drawbacks such as the amount of reagent, the time of standing, non-linearity of Beer's law etc. The above mentioned drawbacks are successfully eliminated in the present Fe (HCPMPTH) $(SCN)_2$ method and offers a rapid and highly selective method for solvent extraction of iron(III) as thiocyanate mixed chelate with *N*-hydroxy--*N*-*p*-chlorophenyl-*N*'-2-methylphenyl-*p*-toluamidine hydrochloride.

EXPERIMENTAL

Apparatus

Absorbance values were measured with an ECIL-UV-VIS spectrophotometer model GS-865 using 1 cm matched quartz and silica cells.

Reagent

N-hydroxy-*N*-*p*-chlorophenyl-*N*'-2-methylphenyl-*p*-toluamidine hydrochloride was prepared by the condensation of equimolar quantities of *N*-2-*m*ethylphenyl-

-*p*-toluimidoyl chloride and *N*-*p*-chlorophenyl hydroxylamine in ether medium following the method of Deb and Mishra[2]. The resulting hydrochloride was crystallised from a minimum volume of absolute ethanol containing a few drops of concentrated hydrochloric acid (BDH, AR) m. p. 192—193 °C yield 60%. The analysis of compound gave satisfactory C, H and N values.

A 0.1% w./v. benzene solution of the reagent was employed for extraction purposes.

Standard Iron(III) Solution

Stock solution of iron(III) was prepared by dissolving 0.5 g pure iron wire (E. Merk) in dilute nitric acid (1 : 3). The oxides of nitrogen were removed by boiling and the solution diluted to 1 litre. It was standardized by 8-hydroxyquinoline[14].

A 5% potassium thiocyanate solution was used throughout the experiment.

Procedure

Place an aliquot of iron(III) solution containing 50 μg of metal in a 125 ml separatory funnel. To this add 5 ml potassium thiocyanate solution and adjust the acidity to 0.1—1.2 mol/dm³ with 2 mol/dm³ hydrochloric acid, keeping the volume of the solution to 25 ml. Add 15 ml of a benzene solution of the reagent and extract for 2 min. Dry the benzene extract over anhydrous sodium sulphate (2 g) in a 50 ml beaker make up the volume to 25 ml and measure the absorbance at 460 nm.

RESULTS AND DISCUSSION

Absorption Spectra

The absorption spectra of the reagent and Fe(HCPMPTH)$(SCN)_2$ ternary complexes are shown in Figure 1. The reagent shows negligible absorption in the 450—700 nm region. The Fe(HCPMPTH)$(SCN)_2$ mixed complex shows a sharp peak at 460 nm with a molar absorptivity of 12565 $dm^3\ mol^{-1}\ cm^{-1}$.

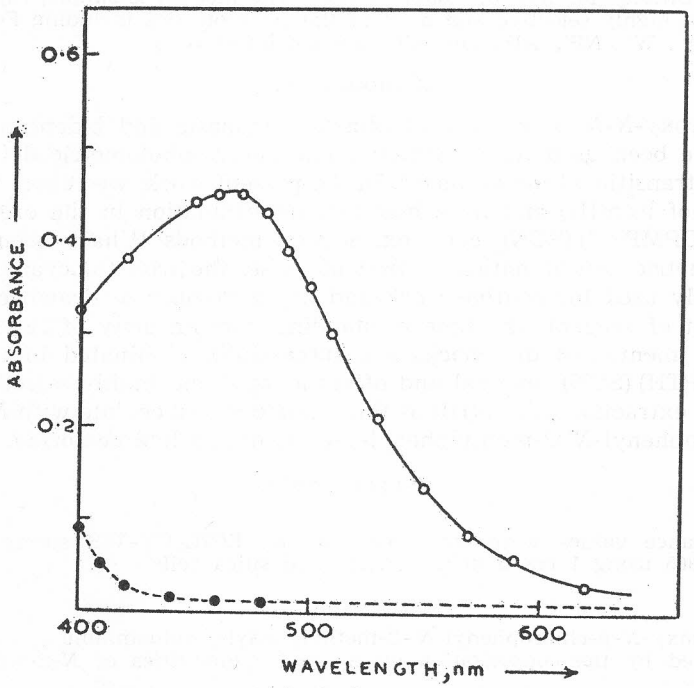

Figure 1. Absorption spectra: A. (—○—○—○—○—) Fe(HCPMPTH)$(SCN)_2$ in benzene, 2 ppm Fe(III). B. (—●—●—●—●—) 0.1% W/V HCPMPTH solution in benzene.

Extracting Solvent Selection

Several organic solvents were tried for the extraction of the Fe (HCPMPTH) $(SCN)_2$ complex; benzene, chloroform and carbontetrachloride were found suitable for the extraction process. Benzene was preferred because the iron : : HCPMPTH : SCN complex gets very rapidly extracted in it.

Effect of Variables

The acidity of the aqueous phase was adjusted with 2 mol/dm^3 hydrochloric acid. The optimum acidity range for the ternary complex was between 0.10—1.2 mol/dm^3 hydrochloric acid of aqueous phase.

A 30 and 240 fold molar excess of HCPMPTH and thiocyanate respectively were adequate for complete extraction of iron(III). Addition of excess reagent caused no diverse effect on λ_{max} and absorbance of the extract. The order of addition of reagent was not critical.

A time of two minutes was sufficient for complete extraction of the mixed complex. Variation of temperature from 20—40 °C did not affect the absorbance of the coloured system. The complex was stable for at least 40 hr at 27 $\pm$ 2 °C.

Beer's law, Optimum Concentration Range, Molar Absorptivity, Sensitivity and Precision

The reagent adhers to Beer's law up to 0.2—4.5 ppm of iron(III). The optimum range for accurate determination, as evaluated from the Ringbom Plot is 0.8—4.0 ppm. The sensitivity of the colour reaction is 0.0044 $\mu g/cm^2$ at 460 nm with a molar absorptivity 12565 dm^3 mol^{-1} cm^{-1}. The precision of the method has been checked by measuring the absorbance of 10 samples each containing a final concentration of 2 ppm of iron/25 ml. The mean absorbance was 0.45 with a standard deviation 0.0033.

Composition

The composition of Fe (HCPMPTH) $(SCN)_2$ was determined by the curve fitting method[15]. To determine the ratio of Fe(III) to HCPMPTH, the concentration of iron(III) was kept constant and SCN was taken in excess and then, the concentration of HCPMPTH was varried. Log absorbance was plotted against log M of HCPMPTH. Similarly the number of SCN attached to Fe(III) were also determined (Figure 2). The results obtained showed the formation of a 1 : 1 : 2 (metal : reagent : thiocyanate) ternary complex in benzene.

Effect of Foreign Ions

The effect of foreign ions was studied in 0.6 M hydrochloric acid by following the above procedure.

Chloride, bromide, nitrate, sulphate, ammonium, phthalate, borate, alkali metals, alkaline earth metals and lanthanides did not interfere up to 2000 ppm. The tolerance limit of other ions are shown in Table I.

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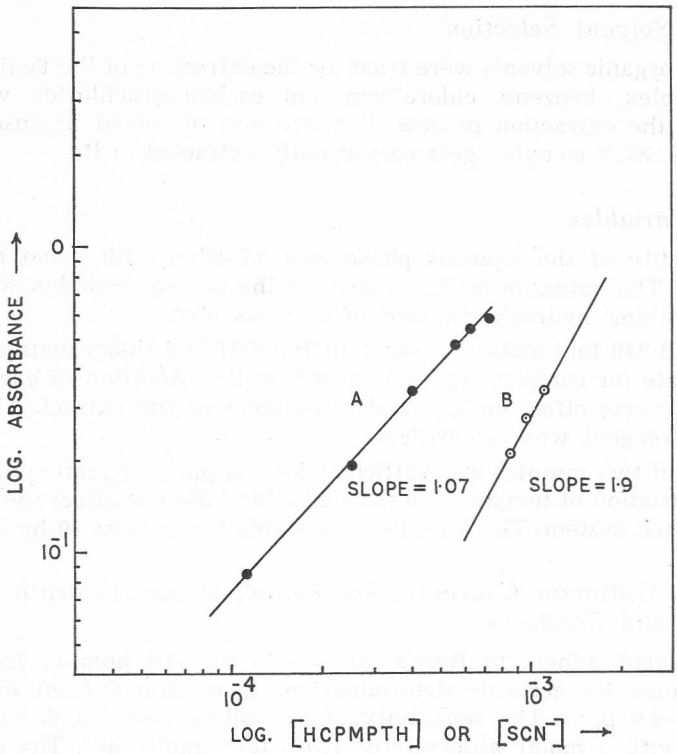

Figure 2. Curve fitting method for determining the ratio of HCPMPTH/SCN of Fe(HCPMPTH)$(SCN)_2$ Complex; 0.3 mol/dm³ HCl.
(A) Log absorbance vs log [HCPMPTH] in the presence of constant excess of thiocyanate (0.04 mol/dm³ in aqueous phase).
(B) Log absorbance vs log [SCN] in the presence of constant excess of HCPMPTH (0.003 mol/dm³ in benzene).

TABLE I

Tolerence Limit of Diverse Ions in the Determination of 2 ppm Iron(III) at 0.6 mol/dm³ Hydrochloric Acid

Ions added	Tolerated* amount ppm	Ions added	Tolerated* amount ppm
Fe^{2+}	800	U^{6+}	400
Co^{2+}	300	Ti^{4+}	80
Ni^{2+}	300	Mo^{6+}	10
Cu^{2+}	10	W^{6+}	50
Zn^{2+}	1600	Al^{3+}	1200
Cd^{2+}	1600	Cr^{3+}	800
Mn^{2+}	600[a]	Th^{4+}	300
Pb^{2+}	1500	Arsanate	1200
Sb^{3+}	1500	Citrate	1200
V^{5+}	80	Tartrate	1200
Zr^{4+}	400	Fluoride	800

* error causing 2%
[a] in the presence of sodium per sulphate.

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SAŽETAK

Ekstraktivno spektrofotometrijsko određivanje željeza(III) *N*-hidroksi-*N*-*p*-klorofenil--*N*'-(2-metil)fenil-*p*-toluamidin hidrokloridom u nazočnosti tiocijanata

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Predložena je nova metoda za ekstrakciju i spektrofotometrijsko određivanje mikrogramskih količina željeza(III) pomoću *N*-hidroksi-*N*-*p*-klorofenil-*N*'-(2-metil)--fenil-*p*-toluamidin hidroklorida (HCPMPTH) u nazočnosti tiocijanata. Narančasti kompleks sastava 1 : 1 : 2 (Fe : HCPMPTH : tiocijanat), koji se ekstrahira benzenom, očituje oštar λ_{max} pri 460 nm, a molarni apsorpcijski koeficijent je 12565 $dm^3\ mol^{-1}\ cm^{-1}$. Metoda je jednostavna, brza i izvanredno selektivna, te većina uobičajenih iona kao što su Fe^{2+}, Mo^{6+}, W^{6+}, Ni^{2+}, Al^{3+}, Zn^{2+} i Cr^{3+} ne smeta.

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