

Selective extraction of iron(III) with N-hydroxy-N-*p*-chlorophenyl-N'-*o*-chlorophenylbenzamidine hydrochloride as a thiocyanato mixed complex from hydrochloric acid media

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Abstract. The thiocyanato complex of iron(III) is selectively extracted with N-hydroxy-N-*p*-chlorophenyl-N'-*o*-chlorophenylbenzamidine hydrochloride into benzene. The 100% extraction of iron(III) is achieved in 0.5-1.4 M hydrochloric acid media of aqueous phase. The molar absorbance of complex is $14000 \text{ l. mol}^{-1} \text{ cm}^{-1}$ at 480 nm with Sandell's sensitivity $0.004 \mu\text{g/cm}^2$. The composition and separation of complex from other ions have been described.

Keywords. Solvent extraction ; hydroxyamidine ; Fe(III)-SCN⁻ complex ; iron(III).

1. Introduction

This paper present a simple, selective and rapid method for the solvent extraction of iron(III) and its subsequent determination in the organic phase as a Fe(III)-HOAm-SCN⁻ complex. In earlier studies, N-hydroxy-N,N'-diarylbenzamidines have been used for the extraction and separation of vanadium(V) (Patel *et al* 1978, 1979a ; Patel and Mishra 1979 ; Kharsan *et al* 1979a) and molybdenum (Kharsan *et al* 1979b, c) as ternary complexes. Although several methods (Sandell 1959 ; Shibata 1960 ; Iwamoto 1961 ; Takeuchi and Shijo 1965 ; Horiuchi and Nishida 1970 ; Otomo 1965 ; Nishida 1970 ; Ishito and Ichinohe 1972 ; Hayashi *et al* 1972 ; Oka and Miyamoto 1954 ; Torii 1955 ; Korenaga *et al* 1973) for the extraction of iron are known, these are sensitive but not selective. However, the iron(III)-SCN⁻ method is commonly used for routine work and has many drawbacks such as amounts of reagents, standing time, nonlinearity of Beer's law, etc. The proposed method eliminates these drawbacks and offers a rapid and reasonably selective method for the solvent extraction of iron(III) as thiocyanato mixed complex with N-hydroxy-N-*p*-chlorophenyl-N'-*o*-chlorophenyl benzamidine hydrochloride. The method is also useful for the analysis of ore and alloys.

2. Experimental

2.1. Apparatus, chemicals and reagents

An ECIL spectrophotometer model GS-865 equipped with 1-cm matched quartz and silica cells was employed for absorbance measurements. The pH values were determined with a Systronic pH meter type-322. The stock solution of iron(III) was prepared by dissolving iron wire (E Merck) in 30% nitric acid. The oxides of nitrogen were removed by boiling. The metal content of the solution was determined using 8-hydroxyquinoline (Vogel 1961). N-hydroxy-N-*p*-chlorophenyl-N'-*o*-chlorophenyl-benzamidine hydrochloride was synthesised by condensing an equimolar ratio of *N*-*o*-chlorophenylbenzimidoyl chloride and *N*-*p*-chlorophenylhydroxylamine as described in literature (Deb and Mishra 1976). A 0.003 M solution of reagent in benzene and 0.05 M solution of potassium thiocyanate in water respectively were used for experimental work. All the chemicals and reagents used were of BDH A.R. quality.

2.2. Procedure

An aliquot of the solution containing 50 μg of iron(III) was transferred in a 100 ml separatory funnel. To this were added concentrated HCl (2 ml) and potassium thiocyanate solution (5 ml) in a final volume of 25 ml aqueous phase. The aqueous phase was extracted with 25 ml benzene solution of reagent for 2 min. The layers were allowed to separate and the organic phase was transferred over anhydrous sodium sulphate (2 g) in a 50 ml beaker. The value of iron was determined photometrically by measuring absorbance at 480 nm against reagent blank.

3. Results and discussion

3.1. Absorption spectra

The absorption spectra of reagent and complex are shown in figure 1. The red-orange Fe(III)-HOAm-SCN⁻ complex shows a sharp λ_{max} at 480 nm

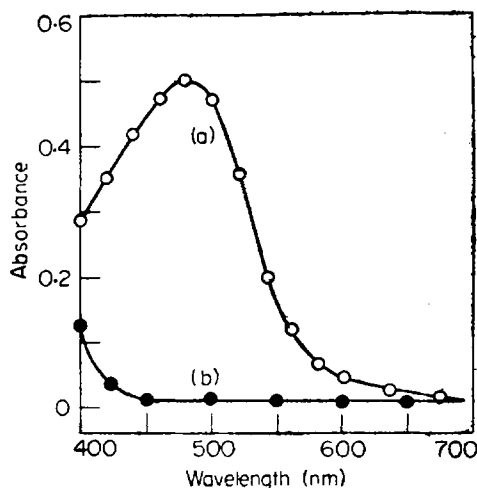


Figure 1. Absorption spectra of reagent and its complex. (a) Iron (3.58×10^{-5} M) + HOAm (3×10^{-3} M) + thiocyanate (0.1 M). (b) HOAm (3×10^{-3} M) in benzene.

with ϵ , 14000 l. mol⁻¹ cm⁻¹. The reagent has negligible absorption between 450–700 nm.

3.2. Effect of experimental variables

Various organic solvents were tested. Of these benzene was found to be the best as the iron(III)-HOAm-SCN⁻ complex had high distribution ratio in it. The acidity was maintained with A.R. HCl. Other mineral acids were unsuitable for extraction work as the complex showed low colour intensity. The optimum acidity range was between 0.5–1.4 M HCl. The effect of acidity of HCl on the extraction of iron(III)-SCN⁻ complex with HOAm is shown in table 1.

A 35-fold molar excess of HOAm in the presence of constant excess of 0.05 M thiocyanate at 0.8 M hydrochloric acid was necessary for complete extraction of iron(III). Similarly 130-fold molar excess of thiocyanate in the presence of constant large amount of HOAm (0.003 M) at 0.8 M HCl was sufficient for complete extraction of the metal. The order in which reagents were mixed is not critical. Addition of thiocyanate upto 2 M had no adverse effect.

The addition of NaCl or KCl (2.0 M) has no appreciable effect on the extraction of iron with varying concentration of HCl. The variation of volume ratio of aqueous phase from 10–60 ml and temperature from 20–40° did not affect the λ_{\max} and absorbance of the coloured system. A time of 1 min was sufficient for complete extraction of metal. The red-orange extract was stable atleast for 40 h at 27 ± 2°.

3.3. Beer's law, optimum concentration range, sensitivity and precision

The system conformed to Beer's law over the concentration range investigated, namely 0.4–4.0 ppm. The optimum working concentration range on the basis of Ringbom plot is 0.6–3.6 ppm of iron. The sensitivity of the method is found to be 0.004 $\mu\text{g}/\text{cm}^2$ of metal. The precision of the method is tested by measuring

Table 1. Effect of acidity on the extraction of the Fe(III)-HOAm-SCN⁻ complex. Fe(III) = 50 μg ; SCN⁻ = 0.05 M; HOAm = 0.003 M; λ_{\max} = 480 nm.

Concentration of hydrochloric acid M	Extraction <i>E</i> %	Distribution ratio <i>D</i>
0.1	80.0	4.0
0.3	88.0	7.2
0.4	94.3	16.5
0.5	100.0	<i>a</i>
0.8	100.0	<i>a</i>
1.0	100.0	<i>a</i>
1.2	100.0	<i>a</i>
1.4	100.0	<i>a</i>
1.5	96.4	26.9
1.8	92.8	13.0
2.0	85.7	6.0

the absorbance values of 10 samples, each containing 50 μg of iron(III) and the relative standard deviation is obtained $\pm 0.86\%$.

3.4. Molar composition

The ratio of thiocyanate and hydroxyamidine in iron(III)-HOAm-SCN⁻ complex was determined by the curve fitting method by plotting $\log D$ vs $\log M$ of thiocyanate/reagent added (Sillen 1956). The results obtained showed the formation of 1 : 1 : 2 (metal : HOAm : SCN⁻) complex in benzene.

3.5. Effect of diverse ions

To examine the effect of foreign ions on the determination of 2 ppm of iron (III), the extraction was carried out according to the recommended procedure. Chloride, bromide, nitrate, sulphate, borate, phthalate, alkali and alkaline-earth elements did not interfere in the present studies. The tolerance limits for other ions are given below in paranthesis (in ppm) : Fe(II), (1500); Zn(II) (2400); Cd(II) (2200); Ni(II), Co(II), Pb(II), Al(III), Cr(III), Th(IV), Bi(III), Sb(III), urea (2000); Mn(II), U(VI), selenate arsenate (1600); Zr(IV), Ga(III), In(III), fluoride, iodide, oxalate, citrate, tartrate, thiourea (1200); Cu(II) (100); Ti(IV) (150); Mo(VI), Nb(V) (in presence of sodium oxalate), Ta(V), (120); W(VI) (60); V(V) (30); phosphate (1500); EDTA (100).

3.6. Application of the method

The validity of the method was checked by analysing various BCS steel samples. The sample was dissolved in 30% nitric acid, in aquaregia, if necessary. Precipitated silica, hydrated tungstic acid and other insoluble residue were filtered off. The filtrated solution was diluted to a known volume after removal of nitrogen oxide. The metal content of the solution was evaluated as described earlier. Results are shown in Table 2.

Table 2. Determination of iron in various samples.

Sample	Certified value (%)	Found* %	Standard deviation
BCS 241/1	65.87	65.78	± 0.011
BCS 19d Cupro-nickel	0.82	0.80	± 0.008
Hametite ore**	67.50	67.58	± 0.009

BCS = British Chemical Standard, Bureau of Analysed samples Ltd., Newhamhall, Middlesbrough, Yorks.

* = An average of 6 determinations.

** = Obtained from Rajhara Mines, M.P. India.

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