Art. XVI.—*The Oxidimetric Determination of Thorium precipitated as the Oxalate;* by F. A. Gooch and Matsusuke Kobayashi.

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There appears to be in the literature no account of an oxidimetric method for the determination of thorium, based upon the precipitation of that element as the oxalate, by procedure similar to that which is applicable in the case of many oxalates of definitely known constitution. In the well-known gravimetric method in which thorium is precipitated as oxalate and weighed as thorium dioxide the exact constitution of the precipitated oxalate is not a matter of moment since the final product will be definite whatever the form of the precipitated oxalate may be. It is necessary, however, that definiteness in the constitution of the precipitate shall be assured in order that the determination may be made to depend upon the oxidimetric measurement of the oxalate. The following account gives the results of a study made to fix the conditions under which an accurate determination of thorium may be made by estimating either the oxalate radical combined in thorium oxalate or the excess of oxalic acid remaining from a known amount of oxalic acid used to effect the precipitation of the thorium.

In the experiments to be described a solution of thorium nitrate was made by dissolving 10 grm. of that salt (hydrous) in a liter of cold water acidified with 1 cm^3 of concentrated sulphuric acid and this solution was standardized accurately by the gravimetric method in which thorium oxalate is precipitated by oxalic acid and ignited and the residue weighed as thorium dioxide, ThO_2.

Potassium permanganate, made up in approximately N/10 solution, and standardized against pure sodium oxalate, was used as the oxidizing reagent and the solution of oxalic acid employed as the precipitant was standardized against the permanganate. In making use of these solutions, the burette readings were corrected for any change of temperature from that prevailing at the time of standardization.

In all the experiments the precipitation was brought about by the reaction of measured amounts of the standard oxalic acid with measured amounts of the solution of thorium nitrate and the mixtures were allowed to stand on the steam bath for intervals varying from fifteen to thirty minutes. The precipitated oxalate was filtered off on asbestos in the perforated crucible and washed with cold water containing in every 25 cm^3 a drop of concentrated sulphuric acid. The oxalic acid in the filtrate and the thorium oxalate of the precipitate were oxidized separately, by the standard permanganate. In the former case the amount of permanganate measured directly the oxalic acid radical of precipitated oxalate; in the latter case the amount of permanganate used measured that part of the known amount of standard oxalic acid which remained uncombined, the difference between the amount of oxalic acid taken and that found in the filtrate representing also the combined oxalic acid radical.

In the treatment of the precipitate, the crucible and precipitate were put into a beaker containing 100 cm^3 of water, the whole was heated to a temperature of about 85°, sulphuric acid (5 cm^3 of the 1:1 acid) added, the measured permanganate solution run in until the larger part of the precipitate had been oxidized, the mixture again heated to facilitate the oxidation of the precipitate (retained by the cooling of the mixture during the titration) and the titration continued to an end-point (which is very sharp if the liquid is kept hot). The coloration was matched with that obtained by adding a definite amount of N/10 permanganate (0·02 cm^3 to 0·04 cm^3) to an emulsion of asbestos in 100 cm^3 of water.

The filtrate from the precipitated thorium oxalate was diluted to a volume of 200 cm^3, heated to about 85°, and sulphuric acid (10 cm^3 of the 1:1 acid) was added. The titration with permanganate was continued to the end-point, since in the titration of the soluble oxalic acid in the filtrate there is no need of reheating as is the case in the titration of the insoluble oxalate.

In the experiments of Series I, A, in which the oxalic acid was added to the hot solution of thorium nitrate, the results show a deficiency amounting in the average to 2·75% of the oxalate radical which should be in combination with thorium, upon the hypothesis that the precipitate is the normal oxalate $Th(C_2O_4)_2$.

The results of the experiments in Series I, B, in which the oxalic acid was added to the cold solution of the thorium salt, though more regular, point to a deviation of

SERIES I.

Precipitation by Addition of Oxalic Acid to Thorium Nitrate.

ThO_2 taken as nitrate grm.	ThO_2 found in treatment of precipitate grm.	ThO_2 found in treatment of filtrate grm.	Error in treatment of precipitate grm.	Error in treatment of filtrate grm.
		A.		
		Precipitation in hot solution.		
0·0216	0·0213	0·0210	—0·0003	—0·0006
0·0430	0·0425	0·0418	—0·0005	—0·0012
0·1074	0·1043	0·1040	—0·0031	—0·0034
0·1721	0·1670	0·1669	—0·0051	—0·0052
		B.		
		Precipitation in cold solution.		
0·0237	0·0235	0·0234	—0·0002	—0·0003
0·0242	0·0241	0·0236	—0·0001	—0·0006
0·0474	0·0471	0·0471	—0·0003	—0·0003
0·0474	0·0467	0·0470	—0·0007	—0·0004

the precipitated oxalate from the normal form amounting to about 1%.

In the experiments of Series II, the order of addition was reversed and the thorium nitrate solution was added gradually to the oxalic acid with the intent to keep the latter reagent in excess during the precipitation. The mean error of the results shown in the experiments of section B in which the precipitation was made in cold solution amounts to about 0·1% while that of the experiments of section A, made in hot solution, is practically negligible.

SERIES II.

Precipitation by Addition of Thorium Nitrate to Oxalic Acid.

ThO_2 taken as nitrate grm.	ThO_2 found in treatment of precipitate grm.	ThO_2 found in treatment of filtrate grm.	Error in treatment of precipitate grm.	Error in treatment of filtrate grm.
		A.		
		Precipitation in hot solution.		
0·0216	0·0217	0·0212	+0·0001	—0·0004
0·0431	0·0432	0·0428	+0·0001	—0·0003
0·0646	0·0646	0·0643	0·0000	—0·0003
0·0860	0·0861	0·0858	+0·0001	—0·0002
0·1075	0·1074	0·1075	—0·0001	0·0000

A. (*Continued*).

Precipitation in hot solution.

ThO_2 taken as nitrate grm.	ThO_2 found in treatment of precipitate grm.	ThO_2 found in treatment of filtrate grm.	Error in treatment of precipitate grm.	Error in treatment of filtrate grm.
0·1290	0·1291	0·1290	+0·0001	0·0000
0·1506	0·1505	0·1504	—0·0001	—0·0002
0·1722	0·1723	0·1720	+0·0001	—0·0002
0·1937	0·1944	0·1937	+0·0007	0·0000
0·2151	0·2153	0·2151	+0·0002	0·0000

B.

Precipitation in cold solution.

0·0238	0·0236	0·0236	—0·0002	—0·0002
0·0474	0·0475	0·0472	+0·0001	—0·0002
0·0711	0·0707	0·0709	—0·0004	—0·0002
0·0711	0·0710	0·0711	—0·0001	0·0000
0·0947	0·0946	0·0945	—0·0001	—0·0002
0·1183	0·1180	0·1184	—0·0003	+0·0001
0·1419	0·1417	0·1416	—0·0002	—0·0003
0·1658	0·1654	0·1658	—0·0004	0·0000
0·1895	0·1888	0·1890	—0·0007	—0·0005
0·2130	0·2128	0·2133	—0·0002	+0·0003
0·2366	0·2365	0·2368	—0·0001	+0·0002

The work described shows that thorium may be estimated by an oxidimetric titration based upon the precipitation of thorium oxalate, provided that the precaution is taken to add the thorium salt gradually during the process of precipitation to an excess of oxalic acid. In the reverse procedure the tendency of thorium oxalate to fall as a basic salt is manifest and this tendency is especially marked in hot solutions. An accurate determination may be made either by the direct oxidation of the precipitated thorium salt, $Th(C_2O_4)_2$, or by determining the excess remaining in solution from a known amount of oxalic acid, after filtering and washing the precipitate.