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Original Scientific Paper

Application of 1-(4-Tolyl)-2-methyl-3-hydroxy-4-pyridone for the Extraction and Spectrophotometric Determination of Iron(III)

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The application of 1-(4-tolyl)-2-methyl-3-hydroxy-4-pyridone (HY) to the extraction and spectrophotometric determination of iron(III) are described.

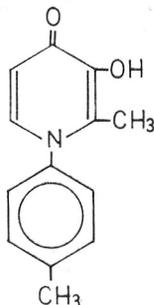
In the aqueous phase iron(III) and HY form two different complexes; FeY^{2+} and FeY_2^+ , depending on the iron—HY concentration ratio and the pH of the solution. It was found that only the FeY_2^+ complex is extracted into chloroform.

INTRODUCTION

In our previous publications¹⁻⁷, the application of 2-carbethoxy-5-hydroxy-1-(4-tolyl)-4-pyridone and 1-phenyl-2-methyl-3-hydroxy-4-pyridone to the extraction and spectrophotometric determination of niobium(V), tantalum(V), zirconium(IV), thorium(IV), protactinium(V), gallium(III), vanadium(V) and iron(III) were described.

While the above-cited reagents form three different complexes with iron(III) in the aqueous phase, the new reagent, 1-(4-tolyl)-2-methyl-3-hydroxy-4-pyridone (HY), forms only two complexes. The formation and properties of these complexes and the application of this new reagent for the extraction and spectrophotometric determination of iron(III) are described in this paper.

This reagent is very selective for the extraction and spectrophotometric determination of certain metals⁸ and its synthesis is very simple.



1-(4-Tolyl)-2-methyl-3-hydroxy-4-pyridone

EXPERIMENTAL

Reagents

The synthesis and physical properties of 1-(4-tolyl)-2-methyl-3-hydroxy-4-pyridone were described previously⁹. Radionuclides ^{55,59}Fe (Institute »Boris Kidrič«,

Vinča, Yugoslavia) in chloride form were used to study the extraction. The inactive iron(III) solution was standardized gravimetrically. 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

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 of the iron(III) solution at pH about 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. C₂₆H₂₄O₄N₂ClFe (519.78) calc'd: C 60.07; H 4.66; N 5.39; Cl 6.82; Fe 10.75%.
found: C 60.58; H 4.70; N 5.43; Cl 6.68; Fe 10.45%.

Procedure for the spectrophotometric determination of iron(III)

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 a glycooll buffer pH 2.2 (2 ml) was added. The aqueous solution was shaken for 2 min. with 5 ml of 5×10^{-3} M HY 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 transferred to the same volumetric flask. The solution was filled to volume with chloroform and absorbance measured at 418 or 465 nm.

RESULTS AND DISCUSSION

Iron(III) reacted in a moderately acidic solution with HY in 50% ethanol. Gradually a violet colour appears, which changes to orange-yellow. These effects were studied spectrophotometrically and results of these measurements are given in Table I. They indicate that, in a water—ethanol solution

TABLE I

The dependence of λ_{\max} on Fe(III)—HY molar ratio at varied pH.
Concentration of iron(III) is 1×10^{-4} M

pH	λ_{\max}/nm			
	[Fe] : [HY] 1 : 1	[Fe] : [HY] 1 : 2	[Fe] : [HY] 1 : 3	[Fe] : [HY] 1 : 10
0.2	colourless			
0.5	575	575	575	575
1.0	575	575	575	579
1.5	572	570	560	560
2.0	570	530	525	520
2.5	560	520	520	490
3.0	560	520	510	480
3.5	520	510	480	470
5.0	480	470	470	470

iron(III) and HY form different complexes depending on the iron-HY concentration ratio and the pH of the solution. The composition of these complexes was determined by a modification of Job's method¹⁰⁻¹² and by the Harvey and Manning's method¹³. Obtained results indicate the existence of two complexes: FeY^{2+} and FeY_2^+ . At pH = 1.0 only a violet complex FeY^{2+} , with absorption maximum at 575 nm is formed. At pH higher than 1.5, two complexes are always present in solution. With an increase of the pH in solution and the initial HY-iron concentration ratio, the concentration of HY_2^+ increase. At a higher HY-iron concentration ratio and at pH higher than 2.5, the orange-yellow FeY_2^+ complex with absorption maximum at 470 nm is practically the only species present in the solution.

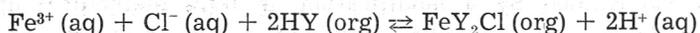
The extraction of iron(III) with HY in chloroform was studied spectrophotometrically and radiometrically. The results of these determinations show that the optimal pH for the extraction is 1.8—2.6. Quantitative back-extraction of iron was carried out with a 5 M concentration of HCl, HNO_3 or HClO_4 . The visible spectrum of the extracted complex in chloroform has two maxima, at 418 and 465 nm. The composition of the iron extractable complex was studied spectrophotometrically by Job's method and by the dependence of the iron distribution ratio, D , on the HY concentration in the organic phase. A curve with a slope of 2 was obtained, indicating that two molecules of the reagent are bound to one atom of iron.

TABLE II

*Influence of anions on the spectrophotometric determination of iron(III).
Concentration of iron(III) 5×10^{-5} M, HY 2.5×10^{-3} M.*

Anion	Iron-anion molar ratio	Absorbance at 418 nm	Absorbance at 465 nm
—	—	0.306	0.308
Nitrate	1 : 10000	0.306	0.307
Sulphate	1 : 10000	0.308	0.308
Chloride	1 : 10000	0.307	0.308
Phosphate	1 : 10000	0.310	0.307
Perchlorate	1 : 10000	0.307	0.307
Citrate	1 : 10000	0.265	0.266
	1 : 1000	0.305	0.307
Tartarate	1 : 10000	0.269	0.269
	1 : 1000	0.302	0.303
Acetate	1 : 10000	0.265	0.266
	1 : 1000	0.298	0.297
	1 : 100	0.306	0.307
Fluoride	1 : 1000	0.296	0.298
	1 : 100	0.307	0.308
Bromide	1 : 1000	0.303	0.304
Cyanide	1 : 100	0.260	0.261
	1 : 10	0.275	0.277
	1 : 1	0.292	0.292
Oxalate	1 : 100	0.084	0.083
	1 : 10	0.272	0.272
	1 : 1	0.290	0.290

These results show that only the FeY_2^+ complex is extracted into chloroform, and the extraction mechanism can be represented as:



The quantitative analysis of the complex isolated from chloroform was consistent with the formula FeY_2Cl .

The solution of the FeY_2Cl complex in the organic phase obeys Lambert-Beer's law. The optimal iron concentrations are 1–10 $\mu\text{g}/\text{ml}$. The molar absorptivity amounts to 6120 at 418 and 465 nm. The absorbance of the solutions are stable for at least several days. Constant absorbance occurs at molar ratio $\text{Fe}:\text{HY} = 1:10$. The reproducibility of the method, expressed by standard deviation is 0.2–2% depending on the iron concentration. The influence of various ions on the spectrophotometric determination of iron by HY is shown in Table II and III. The majority of cations and anions have no influence on the determination of iron. Nb(V), Zr(IV) and Ga(III) are extracted with HY forming colourless complexes. In those cases an amount of HY sufficient for the complete extraction of iron should be added. U(VI), Ti(IV), V(V), Mo(VI), Ta(V), cyanide and oxalate interfere in the determination of iron.

TABLE III

*Influence of cations on the spectrophotometric determination of iron(III).
Concentration of iron(III) 5×10^{-5} M, HY 2.5×10^{-3} M.*

Cation	Iron-cation molar ratio	Absorbance at 418 nm	Absorbance at 465 nm
—	—	0.306	0.308
Na(I)	1 : 10000	0.306	0.308
K(I)	1 : 10000	0.310	0.311
NH_4^+	1 : 10000	0.310	0.310
Mg(II)	1 : 10000	0.306	0.307
Ca(II)	1 : 10000	0.307	0.308
Ni(II)	1 : 10000	0.306	0.306
Al(III)	1 : 10000	0.307	0.307
Cd(II)	1 : 10000	0.305	0.306
Ba(II)	1 : 10000	0.302	0.304
Mn(II)	1 : 5000	0.310	0.311
Zn(II)	1 : 5000	0.309	0.310
Co(II)	1 : 10000	0.310	0.309
Cr(III)	1 : 1000	0.315	0.315
Cu(II)	1 : 1000	0.492	0.369
	1 : 100	0.323	0.325
	1 : 10	0.320	0.315
Pb(II)	1 : 100	0.301	0.303
Mo(VI)	1 : 10	0.645	0.032
U(VI)	1 : 1	0.406	0.380
Ti(IV)	1 : 1	0.890	0.405
V(V)	1 : 1	0.496	0.509
Zr(IV)	1 : 1	0.313	0.311
Nb(V)	1 : 1	0.315	0.309
Ta(V)	1 : 1	0.009	0.007
Ga(III)	1 : 1	0.310	0.308

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SAŽETAK

Primjena 1-(4-tolil)-2-metil-3-hidroksi-4-piridona za ekstrakciju i spektrofotometrijsko određivanje željeza(III)

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Opisana je primjena 1-(4-tolil)-2-metil-3-hidroksi-4-piridona (HY) za ekstrakciju i spektrofotometrijsko određivanje željeza(III). U vodenoj otopini željezo(III) i HY stvaraju dva različita kompleksa; FeY^{2+} i FeY_2^+ , ovisno o molnom omjeru željeza i reagensa i o pH otopine. Utvrđeno je da se u organsku fazu ekstrahira samo kompleks FeY_2^+ .

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