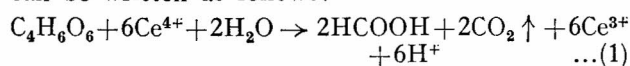


TABLE 1 — ESTIMATION OF BORON

Boron (mg)		Error (%)
Taken	Found	
0.100	0.1014	+1.4
0.2500	0.2540	+1.6
0.500	0.505	+1.0
1.00	1.00	0.0
2.00	2.00	0.0
5.00	5.03	+0.6
10.00	10.22	+2.2

been developed for the precipitation of barium borotartrate complex ($Ba_2B_2C_{16}H_8O_{24}$) as a stoichiometric compound². Bovalini and Piazzzi³ suggested that the barium borotartrate complex contains two moles of tartaric acid per atom of boron. From our previous studies and also the present study, it was found that six equivalents of Ce^{4+} are consumed per mole of tartaric acid, the products being formic acid and carbon dioxide. The oxidation reaction can be written as follows:



The amount of $Ce(IV)$ consumed gives a measure of tartrate ion liberated from the borotartrate complex and indirectly furnishes the amount of borate ion and also boron in boron solutions.

Procedure — Aliquot solutions prepared from recrystallized, fused boric acid, containing 1 mg of boron/ml were taken in a polyethylene beaker. To this solution was added 8-10 volumes of the buffered tartaric acid and the pH adjusted to 8.8. Buffered tartaric acid was prepared by dissolving tartaric acid (AR, 14 g), ammonium chloride (240 g) and $BaCl_2 \cdot 2H_2O$ (13 g) in a litre of solution and aged for 24 hr, filtered and stored in a polyethylene bottle. To facilitate complete precipitation the solutions were thoroughly agitated at room temperature. The precipitated barium borotartrate complex was collected on a Whatman No. 40 filter paper and washed with about 30 ml wash solution (2:1:1, conc. ammonium hydroxide, acetone and water). The precipitate was dissolved in 0.5M nitric acid (50 ml). For oxidation with standard cerate, a measured excess of the 0.1M cerate solution was added with overall 0.5M nitric acid and heated to 55-60° for 30 min. The mixture was cooled, dilute sulphuric acid (5N, 20 ml) added and excess of $Ce(IV)$ back-titrated with iron(II) solution in sulphuric acid with ferroin as indicator. The results obtained are presented in Table 1.

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Salicylic Acid, Sulphosalicylic Acid & Salicylamide as Indicators for Direct Titration of Fe^{3+} with Diethylene Triaminepentaacetic Acid

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Working conditions for the use of salicylic acid, sulphosalicylic acid and salicylamide as indicators for the direct titration of Fe^{3+} with diethylene triaminepentaacetic acid (DTPA) are reported. These indicators give a sharp colour change at the end point and can be used for microtitration of iron, the lowest permissible concentration being 0.056 mg/ml. A large number of diverse ions are tolerated. The procedure has been used for the determination of iron in synthetic solutions, an ore and some pharmaceutical samples.

WHILE a number of substances have been investigated as indicators for the direct EDTA titration of Fe^{3+} , no indicators have been reported for the direct titration of diethylene triaminepentaacetic acid (DTPA) with ferric ions. The present note reports the use of salicylic acid, sulphosalicylic acid and salicylamide as indicators for the direct DTPA titration of ferric ions.

Solutions (0.1M) of ferric nitrate and DTPA were prepared in distilled water. Ethanolic (1%) solutions of the indicators were used. The solutions were stable up to four weeks. Metal salt solutions (0.2M) were used for the study of interference of foreign ions.

Procedure — An aliquot of solution containing ferric ions was taken, the pH was adjusted to 1.0-2.0 and four drops of the indicator solution added. Titration was carried out against standard DTPA solution to a deep yellow end point. Accurate results were obtained in the pH range 1.0-3.0.

Effect of $[Fe^{3+}]$ — Accurate results were obtained in the concentration range $[Fe^{3+}] = 0.01$ to $0.001M$. At 0.005M concentration of Fe^{3+} the end point was not very sharp. However, titration of 1.0 ml of 0.001M ferric nitrate could be accurately performed with a sharp end point. Thus microtitration of ferric ions with DTPA is feasible using these indicators.

Satisfactory results were obtained in the temperature range 0-70°.

Effect of foreign ions — Synthetic solutions containing 2.8 mg of Fe^{3+} were titrated at pH 1.0. It was found that 100-fold excess of Na^+ , K^+ , NH_4^+ , Be^{2+} , UO_2^{2+} , Cl^- , Br^- , ClO_4^- and NO_3^- ; 50-fold excess of SO_4^{2-} ; 20-fold excess of Ba^{2+} , Sr^{2+} , Zn^{2+} , Ca^{2+} , Mg^{2+} , Cd^{2+} , Mn^{2+} , Ni^{2+} , Co^{2+} ; 10-fold excess of Pb^{2+} and Al^{3+} and 5-fold excess of Cr^{3+} could be tolerated. Th^{4+} ; Zr^{3+} , PO_4^{3-} , CO_3^{2-} , F^- and NO_2^- interfere at all levels.

The above procedure was used to estimate iron in synthetic samples. DTPA titrations could tolerate higher amounts of interfering radicals as compared to EDTA titrations under similar conditions (Table 1).

TABLE 1 — COMPARISON OF THE TOLERANCES OF VARIOUS INTERFERING IONS IN THE ESTIMATION OF IRON IN SYNTHETIC MIXTURES USING EDTA AND DTPA AS TITRANTS

{Amount of Fe³⁺ taken = 2.8 mg; pH of titration = 1.0; [titrant] = 0.01M}

EDTA titration		DTPA titration	
Cu ²⁺ (3.16), Ni ²⁺ (14.60)	Cu ²⁺ (15.87), Ni ²⁺ (58.7)	Mn ²⁺ (13.70), Ni ²⁺ (14.60)	Mn ²⁺ (55.00), Ni ²⁺ (58.7)
Cu ²⁺ (3.16), Mn ²⁺ (13.70)	Cu ²⁺ (15.87), Mn ²⁺ (55.0)	Cu ²⁺ (3.16), Zn ²⁺ (6.55)	Cu ²⁺ (15.87), Zn ²⁺ (65.5)
Cu ²⁺ (3.16), Al ³⁺ (13.5)	Cu ²⁺ (15.87), Al ³⁺ (13.5)	Mn ²⁺ (13.7), Al ³⁺ (13.5)	Mn ²⁺ (55.00), Al ³⁺ (27.0)
Cr ³⁺ (2.6), Al ³⁺ (13.5)	Cr ³⁺ (7.8), Al ³⁺ (27.0)	Zn ²⁺ (9.8), Al ³⁺ (13.5)	Zn ²⁺ (65.0), Al ³⁺ (27.0)
Cr ³⁺ (2.6), Mn ²⁺ (5.5)	Cr ³⁺ (5.2), Mn ²⁺ (5.5)	Cu ²⁺ (3.16), Cr ³⁺ (2.6)	Cu ²⁺ (15.87), Cr ³⁺ (7.8)
Cr ³⁺ (2.6), Ni ²⁺ (58.7)	Cr ³⁺ (7.8), Ni ²⁺ (58.7)	Cr ³⁺ (2.6), Co ²⁺ (58.9)	Cr ³⁺ (7.8), Co ²⁺ (58.9)

Figures in parentheses indicate amounts in mg of the interfering ions tolerated.

TABLE 2 — ANALYSIS OF DRUGS CONTAINING IRON BY DIRECT TITRATION WITH DTPA

Name of the drug (mode of occurrence of iron)	Fe (g)			
	Present	Found*	Found†	Found‡
Polycytol tablet (ferrous sulphate)	0.195	0.194	0.194	0.191
Iberol tablet (ferrous sulphate)	0.525	0.522	0.520	0.522
Iberol liquid (ferrous sulphate)	0.131	0.130	0.130	0.130
Ferrolindione tablet (ferrous fumarate)	0.200	0.197	0.197	0.197
Microfer tablet (ferrous gluconate)	0.195	0.194	0.194	0.194
Tonoferon drops (colloidal iron hydroxide)	0.050	0.047	0.047	0.047

*Indicator, salicylic acid.
†Indicator, salicylamide.
‡Indicator, sulphosalicylic acid.

Analysis of pharmaceuticals containing iron — The above procedure was applied to the analysis of pharmaceuticals containing iron in the form of colloidal iron hydroxide, ferrous gluconate, ferrous fumarate or ferrous sulphate. Liquid drugs containing ferrous sulphate or ferric hydroxide were diluted with distilled water, and 2.0 ml of conc. HNO₃ was added. The mixture was heated for 10-15 min and after cooling, diluted to 100 ml.

Tablets or capsules containing ferrous sulphate, ferrous fumarate or ferrous gluconate were treated with 10 ml of conc. HNO₃ and 2 ml of HClO₄. The mixture was evaporated to dryness. The residue was diluted to 50 ml. Aliquots (5 ml) of the dilute solution were used and titration carried out using the general procedure. Results are given in Table 2.

Ore — Hematite ore (1.73 g) was fused with 10.0 g of fusion mixture and treated with conc. HCl. Nitric acid (2 ml) was added to oxidize Fe²⁺ to Fe³⁺, the solution filtered and the filtrate diluted to 1000 ml. An aliquot (5.0 ml) was taken and titration carried out using the general procedure indicated above (Found: Fe₂O₃, 92.4. Expected: Fe₂O₃, 92.3%).

The above results indicate that DTPA is an excellent titrant for the direct titration of ferric ions. A large number of diverse ions are tolerated. The

titration is rapid and colour change at the end point is very sharp.

Among the present indicators salicylamide gives the best results. An important advantage of this indicator is that titration can be carried out at very low pH (1.0-1.5) which is of importance when interfering elements are present. Salicylamide has been previously investigated as an indicator for direct titration of Fe³⁺ with EDTA¹, CyDTA², NTA³ and HEDTA⁴. A comparison of the tolerance of various cations in the determination of Fe³⁺ with EDTA, HEDTA, NTA, CyDTA and DTPA was carried out and it was found that most efficient titrant is DTPA.

This view is confirmed by a comparison of the results of EDTA and DTPA titrations in the presence of various interfering ions. Table 1 clearly shows that DTPA has a greater tolerance than EDTA.

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