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Extraction and Spectrophotometric Determination of Iron(III) by 1-phenyl-2-methyl-3-hydroxy-4-pyridone

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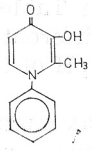
The extraction and spectrophotometric determination of iron (III) by 1-phenyl-2-methyl-3-hydroxy-4-pyridone (HX) are described. At pH > 1.5 97% of the iron(III) can be extracted. A quantitative reextraction of iron from the organic phase is possible with an acid concentraion higher than 1 M. The composition of the iron(III)-HX complex formed in the organic phase was investigated spectrophotometrically, radiometrically and by a quantitative analysis of the isolated species. In the aqueous phase iron(III) and HX form three different complexes, depending on the initial iron(III)-HX concentration ratio and the pH of the solution. They are the violet FeX^{2+}, the orange-red FeX_2^+ and the orange-yellow FeX_3. The latter is identical with the complex found in the organic phase.

INTRODUCTION

In our previous papers[1–6] it was reported that 2-carbethoxy-5-hydroxy--1-(4-tolyl)-4-pyridone appears to be a very suitable agent for the selective extraction of certain metals: niobium(V), tantalum(V), zirconium(IV), thorium(IV), protactinium(V), gallium(III), iron(III) and vanadium(V). Organic extracts of iron(III) and vanadium(V) by this reagent are suitable for spectrophotometric determination of these metals[5,6]. This paper describes the application of a new reagent, 1-phenyl-2-methyl-3-hydroxy-4-pyridone (HX), for the extraction and spectrophotometric determination of iron(III). The composition of the complexes formed in aqueous and organic phase was characterized in the solutions as well as by quantitative analysis of the isolated crystalline compound.

The advantage of this new extractant in comparison to others described in the literature is in its high selectivity and facile separation[7]. Its simple and efficient synthesis[8] also make it preferable to 2-carbethoxy-5-hydroxy-1-(4--tolyl)-4-pyridone described in our previous papers[1–6].



1-phenyl-2-methyl-3-hydroxy-4-pyridone (HX)

EXPERIMENTAL

Reagents

The synthesis and physical properties of 1-phenyl-2-methyl-3-hydroxy-4-pyridone (HX) were described previously[8]. Solutions of this reagent in chloroform served as

the organic phase and its stock solution in ethanol was prepared for the measurements in a water-ethanol mixture.

Radionuclides $^{55,59}Fe$ (Institute »Boris Kidrič«, Vinča, Yugoslavia) in chloride form were used to study the extraction. Inactive iron(III) solution was standardized gravimetrically and by titration with 0.05 M EDTA. To prevent the formation of iron(III) hydrolysed species in water, diluted $FeCl_3$ solutions were always freshly prepared from a 0.1 M $FeCl_3$ stock solution in 0.1 M hydrochloric acid. All of the reagents were of analytical purity.

Apparatus

Absorbance measurements were made on a Beckman Spectrophotometer, model DU-2. A pH-meter, Radiometer, model TTT 1 was used for pH measurements.

Determination of distribution ratios

Two equal volumes (3 ml) of the organic and aqueous solutions were shaken for 15 min although the equilibrium is attained in several minutes. The phases were separated and an aliquot (1 ml) of each phase was counted in a well-type gamma scintillation counter. The distribution ratio, *D*, for a given radionuclide was calculated from the counts per 100 s of samples of each phase.

Spectrophotometric determination of Fe(III) in the organic phase

The pH of the (8 ml) solution containing 10—100 μg of iron(III) was adjusted to 2—2.5 by NaOH or HCl and glycine buffer pH = 2.2 (2 ml) was added. The aqueous solution was shaken for 2 min with 5 ml of 0.01 M HX in chloroform. The phases were separated and the chloroform solution was transferred into a 10 ml volumetric flask. The remaining aqueous phase was shaken with *ca.* 3 ml of chloroform, and this extract was transferred to the same volumetric flask. The solution was filled to volume with chloroform and absorbance measured at 420 or 470 nm.

Isolation of iron(III) extracted species

The iron(III) extracted species was obtained by shaking a chloroform solution of the reagent (0.05 M) with an equal volume iron(III) solution at pH ≈ 2.2. Iron was in excess of the reagent. The organic phase was separated and the solvent evaporated in vacuo. The solid product was recrystallized from chloroform-ligroin mixture (1 : 2) and analyzed.

Anal. $C_{36}H_{30}O_6N_3Fe$ (656.47) Calc'd.: C 65.86; H 4.61; N 6.40; Fe 8.51%
Found: C 65.10; H 4.41; N 6.32; Fe 7.90%

RESULTS AND DISCUSSION

The iron(III)-HX complexes formed in the aqueous phase

When a solution of the reagent in ethanol is gradually added to a moderately acidic solution of iron(III), a violet colour appears, which changes to orange-red and finally to orange-yellow.

In order to study these effects quantitatively a series of solutions were prepared in which the molar ratios of iron to reagent were 1 : 1, 1 : 2, 1 : 3, 1 : 6 and 1 : 10, respectively, and visible spectra of these solutions at varied pH were recorded. Results of these measurements presented in Table I indicate, that, in water-ethanol solution iron(III) and HX form different complexes depending on both the iron-HX concentration ratio and the pH of the solution, respectively.

At $0.6 \leqslant pH \leqslant 1.5$ a violet complex with absorption maximum at 570 nm was formed. The formation of this complex was independent of the iron--reagent concentration ratio. At $pH > 1.5$ the composition of the complex depends on both the iron-reagent concentration ratio and on the pH of the solution, respectively.

TABLE I

The dependence of λ_{max} on Fe(III)-HX molar ratio at varied pH. Concentration of iron(III): 10^{-4} M.

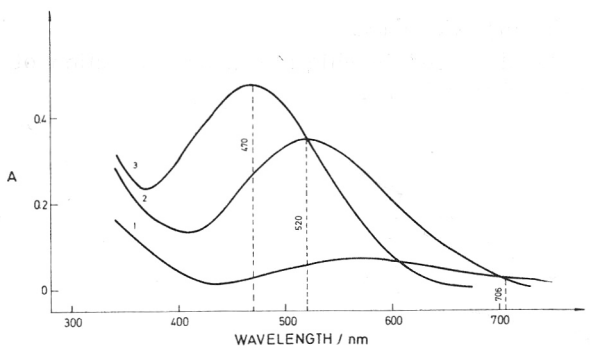
pH	λ_{max}/nm				
	[Fe] : [HX] 1 : 1	[Fe] : [HX] 1 : 2	[Fe] : [HX] 1 : 3	[Fe] : [HX] 1 : 6	[Fe] : [HX] 1 : 10
0.3			colourless		
0.6	570	570	570	570	570
1.0	570	570	570	570	570
1.5	565	560	560	560	560
2.0	560	540	515	510	510
2.5	555	510	505	505	500
3.0	555	505	505	490	480
3.5	530	505	490	480	470
4.0	510	490	470	470	470
4.5	490	480	470	470	470
5.0	480	475	470	470	470

The composition of the complexes formed in the aqueous solution at different pH was determined by (modified) Job's method[9–11]. Series of isomolar solutions containing Fe(III) and HX at pH = 1.0, 2.5 and 4.0, respectively, were prepared and their absorption was measured at 470, 520 and 706 nm, respectively (Fig. 1).

The results of these measurements are given in Figs. 2—4 together with the corrected Y curves[9].

They indicate the existence of three complexes at pH = 2.5 and 4.0: FeX^{2+}, FeX_2^{+} and FeX_3. At pH = 1.0 only a violet complex FeX^{2+} with absorption maximum at 570 nm is formed. The existence of the FeX^{2+} complex only at pH = 1 was also proved by the method of Harvey and Manning[12] (Fig. 5).

At pH > 1.5 three complexes are always present in solution. With an increase of the pH in solution and the initial iron(III)-HX concentration ratio,



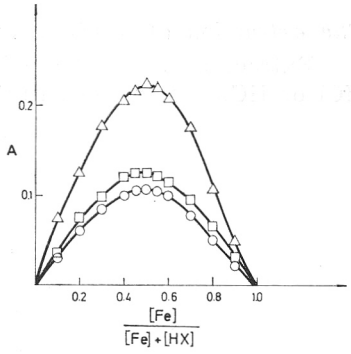


Fig. 1. Absorption spectra of iron (III)-HX complexes in aqueous solution containing 20% ethanol. Concn. Fe (III) : 1×10^{-4} M, concn. HX : 1×10^{-4} M, pH = 1.0 (1), concn. HX : 2×10^{-4} M, pH = 2.5 (2) and concn. HX : 3×10^{-4} M, pH = 4.0 (3).

Fig. 2. Determination of iron (III)-HX complexes in aqueous solution containing 20% ethanol at pH = 1. [Fe] + [HX] = 5×10^{-4} M, λ = 470 nm (○), 520 nm (△) and 706 nm (□).

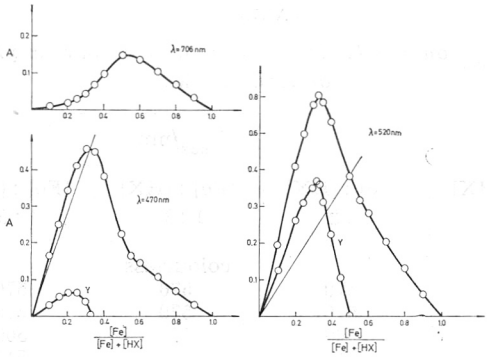


Fig. 3. Determination of iron (III)-HX complexes in aqueous solution containing 20% ethanol at pH = 2.5 [Fe] + [HX] = 5×10^{-4} M. Upper curve: experimental values; lower (Y) curve: corrected values.

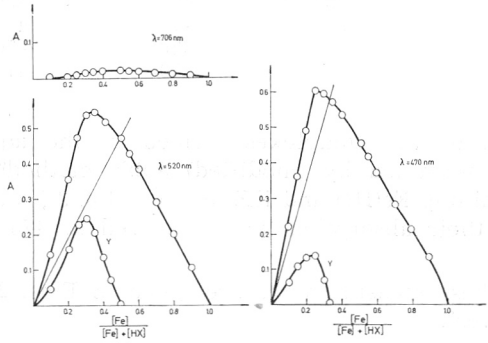


Fig. 4. Determination of iron (III)-HX complex in aqueous solution containing 20% ethanol at pH 4.0 [Fe] + [HX] = 5×10^{-4} M, Upper curve; experimental values; lower (Y) curve: corrected values.

respectively, the concentration of FeX_2^+ and FeX_3 increase. At a higher iron(III)--HX concentration ratio and at pH $>$ 2.5, the orange-yellow FeX_3 complex with absorption maximum at 470 nm is practically the only species present in the solution.

The extraction of iron(III) into the organic phase

Extraction of iron(III) with HX dissolved in chloroform as a function of HCl or $HClO_4$ acid concentration is shown in Fig. 6.

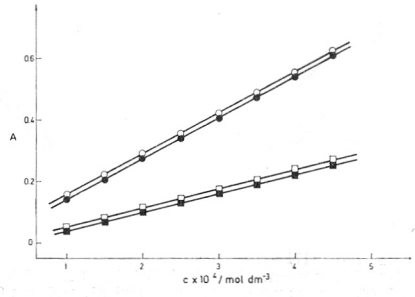
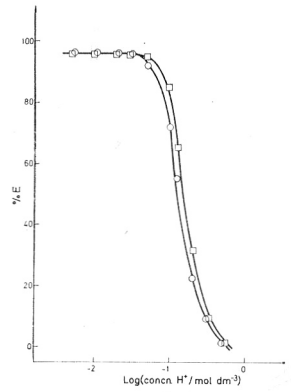


Fig. 5. Determination of complex composition by slope-ratio method at pH = 1.0. Concn. HX 5×10^{-4} M, concn. Fe (III) is varied, λ = 570 nm (○) and 470 nm (□). Cocn. Fe (111), 5×10^{-4} M, concn. HX is varied, λ = 570 nm (●) and 4707 nm (■).

At pH $>$ 1.5 iron(III) is 97% extracted. By increasing the acid concentration, the extraction of iron decreases and at 1 M acid practically all the iron remains in the aqueous phase. D_{Fe} is inversely third-power dependent upon the hydrogen ion concentration in the aqueous phase (Fig. 7) indicating that three protons are released on formation of an extractable complex.



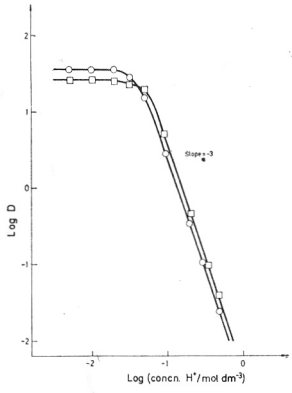


Fig. 6. Extraction dependence of iron (III) on the concentration of HCl (O) and $HClO_4$ (□). Concn. Fe (III) 1×10^{-4} M, concn. HX 5×10^{-3} M.

Fig. 7. The dependende of distribution ratio, D, of iron (III) on the concentration of HCl (O) and $HClO_4$ (□). Concn. Fe (III) 1×10^{-4} M, concn. HX 5×10^{-3} M.

The visible spectrum of the extracted complex in chloroform has two maxima: at 420 and 470 nm (Fig. 8).

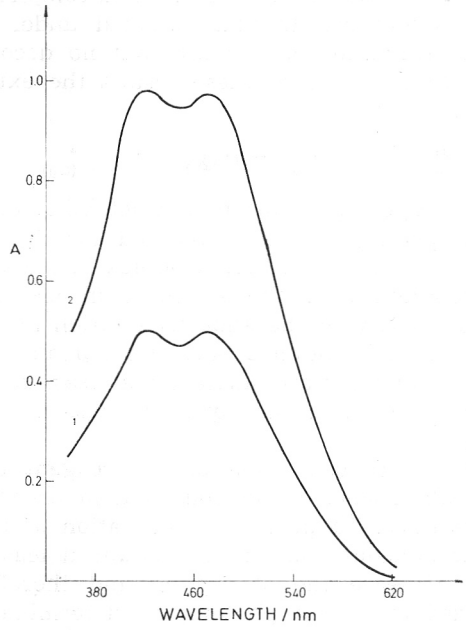


Fig. 8. Absorption spectrum of iron (III)-HX complex in chloroform. Concn. HX 5×10^{-3} M, concn. Fe (III) 8×10^{-5} M (1) and 1.6×10^{-4} M (2).

The composition of this complex was also determined spectrophotometrically by Job's method of continuous variations (Fig. 9). The results obtained show that only the FeX_3 complex is extracted into chloroform.

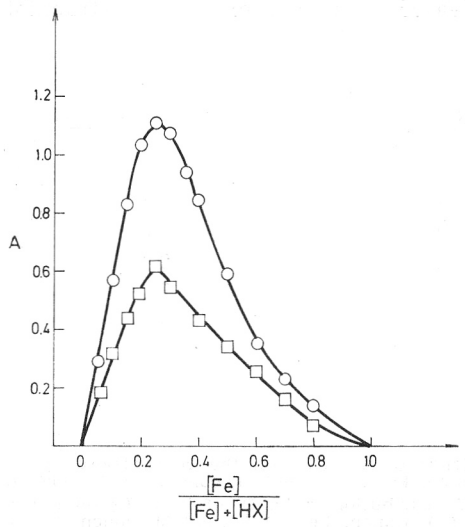


Fig. 9. Determination of complex composition in chloroform by Job's method. [Fe] + [HX] = $= 1 \times 10^{-3}$ M, $\lambda = 420$ nm 470 nm (○) and [Fe] + [HX] = 6×10^{-4} M, $\lambda = 420$ and 470 nm (□).

The quantitative analysis of the complex isolated from the organic phase was consistent with the formula FeX_3. If the isolated complex is dissolved again, the visible spectrum is identical to that obtained under the conditions for spectrophotometric determination confirming that no decomposition occurred during the isolation. On the basis of these results the extraction mechanism can be represented as:

$$Fe^{3+}_{(aq)} + 3\,HX_{(o)} \rightleftarrows FeX_{3(o)} + 3\,H^{+}_{(aq)}$$

The formation of the FeX_3 complex and its extractability into chloroform were utilized to develop a spectrophotometric method for the quantitative determination of iron. The solution of the FeX_3 complex in the aqueous and organic phases obeys Lambert-Beer's law. The optimal iron concentrations are 1—10 μg/ml. The molar absorptivity in the aqueous solution at 470 nm amounts to 6100, and in the chloroform solution at 420 and 470 nm, it amounts to 6300. The absorbances of the solutions are stable for at least several days. Optimal pH for the formation of FeX_3 in the aqueous phase is 2.5—3.0 and for the extraction is 1.5—2.7.

The influence of the concentration of the reagent on absorbance was established. Constant absorbance in aqueous and in organic phase occurs at molar ratio Fe : HX = 1 : 30. To prevent precipitation of the reagent as well as of the complex, the aqueous phase must contain at least 10% ethanol. The quantity of ethanol influence the absorption and therefore the extraction method is recommended for spectrophotometric determination. The influence of various ions on the spectrophotometric determination of iron by extraction is shown in Tables II and III.

TABLE II

Influence of anions on the spectrophotometric determination of iron(III). Concentration of iron(III): 5×10^{-5} M, *HX:* 3.5×10^{-3} *M.*

Anion	Iron-anion molar ratio	Absorbance at 420 nm	Absorbance at 470 nm
—	—	0.315	0.314
Nitrate	1 : 10000	0.314	0.313
Sulphate	1 : 10000	0.313	0.313
Chloride	1 : 10000	0.312	0.312
Acetate	1 : 10000	0.311	0.310
Tartrate	1 : 10000	0.313	0.312
Perchlorate	1 : 10000	0.310	0.309
Citrate	1 : 10000	0.306	0.305
Phosphate	1 : 10000	0.315	0.314
Fluoride	1 : 1000	0.236	0.235
	1 : 100	0.296	0.296
	1 : 10	0.298	0.297
Cyanide	1 : 200	0.267	0.265
	1 : 100	0.297	0.296
	1 : 10	0.307	0.305
Oxalate	1 : 200	0.265	0.264
	1 : 100	0.298	0.299
	1 : 10	0.300	0.299

TABLE III

Influence of cations on the spectrophotometric determination of iron(III). Concentration of iron(III): $5 \times ^{-5}$ M, *HX:* 3.5×10^{-3} M.

Cation	Iron-cation molar ratio	Absorbance at 420 nm	Absorbance at 470 nm
—	—	0.315	0.314
K (I)	1 : 10000	0.315	0.314
Na (I)	1 : 10000	0.314	0.313
NH_4^+	1 : 10000	0.312	0.311
Co (II)	1 : 5000	0.315	0.314
Zn (II)	1 : 5000	0.314	0.313
Al (III)	1 : 5000	0.315	0.314
Mn (II)	1 : 5000	0.314	0.312
Ni (II)	1 : 5000	0.314	0.312
Ca (II)	1 : 5000	0.312	0.311
Cd (II)	1 : 5000	0.313	0.311
Cr (III)	1 : 5000	0.314	0.312
Mg (II)	1 : 5000	0.313	0.312
Ba (II)	1 : 5000	0.315	0.314
Pb (II)	1 : 5000	0.330	0.313
Cu (II)	1 : 5000	0.550	0.380
U (VI)	1 : 10	0.608	0.427
	1 : 1	0.352	0.319
Ti (IV)	1 : 1	0.457	0.346
V (V)	1 : 1	0.446	0.448
Mo (VI)	1 : 100	0.720	0.033
Ta (V)	1 : 1	0.008	0.003
Nb (V)	1 : 1	0.312	0.311
Ga (III)	1 : 1	0.310	0.309
Zr (IV)	1 : 1	0.314	0.313

The results obtained show that nitrates, sulphates, chlorides, acetates, tartrates, perchlorates, citrates and phosphates do not interfere; while fluorides, cyanides and oxalates interfere only if present in higher concentrations. The majority of cations do not react with HX and have no influence on the determination of iron. U(VI), Ti(IV), V(V), Mo(VI), Ta(V) and Cu(II) interfere in the determination of iron. Nb(V), Ga(III) and Zr(IV) are extracted with HX forming colourless complexes. In those cases an amount of HX sufficient for the complete extraction of iron should be added.

The reproducibility of the method, expressed as standard deviation is 0.2%—2%, depending on the iron concentration.

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IZVOD

Ekstrakcija i spektrofotometrijsko određivanje željeza(III) 1-fenil-2-metil-3-hidroksi-4-piridonom

B. Tamhina i M. J. Herak

Opisana je ekstrakcija i spektrofotometrijsko određivanje željeza(III) 1-fenil-2-metil-3-hidroksi-4-piridonom (HX). Željezo(III) se 97% ekstrahira kod pH > 1.5. Kvantitativna reekstrakcija željeza iz organske faze postiže se mućkanjem s kiselinama veće koncentracije od 1 M. Sastav željezo(III)-HX kompleksa u organskoj fazi ispitan je spektrofotometrijski, radiometrijski i kvantitativnom analizom izoliranog kompleksa u čvrstom stanju.

U vodenoj otopini željezo(III) s HX stvara tri različita kompleksa ovisno o početnom molarnom omjeru koncentracija željeza(III) i reagensa i o pH otopine. Nastaju slijedeći kompleksi: ljubičasti FeX^{2+}, narančastocrveni FeX_2^+ i narančastožuti FeX_3. Od navedenih kompleksa samo se FeX_3 ekstrahira u organsku fazu.

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