

Some Phenones and their Derivatives as Indicators for Volumetric Determination of Fe(III) with Diethylenetriamine Pentaacetic Acid

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2-Hydroxy-4-n-butoxyacetophenone, 2-hydroxy-4-n-butoxypropiofenone, 2-hydroxy-4-n-butoxy-5-nitroacetophenone, 2-hydroxy-4-n-butoxy-5-nitropropiofenone, 2-hydroxy-4-n-butoxyacetophenone ethylenediamine and 2-hydroxy-4-n-butoxyacetophenone thiosemicarbazone have been used as indicators for the direct diethylenetriamine pentaacetic acid (DTPA) titration for Fe(III). Fe(III) can be quantitatively determined with an error of measurement of $\leq \pm 0.4\%$ from solutions containing 280 ppm or more of iron in the pH range 1.5-3.0. A number of diverse ions can be tolerated but Ca^{2+} , Ba^{2+} , Sr^{2+} , Cu^{2+} , Zn^{2+} phosphate, tartrate, vanadate, oxalate and citrate interfered. The indicators can also be used for determination of iron present in pharmaceuticals preparations.

INTRODUCTION

Among earlier methods for the determination of Fe(III), iron mention should be made of the use of mercurous perchlorate, titanous sulphate or chloride and vanadous sulphate as titrants in the direct method and potassium dichromate and sodium thiosulphate as titrants in the indirect determination¹. With the advent of the complexometric methods of volumetric analysis, titrants like ethylenediamine tetraacetic acid (EDTA), diethylenetriamine pentaacetic acid (DTPA), nitrilo triacetic acid (NTA), ethyleneglycol bis-(β -aminoethylether)-tetraacetic acid (EGTA), cyclohexane diaminotetraacetic acid (DCyTA), etc. have been employed making use of varamine blue-B, ferron, 8-quinolinol, salicylic acid, *o*-cresotic acid etc., as indicators^{1,2}. Of late substituted 2-hydroxy phenones and their oximes, anils, chalcones as well as thiosemicarbazones have been suggested as indicators in the complexometric titration of Fe(III)³⁻¹⁶.

In earlier communications^{17, 18} 2-hydroxy-4-n-butoxyacetophenone (HBA) and 2-hydroxy-4-n-butoxypropiofenone (HBP) have been reported as reagents for spectrophotometric determination of Fe(III). The use of HBP as an indicator for the volumetric determination of Fe(III) with EDTA has also been reported¹⁹. In the present work phenones like HBA and HBP and their derivatives such as 2-hydroxy-4-n-butoxy-5-nitroacetophenone (HBNA) 2-hydroxy-4-n-butoxy-5-nitropropiofenone (HBNP), 2-hydroxy-4-n-butoxyacetophenone ethylenediamine (HBAE) and 2-hydroxy-4-n-butoxyacetophenone thiosemicarbazone (HBAT) have been described as visual indicators for the complexometric titration of Fe(III) with DTPA.

EXPERIMENTAL

All the chemicals used were of A.R./B.P. grade and recrystallized wherever necessary. Double distilled water was used throughout the experiment. A 0.1 M stock solution of Fe(III) was prepared by dissolving ferric ammonium sulphate (A.R.) in distilled water containing 1–2 mL of nitric acid. The amount of Fe(III) in this solution was determined volumetrically with EDTA¹ using varamine blue-B as an indicator and gravimetrically with cupferron¹. A stock solution of 0.1 M DTPA was prepared by weighing 9.83 g of DTPA, dissolving in 100 mL 0.5 M sodium hydroxide and finally diluting the solution to 250 mL with distilled water. Each of the indicators was synthesised from resorcinol following standard procedures²⁰. A 1% solution of the indicator in methanol was prepared by dissolving the recrystallized compound.

Titration Procedure

An aliquot of Fe(III) was taken in a standard measuring flask, and distilled water, methanol and a few drops of dilute nitric acid were added to it in such a way that the final solution after dilution to the mark was 60% in methanol and had a predetermined pH. 5 mL of this diluted solution were taken in a conical flask, two drops of 1% indicator solution in methanol were added and the solution titrated with 0.01 M DTPA. A sharp colour change was observed at the equivalence point in the case of the indicators as shown below:

<i>Indicator</i>	<i>Colour change at the equivalence point</i>
HBA	Reddish violet to pale yellow
HBP	Reddish violet to pale yellow
HBNA	Red to pale yellow
HBNP	Red to pale yellow
HBAE	Reddish violet to pale yellow
HBAT	Brown to pale yellow

In the case of chalcone (HBA with *p*-anisaldehyde) and its oxime the colour change was not so sharp and the results appeared to be lower by about 5%.

RESULTS AND DISCUSSION

Results are given in Tables 1–4.

pH for titration

To determine the pH range or exact pH for volumetric determination of iron with DTPA using HBA, HBP, HBNA, HBNP, HBAE and HBAT as indicators, titrations were carried out at pH values ranging from 1.0 to 3.0. At pH higher than 3.0 the complex appeared to decompose as indicated by the disappearance of the colour. At pH higher than 5.0 a slight turbidity appeared, perhaps due to the precipitation of ferric hydroxide. From the results given in Table-1, it is apparent that except HBNA and HBNP all the compounds used as indicators give satisfactory results (error = $\pm 0.36\%$) in the pH range 1.0 to 3.0. As the error was

higher in the range 1.0 to 1.25 in the case of HBNA and HBNP, a pH of 2.0 was selected for further work.

TABLE-1
EFFECT OF pH ON VOLUMETRIC DETERMINATION OF Fe(III) WITH DTPA USING DIFFERENT INDICATORS [Fe(III) taken: 2.79 mg in 5 mL solution]

pH	HBA Fe(III) found, mg (Error %)	HBP Fe(III) found, mg (Error %)	HBNA Fe(III) found, mg (Error %)	HBNP Fe(III) found, mg (Error %)	HBAE Fe(III) found, mg (Error %)	HBAT Fe(III) found, mg (Error %)
1.00	2.80 (0.36)	2.79 (0.00)	2.83 (1.43)	2.85 (2.15)	2.78 (-0.36)	2.79 (0.00)
1.25	2.79 (0.00)	2.79 (0.00)	2.77 (0.72)	2.78 (-0.36)	2.79 (0.00)	2.80 (0.36)
1.50	2.79 (0.00)	2.80 (0.36)	2.79 (0.00)	2.79 (0.00)	2.80 (0.36)	2.78 (-0.36)
2.00	2.80 (0.36)	2.80 (0.36)	2.80 (0.36)	2.79 (0.00)	2.79 (0.00)	2.79 (0.00)
2.50	2.79 (0.00)	2.80 (0.36)	2.80 (0.36)	2.80 (0.36)	2.80 (0.36)	2.79 (0.00)
3.00	2.79 (0.00)	2.79 (0.00)	2.80 (0.36)	2.79 (0.00)	2.79 (0.00)	2.80 (0.36)

TABLE-2
EFFECT OF IRON CONCENTRATION ON THE VOLUMETRIC DETERMINATION OF Fe(III) WITH DTPA
(pH for titration: 2.0)

Indicator	Fe(III) taken in 5 mL solution. (ppm)							
	2792.5 (558.5 ppm)		1396.3 (279.3 ppm)		279.3 (55.9 ppm)		139.6 (27.9 ppm)	
	Fe(III) found, g	Error %	Fe(III) found, g	Error %	Fe(III) found, g	Error %	Fe(III) found, g	Error %
HBA	2792.5	0.00	1401.8	0.40	281.5	0.80	141.3	1.20
HBP	2803.7	0.40	1396.3	0.00	280.4	0.40	141.9	1.60
HBNA	2803.7	0.40	1407.4	0.80	282.6	1.20	144.1	3.20
HBNP	2792.5	0.00	1401.8	0.40	283.7	1.60	145.2	4.00
HNAE	2792.5	0.00	1396.3	0.00	280.4	0.40	140.2	0.40
HBAT	2803.7	0.40	1401.8	0.40	279.3	0.00	140.8	0.80

TABLE-3
REPRODUCIBILITY OF THE RESULTS

Indicator	Average Fe(III) found* mg	Average error %	Standard deviation
HBA	2.79	0.12	0.01
HBP	2.80	0.18	0.01
HBNA	2.80	0.18	0.01
HBNP	2.80	0.24	0.02
HBAE	2.80	0.18	0.01
HBAT	2.79	-0.06	0.01

*Average of six determinations.

TABLE-4
DETERMINATION OF IRON FROM PHARMACEUTICAL PREPARATIONS

Indicator	Pharmaceutical Preparation			
	A (Iron present, 3.013 mg)		B (Iron present, 3.01 mg)	
	Iron found mg	Error %	Iron found mg	Error %
HBA	3.028	0.50	3.009	-0.13
HBP	2.020	0.23	3.031	0.60
HBNA	2.994	-0.63	3.039	0.86
HBNP	2.998	-0.50	3.020	0.86
HBAE	3.009	-0.13	3.020	0.23
HBAT	3.013	0.00	3.006	-0.23

Effect of Fe(III) concentration

To determine the feasibility of the method for determination of iron from aqueous solution of different concentrations, titrations were performed using 5 mL of aqueous solutions containing from 27.9 to 5588.5 ppm of iron. From the results given in Table-2, it may be generalised that Fe(III) can be quantitatively determined (error $\leq \pm 0.4\%$) by titration with DTPA from solutions containing approximately 280 ppm or more of iron making use of the suggested indicators. Further, HBAE could be used at concentrations as low as 28 ppm, while HBP is useful at concentrations of 55 ppm or higher. From the values of % error given in Table-2, it can also be generalised that the efficiencies of the various indicators studied increase in the order:



Effect of indicator concentration

To ascertain the effect of indicator concentration on the titre value, titrations were carried out by adding 1, 2 or 3 drops of 1% indicator to the Fe(III) solution. The results (not reported here) show that best results could be obtained by adding two drops of any of the indicators suggested.

Effect of temperature

To study the effect of temperature on the feasibility of the method, titrations were carried out in different temperature ranges like 5–10°C, 30–35°C, 40–45°C and 50–55°C. It was found that the indicator and that way the method works quite efficiently in the range 5–55°C with an error of measurement of $\pm 0.4\%$.

Reproducibility of method

To determine the reproducibility of the method six replicate determinations were carried out using the same concentration of Fe(III) and DTPA solutions. The average error (%) and the standard deviation calculated are given in Table-3. From the data it is apparent that about 2.79 mg of iron can be quantitatively determined by titration with DTPA making use of these indicators with an average error of $\leq 0.24\%$. The standard deviation was found to be 0.01 mg for each of the indicators except HBNP, which showed $\sigma = 0.02$.

Effect of diverse ions

The interference due to the presence of other ions on the determination of ferric ions has also been studied using the suggested indicators. A difference of more than 1.5% in the results has been considered as interference. According to this criterion, the tolerance limits of various ions, expressed in mg, for a solution containing 2.79 mg Fe(III) are as follows.

500 mg: Na^+ , K^+ , NH_4^+ , NO_3^- , SO_4^{2-} , CH_3COO^- ;

100 mg: Fe^{2+} , Pd^{2+}

50 mg: Ag^+ ;

10 mg: Cd^{2+} , Al^{3+} , Co^{2+} , Ni^{2+} , Cr^{3+} ;

5 mg: Ca^{2+} , Ba^{2+} , Sr^{2+} , Cu^{2+} , Zn^{2+} .

PO_4^{3-} , tartrate, vanadate, oxalate and citrate interfere at all levels.

Fe(III) could also be satisfactorily determined from synthetic mixtures containing Fe^{3+} , Pd^{2+} and Cr^{3+} ; Fe^{3+} , Na^+ , Ni^{2+} and Ca^{2+} and also Fe^{3+} , K^+ , Cu^{2+} and Ag^+ .

Determination of iron from pharmaceutical preparations

To determine the usefulness of the various indicators in estimating iron from various pharmaceutical preparations, capsules/tablets containing iron as ferrous sulphate were taken and their iron content was determined by volumetric titration with DTPA using these indicators. For this purpose a known weight of the sample was taken, about 5 mL concentrated nitric acid was added and the mixture was

evaporated to dryness. The residue was dissolved in distilled water containing a drop or two of nitric acid and filtered. The filtrate was diluted to 50 mL. 5 mL of this diluted solution was titrated as described before. The results given in Table-4 show that the amount of iron present in pharmaceutical preparations can be calculated with an error of measurement of $\leq \pm 0.86\%$ with each of these indicators.

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