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Extraction and Photometric Studies of Fe-Cyanex 923 Complex

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A detailed study of extraction of iron was carried out using Cyanex 923 in chloroform as an extractant. The Fe(III) content in the extracted colourless complex can be estimated using direct spectrophotometric method. Various parameters for extraction of iron were studied *viz.*, HCl study, effect of reagent concentration, effect of various diluents and equilibration period. These conditions were optimized to obtain the quantitative extraction. The probable nature of the extracted species was found out by a plot of log D *vs.* log C. The interference of foreign ions on extraction of Fe(III) was studied. The method can be used to separate Fe(III) from Mn(II), Ni(II), Co(II) and Mg(II) in their binary mixtures. Analysis of Fe(III) in ores, alloys and pharmaceutical products have been performed successfully and are in good agreement with certified values.

Key Words: Extraction, Photometric Studies, Fe(III), Cyanex 923.

INTRODUCTION

An extensive literature survey showed that a large number of extractants are useful for the extraction of iron. These include neutral extractants, high molecular weight amines, acidic extractants, *etc*. These methods however suffer from drawbacks such as longer extraction periods[1-3], interferences from common ions[4-8], less stability[9], low sensitivity[10] and use of carcinogenic solvents[11-19].

The present study reported an extraction method of iron from hydrochloric acid medium using Cyanex 923 in chloroform as an extractant. The extracted metal complex was determined spectrophotometrically. The proposed method successfully applied for the separation of iron from other metal ions in their binary mixtures and also applicable for the determination of iron in ores, alloys and pharmaceutical samples.

EXPERIMENTAL

All the chemicals used were of analytical grade from E. Merck. The stock solution of iron(III) solution was prepared by dissolving 4.317 g of ferric ammonium sulphate in double distilled water containing 5 mL of conc. sulphuric acid. The solution was diluted to 500 mL using double distilled water. The solution was standardized spectrophotometrically by a standard method[20] and the working standard solutions were prepared by suitable dilution of the stock solution. A 5×10^{-2} M solution of Cyanex 923 (m.w. 348) was prepared by pipetting out 1.98 mL of Cyanex 923 in a 100 mL standard measuring flask and diluting it up to the mark with chloroform.

A Spectronic Genesis 8 UV- Visible spectrophotometer was used for absorbance measurements.

General extraction procedure: To an aliquot of aqueous solution containing iron(III) was added hydrochloric acid to make it 6 M in a total volume of 15 mL. The solution was then transferred into a 125 mL separatory funnel and shaken for 60 s with 15 mL of 0.05 M Cyanex 923 solution in chloroform. After allowing the two phases to separate, the organic phase was collected in a 25 mL standard measuring flask and diluted upto the mark with chloroform. Minimum amount of anhydrous sodium sulphate was added to the 25 mL flasks to absorb all moisture. The absorbance of the extract was measured at 365 nm against reagent blank prepared analogously.

RESULTS AND DISCUSSION

Extraction conditions: The absorption of iron(III) complex was studied over a wavelength range of 300-400 nm. This colourless complex exhibited absorption maxima at 365 nm. At this wavelength the absorption of the reagent was negligible. Therefore, the wavelength of 365 nm was chosen for all further measurements.

The conditions for quantitative extraction of Fe(III) were established by varying parameters like concentration of hydrochloric acid (1-7 M), Cyanex 923 concentration ($0.5\text{-}6.0 \times 10^{-2}$ M), diluents and shaking period. It was observed that Fe(III) is quantitatively extracted from 6 M hydrochloric acid, with 15 mL of 5×10^{-2} M Cyanex 923 dissolved in chloroform.

The study showed that shaking period of 60 s is enough for complete transfer of Fe(III) into the organic phase. Prolonged shaking, however, had no adverse effect on the extraction.

The suitability of various solvents was investigated for the proposed system. It was observed that, extraction was quantitative with chloroform, cyclohexane and benzene but decreased with toluene, xylene and carbon tetrachloride. Chloroform was chosen as a diluent for all studies as it gives a clear phase separation and the lower organic layer is easier to remove.

The optimum extractions conditions are shown in Table-1 and in Figs. 1-4.

TABLE-1
OPTIMUM CONDITIONS FOR EXTRACTION OF IRON

Parameters	Optimum conditions
Iron(II)	10 to 320 µg
Hydrochloric concentration	6 M
Cyanex 923 concentration	5×10^{-2} M
Shaking time	60 s
Diluent	Chloroform

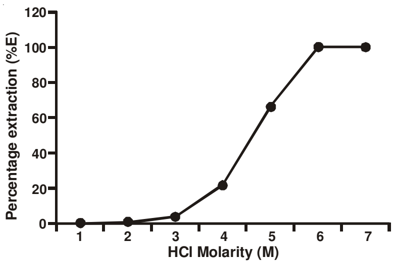

Fig. 1. Extraction behaviour of Fe(III) into Cyaned 923 as a function of the molarity of HCl

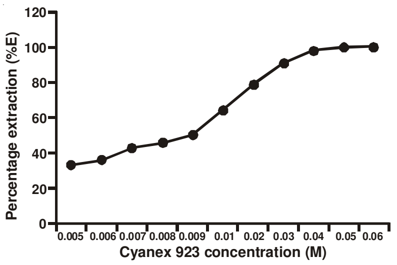

Fig. 2. Extraction behaviour of Fe(III) into Cyaned 923 as a function of Cyanex 923 concentration

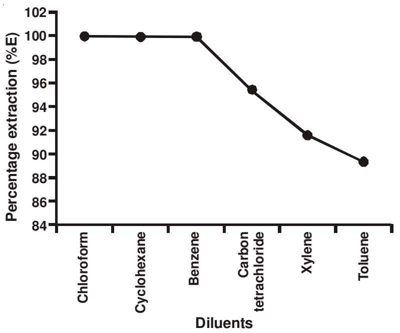

Fig. 3. Extraction behaviour of Fe(III) into Cyaned 923 as a function of different diluents

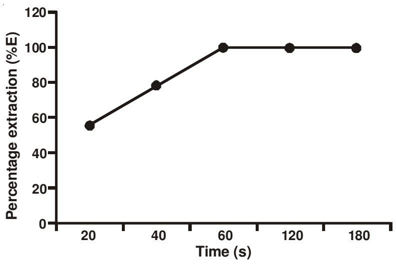

Fig. 4. Extraction behaviour of Fe(III) into Cyaned 923 as a function of shaking time

Spectral characteristics: Iron(III) was extracted with Cyanex concentration ranging from 10-320 µg. It was found that a linear plot is obtained in the concentration range of 10-310 µg of the organic phase. Beyond 310 µg of iron(III), the slope of the plot changes. The colour of the complex is stable for over 24 h. The Sandell's sensitivity and the molar absorptivity was found to be 7.9051 × 10^{-3} µg mL^{-1} cm^{-2} and 7065.06 L mol^{-1} cm^{-1}, respectively. The coefficient of variation was 0.25 % for 50 µg of iron(III).

The spectrophotometric data for the determination of 50 µg of iron(III) after extraction with Cyanex 923 is given in Table-2.

TABLE-2
SPECTROPHOTOMETRIC DATA FOR THE DETERMINATION OF IRON AFTER EXTRACTION WITH CYANEX 923
Fe(III) = 50 µg; Extracting solution = 15 mL of 5 × 10^{-2} M Cyanex 923 in chloroform; [HCl] = 6 M; Shaking time = 60 s

Molar absorptivity	7065.06 L mol^{-1} cm^{-1}
Sandell's sensitivity	7.9051 × 10^{-3} µg mL^{-1} cm^{-1}
Mean absorbance of 6 determinations	0.253
Beer's law range	10-310 µg
Standard deviation	6.324 × 10^{-4}
Coefficient of variation	0.25 %

Nature of the extracted species: An attempt was made to find out the probable composition of the extracted species, from a plot of log D *vs.* log C (Cyanex 923) at fixed acid concentration. The slope of this plot was found to be 2.7 indicating the complex to be 1:3 with respect to Cyanex 923 (Fig. 5).

A further attempt was made to ascertain the nature of the complex spectroscopically. As mentioned earlier, the complex absorbs in the UV region at 365 nm.

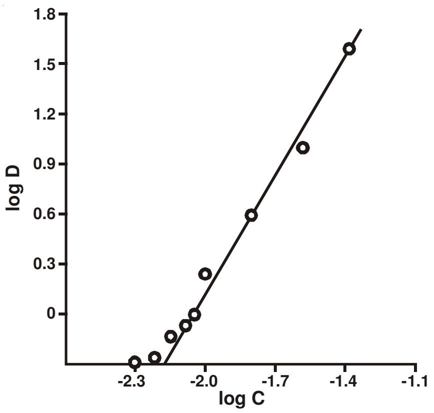

Fig. 5. Distribution ratio of Fe(III) as a function of Cyanex 923 concentration at 6 M HCl

Complexation is between Fe in +3 oxidation state and Cyanex 923. Cyanex 923 is available in a pure form from Cytec Industries, Canada and is composed of four trialkyl phosphine oxides. [$R_3{}^1P = O$ (8 %), $R_3P = O$ (14 %), $R_2{}^1RP = O$ (31 %) and $R_2R^1P = O$ (42 %), where R = hexyl and R^1 = octyl].

An IR spectra of the complex was taken. However, due to the complexity of the reagent itself, it was not possible to derive any conclusion out of it. The ^{31}P NMR spectra of Cyanex 923 alone showed a mixture of peaks at 47.9 ppm which can be attributed to the 4 types of 'P' which are very similar in chemical environment around the phosphorus group of the phosphines.

A similar ^{31}P NMR spectra of the complex shows a shift of the peak from 47.9 to 50.03 ppm . This probably is due to the paramagnetic effect of the *d*-orbitals in iron. Thus, it is possible to confirm the involvement of 'P' in the complex formation.

^1H NMR of the reagent was extremely complex due to the various groups present and also due to 'H-P' coupling. The ^1H NMR of the complex however does not show a major change in NMR signal apart from a slight shift probably due to the paramagnetic effect of the metal ion.

Thus, from the spectral data was confirmed the formation of the complex between Fe and Cyanex 923. However, it was not possible to know as to which out of the four phosphine oxides was actually involved in the complexation.

Effect of foreign ions: The extraction of iron(III) was carried out according to the recommended procedure to examine the effect of interference from various foreign ions. The tolerance limit was set at an amount to cause an error of ± 2 % in the recovery of the metal ion. The results are shown in Table-3. It reveals that a large number of cations and anions are tolerated. However, Fe(II) ion interfere seriously in the extraction of iron(III) and must be absent during the extraction.

TABLE-3
EFFECT OF THE INTEREFERENCE BY FOREIGN IONS ON THE EXTRACTION OF 50 μg OF IRON(III)*

Tolerance limit (μg)	Foreign ions
300	Ce(IV), Mg(II), Bromide, Bi(II), Co(II) and Cd(II).
200	Cu(II), Zn(II), Ba(II), Sr(II), Sn(II), Pb(II), Nitrate, Cr(IV), Phosphate and Ca(II)
100	Mn(II), Al(II), Zr(IV), Rh(III), Ni(II), Ag(II), Th(IV), EDTA and V(V),
Ion not tolerated	Fe(II)

*Spectrophotometric estimation.

Binary separations of iron(III) from manganese(II), nickel(II), cobalt(II) and magnesium(II): Ions such as manganese(II), cobalt(II), nickel(II) and magnesium(II) are not extracted into Cyanex 923 under optimum conditions for iron (III) upto a certain concentration. Hence, it is possible to separate them from their binary mixtures. The unextracted manganese(II), cobalt(II), nickel(II) and magnesium(II) were determined spectrophotometrically[20].

The results of the analysis of binary mixtures are given in Table-4.

TABLE-4
BINARY SEPARATIONS OF IRON

Composition (μg)	Recovery of (Pd(III))* (%)	Coefficient of variation (%)	Recovery of the added ion* (%)	Coefficient of variation (%)	Estimated procedure for the added ion and its reference
Fe(III):Mn(II) 50:50	99.99	0.39	98.14	0.09	Spectrophotometrically with periodate[20]
Fe(III):Co(II) 50:100	99.99	0.10	98.53	0.22	Spectrophotometrically with Nitroso-R-salt[20]
Fe(III):Ni(II) 50:100	99.99	0.14	98.84	0.05	Spectrophotometrically with DMG[20]
Fe(III):Mg(II) 50:50	99.99	0.08	98.16	0.80	Spectrophotometrically with Solochrome black T[20]

*Mean of five determinations.

Analytical applications

Analysis of ores: The sample solution of ilmenite ore was prepared by decomposing 5 g of sample using aqua regia and evaporating it to near dryness. The residue was leached with dilute hydrochloric acid. The solution was diluted to 250 mL using double distilled water. An aliquot of this solution was used for estimation of Fe(III) using the proposed method.

The sample solution of Haematite ore was prepared by taking 1 g of sample moistened with double distilled water and was treated with 50 mL of 1:1 hydrochloric acid. The contents were boiled in a 250 mL conical flask (with a funnel on the neck) till a clear solution was obtained. It was diluted to 250 mL with double distilled water. An aliquot of this solution was used for estimation of Fe(III) using the proposed method.

Analysis of alloys: The EN 8 steel and the iron rod sample solutions were prepared by dissolving 500 mg of the samples separately in aqua regia and then evaporating them to near dryness. The residues were dissolved in 1:1 dilute hydrochloric acid and then finally diluted to 250 mL with double distilled water. An aliquot of this solution was used for estimation of Fe(III) using the proposed method. The results of the ilmenite ore and alloy analysis is given in Table-5.

TABLE-5
DETERMINATION OF IRON(III) IN ORES AND ALLOYS

Samples	Iron found*		Recovery (%)
	Proposed method**	Known method***	
Ores			
Haematite	0.6000	0.6070	98.84
Ilmenite	0.0371	0.0375	98.93
Alloys			
EN 8 Steel	0.895	0.910	98.35
Iron Rod	0.905	0.910	99.45

*mg/g of the sample. **Salicylic Acid method [Spectrophotometric].
***Average of Six determinations.

Analysis of pharmaceutical samples: The proposed method was applied for the determination of iron in pharmaceutical samples such as raricap and livogen capsules.

The contents of the samples were treated with nitric acid with care, evaporated to dryness and extracted with dilute sulphuric acid. From the diluted sample solution, the analysis was carried out using the proposed method. The results of the above sample analysis is reported in Table-6.

TABLE-6
DETERMINATION OF IRON(III) IN PHARMACEUTICAL SAMPLES

Tablet	Sample manufactured by	Composition	A	Amount of Fe(III)*		Amount of Fe(III)	
				B	C	D	C
Raricap	NR Jet Enterprises Ltd.	Ferrous: 278 mg Citrate equivalent to Iron: 25 mg Calcium: 6 mg Follic acid: 0.3 mg	30.22*	28.82*	95.39	29.62	98.02
Livogen	Merck	Ferrous: 152 mg fumerate Folic acid: 1500 mg	38.00*	36.57*	96.24	37.21	97.21

A = Certified value; B = Found* by proposed method; C = Recovery (%);
D = Found by known method. *Average of 6 determinations.

The results for the analysis of iron in the sample *viz.* ores and alloys were also comparable with the known analytical method[20].

The results of the analysis of iron in pharmaceutical samples were also in good agreement with the certified values and those of an independent analysis.

Conclusion

(1) The method is simple, rapid and has good precision. (2) The method has been successfully applied for the separation and determination of iron(III) in its binary mixtures with Mn(II), Co(II), Ni(II) and Mg(II). (3) It is also possible to analyze Fe(III) present in ores, alloys and pharmaceutical samples using the proposed method. (4) The spectroscopic study of the complex with respect to the reagent confirms the formation of the complex.

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