The Complexometric Estimation of Ferric Iron

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(Received March 17, 1964)

1, 2-Diaminocyclohexane-*N*, *N*, *N'*, *N'*-tetraacetic acid (CyDTA) forms a very stable 1 : 1 complex with ferric iron, and the complex serves as a basis for the complexometric determination of this metal. Přibil[1] used salicylic acid as an indicator for the complexometric determination of iron(III) with CyDTA (disodium salt). Martinez and Mendoza[2] suggested the use of sulphosalicylic acid, tiron and potassium thiocyanate as indicators for the determination of ferric iron with CyDTA at pH values from 2 to 5 and at a temperature of 50°C, but they found that the results were 1 to 5 per cent too high. Přibil and Sir[3] determined iron(III) in the presence of aluminium and titanium in a weakly alkaline pyridine solution by masking aluminium and titanium with a two per cent solution of ammonium fluoride. An excess of CyDTA was added and back titrated with zinc chloride or zinc sulphate, using Eriochrome Black T as an indicator. Martinez and Mendoza[4] have also determined ferric iron photometrically with CyDTA at pH 4. Koroz and Poczoc[5] estimated iron(III) in the presence of calcium and magnesium, with sulphosalicylic acid as an indicator, at pH values from 2 to 3 at 60°C.

No more evidence is available in the literature for the determination of ferric iron with

1) R. Přibil, *Chem. Listy*, **49**, 179 (1955).
2) F. B. Martinez and R. Rey Mendoza, *Quim. e. Ind., Bilbao*, **6** (1), 3 (1959).
3) R. Přibil and Z. Sir, *Coll. Czechslov. Chem. Communs.*, **20**, 871 (1955).
4) F. B. Martinez and R. R. Mendoza, *Chemist-Analyst*, **47**, 94 (1958).
5) E. Koros and I. Poczoc, *Magyar Kem. Foly*, **64**, 7, 250 (1958).

CyDTA. In the present work, an attempt has been made to determine ferric iron alone as well as in the presence of various metal ions by titration with CyDTA (disodium salt), using pyrocatechol violet at pH 3.09 or *p*-anisidine-thiocyanate at pH 4.2 as an indicator. The end point of the complexometric titration in both cases is very sharp, and there is no dragging of indicator colour near the end point. The titrations can be successfully made at room temperature.

Experimental

The Preparation of Standard CyDTA (Disodium Salt). — 0.05 M CyDTA (disodium salt) was prepared by dissolving 35.45 g. of CyDTA in 400 ml. of boiling 0.5 N sodium hydroxide and diluting it to two litres in metal-free distilled water. This was further diluted ten times to prepare 0.005 M CyDTA (disodium salt).

The Preparation of a *p*-Anisidine-thiocyanate Indicator Solution.[6]—9.7175 g. of potassium thiocyanate were dissolved in water, and the volume made to 50 ml. In ethyl alcohol 1.2315 g. of *p*-anisidine were dissolved and the total volume of the solution was made to 50 ml. The two solutions were then mixed together, and the mixture used as *p*-anisidine-thiocyanate indicator.

The Preparation of a Pyrocatechol Violet Indicator Solution.—0.1 g. of pyrocatechol violet was dissolved in distilled water, and its volume made to 100 ml.

Results

The Estimation of Ferric Iron in Presence of Other Metal Ions.—An aliquot of a ferric nitrate solution was taken in a conical flask containing 50 ml. of water, and then 2 to 3 drops of pyrocatechol violet or *p*-anisidine-thiocyanate were added to it. A sodium acetate and hydrochloric acid buffer was added to adjust the pH of the solution to 3.09 or 1.42 respectively. The mixture was titrated with 0.005 M CyDTA (disodium salt). The end

TABLE I. THE TITRATION OF FERRIC IRON WITH 0.005 M 1,2-DIAMINOCYCLOHEXANE-TETRAACETIC ACID (DISODIUM SALT)

Metal salts added		Weight of $Fe(NO_3)_3 \cdot 9H_2O$		
		Taken	Found	
			Pyrocatechol violet indicator	*p*-Anisidine-thiocyanate indicator
	g.	g.	g.	g.
		0.0040	0.0040	0.0040
		0.0202	0.0202	0.0202
$BaCl_2 \cdot 2H_2O$	0.0048	0.0081	0.0081	0.0081
	0.0073	0.0121	0.0121	0.0121
$CaCl_2 \cdot 2H_2O$	0.0058	0.0162	0.0162	0.0162
	0.0073	0.0202	0.0203	0.0203
$Sr(NO_3)_2$	0.0021	0.0040	0.0040	0.0040
	0.0042	0.0081	0.0081	0.0081
$Cr(NO_3)_3 \cdot 9H_2O$	0.0120	0.0121	0.0122	0.0121
	0.0160	0.0162	0.0162	0.0162
$Hg(NO_3)_2 \cdot H_2O$	0.0035	0.0040	0.0041	0.0040
	0.0173	0.0202	0.0202	0.0202
$Th(NO_3)_4 \cdot 4H_2O$	0.0220	0.0162	0.0324	0.0324
	0.0275	0.0202	0.0404	0.0404
NaF	0.0012	0.0121	No end point	No end point
	0.0021	0·0202		
$(NH_4)_2C_2O_4 \cdot H_2O$	0.0056	0.0162	No end point	No end point
	0.0071	0.0202		
$CuSO_4 \cdot 5H_2O$	0.0050	0.0081	No end point	No end point
	0.0125	0.0202		
$Ni(CH_3COO)_2 \cdot 4H_2O$	0.0075	0.0124	No end point	No end point
	0.0099	0.0162		
$CoCl_2 \cdot 6H_2O$	0.0042	0.0081	No end point	No end point
	0.0119	0.0202		
$MnCl_2 \cdot 4H_2O$	0.0054	0.0121	No end point	No end point
	0.0099	0.0201		

6) B. Singh, S. S. Sahota and M. S. Mankotia, *Z. anal. Chem.*, **173**, 275 (1960).

point was marked by a sharp colour change from blue to yellow in the case of pyrocatechol violet and from violet to yellow when *p*-anisidine-thiocyanate was used as the indicator. The titration was then performed in the presence of barium chloride, calcium chloride, strontium nitrate, chromium nitrate, mercuric nitrate, magnesium sulphate, thorium nitrate, sodium fluoride, ammonium oxalate, copper sulphate, nickel acetate, cobalt chloride and manganese chloride respectively. Some typical results are given in Table I.

From the data given in Table I it is evident that ferric iron, alone or in the presence of Ba^{2+}, Ca^{2+}, Sr^{2+}, Cr^{3+}, or Hg^{2+}, can be determined volumetrically by titrating it with a CyDTA (disodium salt) solution, using pyrocatechol violet or *p*-anisidine-thiocyanate as an indicator.

Thorium nitrate interferes in this titration, because CyDTA forms a 1:1 complex with thorium as well as with iron(III); the amount of CyDTA used is, therefore, double that required for the estimation of iron(III). In the presence of sodium fluoride and ammonium oxalate, there is no end point in the complexometric determination of ferric iron with CyDTA (disodium salt) because of the formation of stable complexes of iron fluoride and iron oxalate respectively. Because of the presence of coloured compounds (copper sulphate, cobalt chloride and manganese chloride), no end point was detected in these titrations.

Summary

Ferric iron has been determined, alone or in the presence of Ba^{2+}, Ca^{2+}, Sr^{2+}, Cr^{3+} or Hg^{2+}, by titrating it with CyDTA (disodium salt), using pyrocatechol violet and *p*-anisidine-thiocyanate as indicators at pH 3.09 and 1.42 respectively. Th^{4+}, F^-, $C_2O_4^{2-}$, Cu^{2+}, Ni^{2+}, Co^{2+} and Mn^{2+} have been found to interfere in the complexometric estimation of ferric iron with CyDTA (disodium salt).

The authors wish to take this opportunity to thank the Council of Scientific and Industrial Research (India) for the award of Junior Fellowship to one of them (M. S. M.), thus enabling him to pursue the study of complexometric titrations.

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