

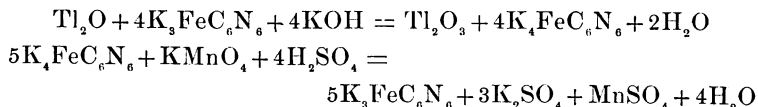
ART. XXXI.—*The Volumetric and Gravimetric Estimation of Thallium in Alkaline Solution by Means of Potassium Ferricyanide*; by PHILIP E. BROWNING and HOWARD E. PALMER.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—cxviii.]

IN a former paper from this laboratory* it was shown that reactions involving oxidation by ferricyanide in alkaline solution and reoxidation by permanganate of the resulting ferrocyanide in acid solution might be applied to the determination of cerium in the presence of the other rare earth compounds.

In the work to be described the same reactions were applied to the volumetric estimation of thallium. A solution of thallium nitrate was made up by dissolving 10 grms. of pure thalious nitrate in water and making up to a liter. This solution was standardized by precipitating definite portions with potassium bichromate in alkaline solution, filtering, and weighing the thalious chromate,† and also by evaporating measured portions of the solution with an excess of sulphuric acid and weighing as the neutral sulphate;‡ the mean of closely agreeing results by both methods was taken as the standard.

Volumetric.—The procedure was as follows: Measured portions of the solution of thalious nitrate were drawn from a burette, water was added to about 100^{cm}³ a sufficient quantity of a solution of potassium ferricyanide to give an excess, and potassium hydroxide to complete precipitation of the brown thallic hydroxide. The precipitate was filtered off on asbestos, generally without settling, and washed thoroughly. The filtrate was acidified with sulphuric acid and titrated with standard permanganate. From the following equations, representing the reactions, the amount of thallium present may be readily calculated:



It was found necessary to apply a correction for the amount of permanganate used to give the first tinge of pink color to the amounts of ferricyanide used in the determinations. This seldom exceeded .1 of 1^{cm}³ of the permanganate.

The following table shows the results obtained with different amounts of the thallium salt:

* Browning and Palmer, this Journal (4), xxvi, 83.

† This Journal (4), viii, 460.

‡ This Journal (4), ix, 137.

	Tl ₂ O taken as the nitrate gram.	Tl ₂ O found gram.	Error gram.
(1)	0·0809	0·0809	+ 0·0000
(2)	0·0809	0·0808	— 0·0001
(3)	0·0809	0·0809	± 0·0000
(4)	0·1213	0·1212	— 0·0001
(5)	0·1213	0·1216	+ 0·0003
(6)	0·1213	0·1218	+ 0·0005
(7)	0·1213	0·1218	+ 0·0005
(8)	0·1213	0·1212	— 0·0001
(9)	0·1213	0·1207	— 0·0006
(10)	0·1618	0·1614	— 0·0004
(11)	0·1618	0·1613	— 0·0005
(12)	0·1618	0·1616	— 0·0002

Gravimetric.—The satisfactory character of the precipitate of thallic hydroxide obtained by this process suggested the possibility of applying it to a gravimetric estimation of thallium. Several precipitations were made according to the method described and the precipitate contained in a perforated platinum crucible upon an asbestos felt was dried over a low flame at about 200° C. to constant weight. The results follow in the table:

	Tl ₂ O ₃ taken as the nitrate gram.	Tl ₂ O ₃ found gram.	Error gram.
(1)	0·1305	0·1309	0·0004 +
(2)	0·1305	0·1314	0·0009 +
(3)	0·1305	0·1308	0·0003 +
(4)	0·0870	0·0872	0·0002 +
(5)	0·1740	0·1741	0·0001 +
(6)	0·1740	0·1739	0·0001 —
(7)	0·1740	0·1742	0·0002 +
(8)	0·1305	0·1307	0·0002 +
(9)	0·1305	0·1309	0·0004 +
(10)	0·1305	0·1308	0·0003 +
(11)	0·0870	0·0872	0·0002 +
(12)	0·0870	0·0874	0·0004 +

In experiments (5) to (12) the precipitated thallic hydroxide was washed with hot water, a procedure to be recommended when large amounts are present.