Determination of Thallium(I) with Iodate in the Presence of Mercuric Ions and with Iodate and Permanganate via Bromide

By Bechu SHARMA

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Most of the current methods, to determine thallium(I), have certain inherent defects. Willm's method¹⁾ based upon titration of thallium(I) in hydrochloric acid with permanganate has been used extensively, but various authors reported unfavorable results. The procedure used by Marshall²⁾ is tedious. Kolthoff³⁾, Zintl and Rienacher⁴⁾, however, titrated it accurately with bromate in hydrochloric acid using methyl orange as indicator. Willard and Young⁵⁾ determined it against ceric sulfate. Berry⁶⁾ titrated various thallous salts with iodate using iodine monochloride end point and reported low results by about 2%. Swift and Garner⁷⁾ employed iodine monochloride procedure in the determination of thallium(I) with iodate, permanganate and ceric sulfate, but precise results were obtained only with iodate. Recently a general application of the amperometric Dead Stop End Point to direct and indirect determination with iodate in the presence of mercuric ions has been reported. Arsenious oxide and hydrazine sulfate are used as direct primary standards and thiosulfate, thiocyanate and thiourea are determined by excessive iodate⁸⁾. Investigations were therefore carried out to adopt the above procedure (iodate procedure in the presence of mercuric ions) in the determination of thallium. Oxidation titration of hydrazine sulfate with permanganate and ceric sulfate in hydrochloric acid via bromide has been carried out amperometrically using "Dead Stop End Point" written as D.S.E.P.⁹⁾ This also suggested a similar oxidizability of thallium.

Experimental

A 0.1 N (0.025 M) solution of potassium iodate was prepared from E. Merck (G. R.) reagent. Its strength was checked against 0.1 N arsenious oxide prepared from E. Merck (G. R.) reagent using iodine monochloride end point. Approximately 0.1 N potassium permanganate solution, prepared from British Drag House (L. R.) reagent, was standardized against 0.1 N arsenious oxide. A 1% thallous acetate solution was prepared from B.D.H. reagent and its strength was determined against potassium iodate using iodine monochloride procedure.

Direct Titration Procedure. — An aliquot of iodate solution was transferred to a 100 ml. titrating vessel, 25~35 ml. of mercuric chloride (8~9%) solution was added followed by such a volume of 12 N hydrochloric acid as to adjust the overall acidity between 0.7~1.5 N. The contents of the vessel were cooled to 25°C completely. The reaction mixture was finally titrated against thallous acetate using the amperometric D.S.E.P. A potential of 0.1 V. was impressed across the indicator electrodes. The indicator current increased toward a maximum as the addition of thallous acetate solution was continued and finally decreased to a minimum at the equivalence point. As iodate is reduced to iodide, the equivalent weight in these titrations is 1/6 the formula weight.

Reverse Titration Procedure. — An aliquot of thallous acetate was taken in a titrating vessel, and mixed with 30~35 ml. mercuric chloride solution (8~9%) and 12 M hydrochloric acid (to maintain overall acidity between 1~2 N). The contents of the vessel were cooled to 25°C completely. The reaction mixture was finally titrated against standard iodate solution using the same electrometric end point. Near the equivalence point the indicator current showed a sudden increase in its value.

A series of experiments in which the acidity and mercuric chloride concentration were varied over a wide range, revealed that 1~2 N overall acid concentration and 25~35 ml. mercuric chloride gave accurate results. The results of one typical series of experiments are summarized in Tables I and II. Direct as well as reverse procedure may be extended to iodine monochloride end point (second end point), the acidity (hydrochloric acid) of the reaction mixture being raised at the iodide end point (first end point) to about 5~6 N.

Determination of Thallium(I) with Iodate and Permanganate via Bromide.—An aliquot of thallous

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TABLE I. DIRECT TITRATION OF THALLIUM(I) WITH IODATE IN THE PRESENCE OF MERCURIC IONS

ml. of 0.025 M iodate	ml. of 8~9% mercuric chloride	Overall acidity N	ml. of thallous acetate		% Difference
			Reqd.	Calcd.	
2	30~35	0.5~1.5	2.78	2.75	1.00
4	30~35	0.5~1.5	5.55	5.50	0.91
5	30~35	0.5~1.5	6.95	7.00	0.71
6	30~35	0.5~1.5	8.30	8.25	0.60
8	30~35	0.5~1.5	11.06	11.00	0.55
10	30~35	0.5~1.5	13.82	13.75	0.51

TABLE II. REVERSE TITRATION OF THALLIUM(I) WITH IODATE IN THE PRESENCE OF MERCURIC IONS

ml. of thallous acetate	ml. of 8~9% mercuric chloride	Overall acidity N	ml. of 0.025 M iodate		% Difference
			Reqd.	Calcd.	
2	25~35	0.5~1.5	1.50	1.46	2.78
4	25~35	0.5~1.5	2.95	2.92	1.03
6	25~35	0.5~1.5	4.40	4.38	0.45
8	25~35	0.5~1.5	5.85	5.84	0.17
10	25~35	0.5~1.5	7.30	7.30	nil

TABLE III. DETERMINATION OF THALLIUM(I) WITH IODATE VIA BROMIDE IN HYDROCHLORIC ACID SOLUTION

ml. of thallium(I)	Wt. of potassium bromide in grams	Overall acidity N	ml. of 0.1 N iodate		% Difference
			Reqd.	Calcd.	
20	2~3	1.50	15.05	15.20	0.95
20	2~3	2.00	15.05	15.20	0.98
20	2~3	3.00	15.10	15.20	0.66
20	2~3	4.00	15.15	15.20	0.33
20	2~3	5.00	15.15	15.20	0.33

TABLE IV. DETERMINATION OF THALLIUM(I) WITH PERMANGANATE VIA BROMIDE IN HYDROCHLORIC ACID SOLUTION

ml. of thallium(I)	Wt. of potassium bromide in grams	Overall acidity N	ml. of permanganate solution		% Difference
			Reqd.	Calcd.	
20	2~3	2.0	12.60	12.65	0.39
20	2~3	3.0	12.65	12.65	nil
20	2~3	4.0	12.70	12.65	0.39
20	2~3	5.0	12.75	12.65	0.79
20	2~3	6.0	12.85	12.65	1.59

acetate was taken in a titrating vessel and 25~35 ml. 12 M hydrochloric acid was added to maintain the final acidity as indicated in Tables III and IV followed by 2~3 g. of potassium bromide. The reaction mixture was then titrated againt standard permanganate or iodate using the amperometric D.S.E.P. A potential of 0.1 V. was impressed across the indicator electrodes. The indicator current remained constant throughout the titration and finally at the equivalent point it showed a sudden increase in its value. Series of experiments in which the acidity was varied over a wide range revealed that the method is accurate for the determination of thallium(I) with iodate and permanganate via bromide at an overall acidity between 3~5 N. In the titration of thallous salt with permanganate at a high acid concentration (above 4 N), the amount of permanganate solution consumed was too high owing to (catalytic) oxidation of hydrochloric acid by permanganate.

Summary

Oxidation of thallium(I) is carried out with iodate in the presence of mercuric ions using the amperometric D.S.E.P. Thallium is oxidized to thallium(III) and iodate is quantitatively reduced to iodide. The procedure is valuable because it gives correct determination for thallium(I) at

a low acid concentration. Oxidation of thallium(I) with permanganate and iodate in hydrochloric acid via bromide is also found to be accurate and quantitative.

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Chemical Laboratories
Banaras Hindu University
India