

Extraction of iron(III) from nitrate media with bis (2-ethylhexyl) phosphinic acid

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Solvent extraction of iron(III) from nitrate media using bis(2-ethylhexyl) phosphinic acid as extractant has been proposed. A critical study of various parameters suggest that iron(III) can be quantitatively extracted in the pH range 2.0-4.5 using 0.009 *M* bis(2-ethylhexyl) phosphinic acid in hexane. The organic phase is stripped using 0.75 *M* HNO₃ and iron(III) determined spectrophotometrically by thiocyanate method. The method is selective and can be applied in the presence of a large number of diverse ions. The method is found to be reproducible when applied for recovery of iron from real samples as well as its separation from other metal ions.

Neutral organophosphorous extractants like tributyl phosphate (TBP)¹ and trioctyl phosphine oxide (TOPO)² have earlier been reported for quantitative extraction of iron(III) from HCl media but they were found to be less effective in the presence of nitrate ion^{3,4}. Although mono (2-ethylhexyl) phosphoric acid⁵ and bis (2-ethylhexyl) phosphoric acid (HDEHP)^{6,7} have been reported; the stripping of iron-loaded organic phase was found to be difficult^{8,9}. In the case of cobalt-nickel separation it has been reported that the phosphinic acid extractants have better separation efficiency than the corresponding phosphoric or phosphonic acid derivatives¹⁰. Mirelles *et al.* have reported the mechanism of extraction of iron(III) by bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex-272)¹¹. Bis (2-ethylhexyl) phosphinic acid (PIA-8) was found to be advantageous as compared to Cyanex-272 for the refining of nickel sulphate solution¹².

Most of the existing extraction methods for iron(III) using different reagents^{13,14} have drawbacks such as long equilibration period, difficult phase separation, multiple extractions, mutual solubility of the two phases, co-extraction of mineral acid etc. In the present note, we report a simple, rapid and reproducible method where high selectivity of PIA-8 was utilized for separation and esti-

mation of iron(III).

Experimental

Bis (2-ethylhexyl) phosphinic acid obtained from Daihachi Chemical Industry, Japan, under the trade name of PIA-8 was used without further purification. It was used after appropriate dilution with *n*-hexane. *n*-Hexane used as diluent was an analytical grade petroleum fraction. All chemicals used were of AR grade. Doubly distilled water was used throughout the study.

Iron(III) stock solution was prepared by dissolving 7.234 g of iron(III) nitrate nonahydrate, [Fe(NO₃)₃·9H₂O], in doubly distilled water containing 10 ml conc. HNO₃ and diluting up to 1000 ml. It was standardized by titration with K₂Cr₂O₇ (ref. 15). Working solutions of iron(III) were prepared by appropriate dilution of the standardized stock solution.

An Elico model (LI-120) pH meter with a PPC-CL51 combined glass electrode was used for pH measurements while a GBC-911A UV visible spectrophotometer with 10 mm quartz cuvettes was used for absorbance measurements.

General procedure

An aliquot containing 50 µg of iron(III) was taken and its pH was adjusted to 2.0 with dil. nitric acid or dil. ammonium hydroxide. The solution was made up to 10 ml and transferred to a separating funnel. It was then equilibrated with 10 ml of 0.009 *M* PIA-8 in hexane for 3 min. After phase separation, iron(III) from the organic phase was stripped back with 0.75 *M* HNO₃ and determined spectrophotometrically by thiocyanate method¹⁵.

Results and discussion

Extraction of iron(III) with 0.009 *M* PIA-8 in hexane was examined over the pH range of 0.1-4.5 and was found to be quantitative in the range 2.0-4.5; precipitation of hydroxy species takes place above pH 5.0.

The effect of reagent concentration on the extraction was observed by varying concentration of PIA-8 from 0.0001-0.1 *M*. Quantitative extraction at pH 2.0 was obtained with a PIA-8 concentration of at least 0.009 *M*.

Table 1 – Separation of iron(III) from multicomponent mixtures

No	Mixture	Amt., μg	pH	Stripping agent	Recovery [†] , %
1	Fe(III)	50	2.0	0.75 M HNO ₃	99.6
	Ti(IV)	100	2.0	2.5 M H ₂ SO ₄ + 3% H ₂ O ₂	96.9
	Ni(II)	50	2.0	Aq. phase / Unextracted	99.9
2	Fe(III)	50	2.0	0.75 M HNO ₃	99.5
	Ti(IV)	100	2.0	2.5 M H ₂ SO ₄ + 3% H ₂ O ₂	97.2
	Ca(II)	30	2.0	Aq. phase / Unextracted	99.7
3	Fe(III)	50	2.0	0.75 M HNO ₃	98.8
	Zn(II)	30	6.0	0.1 M H ₂ SO ₄	99.0
	Cu(II)	50	9.5	0.1 M H ₂ SO ₄	98.4
4	Fe(III)	50	2.0	0.75 M HNO ₃	99.6
	Zn(II)	30	6.0	0.1 M H ₂ SO ₄	98.5
	Mn(II)	25	8.5	0.2 M H ₂ SO ₄	96.7
5	Fe(III)	50	2.0	0.75 M HNO ₃	99.9
	Co(II)	20	0.3 M CH ₃ COONa	1 M HCl	98.3
	Cr(VI)	25	0.3 M CH ₃ COONa	Aq. phase / Unextracted	97.4

[†]Mean of triplicate analysis

Therefore all further studies were carried out using 0.009 M of PIA-8.

The extraction of iron(III) was performed with 0.009 M PIA-8 in different diluents. The extraction was found to be quantitative with diluents like *n*-hexane, benzene, toluene, xylene, nitrobenzene and chloroform. Dichloromethane (98.1%), carbon tetrachloride (90.5%) and cyclohexane (89.4%) were found to be less effective. Hexane was preferred as the diluent for extraction, since it provided better phase separation.

The equilibration period was varied from 0.5- 20 minutes. Quantitative extraction was achieved with shaking for at least of 3 min.; prolonged equilibration showed no change in extraction. Therefore equilibration period of 3 min. was maintained.

Iron(III) was back-extracted from organic phase with different concentrations of mineral acids. The stripping of iron(III) was observed to be quantitative with 0.75-3.0 M HNO₃, 1.0-2.5 M HCl and 1.0-3.0 M H₂SO₄. Among these mineral acids, HNO₃ was preferred as stripping agent as the same concentration of it is required in determination of iron(III) by the thiocyanate method.

Iron(III) was quantitatively extracted in the range of 1.0-20.0 $\mu\text{g cm}^{-3}$ at pH 2.5 with 0.009 M PIA-8. Higher

Table 2 – Determination of iron(III) in some real samples

Sample	Iron(III), %		Recovery, %
	Present [†]	Found [‡]	
Brass	1.78	1.76	98.7
Monel metal	2.00	1.98	99.0
Pyrolusite ore	9.80	9.67	98.7
Bauxite ore	30.25	29.65	98.0
Iron oxide red pigment	69.90	69.60	99.5
Supradyn tablets (Nicholas Piramal India)	9.81 mg	9.67 mg	101.5
Impheron injection (Rallies, India)	50 mg	49.9 mg	99.8

[†] Certified value[‡] Mean of triplicate analysis

concentrations of metals could be extracted with higher concentration of the reagent.

The nature of the extracted species was ascertained by conventional slope analysis method from the graph of log *D* versus log [HR] at fixed pH 2.0. A linear plot with a slope of 2.87 was obtained. Hence the ratio of

iron(III) to PIA-8 in extractable species is proposed as 1:3.

Iron(III) was extracted in the presence of a large number of ions. The tolerance limit was set as the amount of foreign ion causing an interference of $\pm 1\%$ in the extraction of iron(III). The alkali metals (except Rb^+), alkaline earth metals, cadmium(II), mercury(II) and nickel(II) were tolerated up to a weight ratio of 100:1 or more. Cobalt(II), aluminium(III), copper (II), and thallium(I), did not interfere up to a ratio of 50:1. The tolerance limit was found to be 20:1 for rubidium(I), zinc(II) and manganese(II) but only 10:1 for lead(II), vanadium(V), bismuth(III) and tartarate. Chromium(III), gallium(III), indium(III) and citrate were tolerated up to 5:1 ratio. Common anions like chloride, bromide, sulphate, sulphite, sulphide and nitrite did not interfere even up to 100:1 or more. Thus most of the ions were tolerated at high ratios suggesting high selectivity of PIA-8 for iron(III). Titanium(IV) was found to interfere seriously by co-extraction. EDTA and oxalate were not tolerated at and above 1:1 ratio and effectively mask iron(III).

Separation from multi-component mixtures

After a study of the extraction behaviour of PIA-8 towards some metal ions, differences in pH and stripping agents were fully exploited to devise schemes for separation of iron(III) from some binary and ternary mixtures.

A mixture of iron(III), cobalt(II), and chromium(VI) was separated by first extracting iron(III) at pH 2.0; followed by extraction of cobalt(II) from acetate media; at this stage chromium(VI) was not extracted. In a mixture containing iron(III), titanium(IV) and nickel(II), iron(III) and titanium(IV) were extracted at pH 2.0 and further separated by selective stripping of iron(III) with 0.75 M HNO_3 . Titanium(IV) was then stripped with 10 ml of a mixture of 2.5 M H_2SO_4 and 2 ml of 3% H_2O_2 . Nickel(II) was found to remain unextracted. Zinc(II), manganese(II) and copper(II) were extracted at pH 6.0, 8.5 and 9.0 respectively. Thus these metal ions were easily separated from iron(III) by taking advantage of differences in the pH. The details of separation schemes are summarized in Table 1.

Analysis of real samples

The proposed method was applied to analysis of iron samples of different origin (Table 2). The method gave good results and was free from interference caused by other constituents present in pharmaceuticals formulations. The ore and alloy samples were analyzed after applying the separation schemes given in Table 1. The results obtained for different iron concentrations are reproducible.

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