GRAVIMETRIC DETERMINATION OF THORIUM AND ITS SEPARATION FROM URANIUM, CERITE EARTHS AND CERIC SALTS

By G. M. Saxena and T. R. Seshadri, F.A.Sc.

(*Department of Chemistry, University of Delhi, Delhi-8*)

THORIUM has been an important element in the past, particularly in connection with the incandescent mantle industry and it has recently acquired added interest as a source of atomic energy. Hence its determination in its ores and also its separation from accompanying elements has become increasingly important. From a review of the methods of the determination of thorium, Kaufmann[1] and Wenger and Duckert[2] reported that some of the most sensitive reagents precipitate uranium and cerite earths along with thorium. Among those that have been subsequently considered to be effective for separating thorium from rare earths,[3-11] probably the most important are *m*-nitro-benzoic acid and tetrachlorophthalic acid. But even these suffer from interference by ceric ions and hence further processes have to be adopted. Another combination which is frequently found in nature is thorium and uranium. Several organic acids have been reported to be suitable for determining thorium in the presence of uranium: they are ferron,[12] *m*-nitro-benzoic acid,[13] anisic acid,[14] cinnamic acid,[15] benzoic acid[16] and sebacic acid.[17] But they are not useful in the presence of cerite earths or ceric salts and hence have not got into common use.

As the result of a detailed study of flavone and xanthone derivatives as complexing agents for rare metals,[17a] 1-hydroxy-3-methoxy xanthone has now been found to be a useful reagent for the determination of thorium in the presence of uranium (uranyl ion) and of cerite earths and ceric salts. When an alcoholic solution of this xanthone is added to thorium salt solution, a deep yellow solution is formed which on dilution with water gives a yellow precipitate yielding thorium dioxide on ignition.

Owing to the solubility of the thorium complex in organic solvents, it is not possible to separate the pure complex from the excess of the xanthone added. Hence its composition could not be determined by direct weighing. The spectrophotometric method of Job[18] and Vosburgh and Cooper,[19] however, shows that the complex has the molar composition ThL_4 where L represents the xanthone ligand. The estimation of thorium can be conveniently

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done in the pH range 2·6–3·2 and under these conditions a minimum limit of 10·0 mg. thorium can be estimated with accuracy. Since ceric salts and cerite earths do not react with 1-hydroxy-3-methoxy xanthone, their separation from thorium presents no difficulty. It has been found that 10·0 mg. thorium can be separated from a ten-fold excess of cerite earths and five-fold excess of ceric salts. Uranium also does not get precipitated in this pH range. With a single precipitation a seven-fold excess of uranium salts can be separated. A very large excess (upto fifteen times) of uranium can be separated using double precipitation. For the estimation of thorium or for its separations from the above elements, sulphate ions should not be present in the solution, since complex formation is totally inhibited by them. The estimation can be smoothly carried out in the presence of chloride and nitrate ions.

EXPERIMENTAL

Reagents

(*a*) *Thorium nitrate solution.*—Thorium nitrate (B.D.H.) was purified by the method of Rao and Patel.[20] The thorium content of the solution was determined by the 8-hydroxy-quinoline method.

(*b*) 1-*hydroxy-3-methoxy xanthone.*—It was prepared by the condensation of phloroglucinol-dimethyl ether[21] with salicylic acid in presence of fused zinc chloride.[22] A 2% (almost saturated) solution of the xanthone in alcohol was used.

(*c*) Other reagents used were of A.R. quality.

Procedure for precipitation

To an aqueous thorium nitrate solution (pH adjusted) containing about 0·1 g. of thorium in about 100 c.c., alcohol (30 c.c.) was added. The mixture was heated on a water-bath nearly to boiling and an excess (40–50 c.c.) of the xanthone solution in alcohol was added. The deep yellow solution obtained was heated on a water-bath to remove most of the alcohol. It was then cooled and water (100 c.c.) added when all the thorium complex was precipitated. The flocculent precipitate was filtered and washed repeatedly with water. It was then dried at 120° and ignited in a weighed platinum crucible to constant weight (ThO_2). As the precipitate is voluminous, it is not convenient to take quantities larger than 0·1 g. of thorium. Smaller quantities could be used without any modification in the procedure.

Relative amount of the xanthone required for precipitation

As shown below, the complex formed contains four xanthone units attached to a thorium atom. In order to effect complete precipitation,

therefore, at least six moles of xanthone should be added for each mole of the thorium salt. It is desirable however to add larger proportions of the xanthone.

Effect of pH on the precipitation of thorium

The effect was studied by buffering thorium nitrate solutions with sodium acetate-hydrochloric acid mixture and then precipitating the complex. As thorium salts tend to hydrolyse above pH 4·0 the effect was studied only upto this pH. Precipitation of solutions containing 20·00 mg. of thorium oxide was carried out at different pH values. There was no precipitation below pH 1·0 and it increased upto pH 2·6 when it was complete and continued to be complete upto pH 4·0. Beyond pH 3·5 the procedure for precipitation had to be modified because thorium nitrate underwent hydrolysis on boiling. 1-Hydroxy-3-methoxy xanthone was added in this case in the cold. After about five minutes of thorough stirring the solution was heated on a water-bath to remove the alcohol. Complete removal of alcohol is very necessary as otherwise some of the complex passes through the filter-paper in the colloidal state. The precipitate was then filtered, washed, dried and heated as before.

It could be seen from the above observations that the most convenient range for estimating thorium is 2·6–3·5. In order to avoid any possibility of hydrolysis the most desirable conditions were in the pH range 2·6–3·2.

Molar composition of the complex

X c.c. of xanthone solution $(1·25 \times 10^{-3} \text{ M})$ were mixed with $(10 - \text{X})$ c.c. of thorium solution of the same molarity and the value of X varied from 1 to 9. Optical densities of these mixtures were determined at 400 $m\mu$ employing the xanthone solution as blank. The absorption due to the reacting solutions is small at that wave-length and at the same time the absorption of the complex is maximum (see Fig. 1). The difference between the optical density of the complex and of the reactants, therefore, is the same as the optical density of the complex itself in this case. The values of the optical densities (called the Y value) for the different mixtures were plotted against X. The curve showed a peak when the molar ratio was 8 : 2. The complex should, therefore, have the formula ThL_4, where L represents a unit of the xanthone.

Separation of thorium from cerite earths and ceric salts

Since 1-hydroxy-3-methoxy xanthone does not react with cerite earths and ceric salts it can be used for separating thorium from these elements

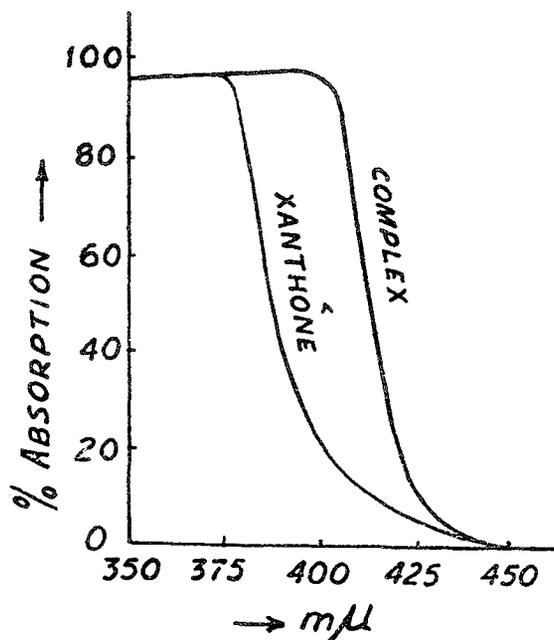The experimental results obtained are given in Table I. All precipitations were carried out at pH 2·8.

FIG. 1. Absorption of the Reagent and the Complex.

TABLE I

S. No.	ThO_2 (taken as thorium nitrate)	Ceric salts present	Cerite earths present	ThO_2 obtained after precipitation with the xanthone
	mg.	mg.	mg.	mg.
1	50·00	50·00	..	50·02
2	50·00	..	50·00	50·03
3	50·00	50·00	50·00	50·03
4	25·00	50·00	50·00	25·02
5	10·00	10·00	10·00	10·01
6	10·00	20·00	20·00	10·02
7	10·00	50·00	20·00	10·12
8	10·00	50·00	50·00	10·14
9	10·00	100·00	50·00	10·30
10	10·00	50·00	100·00	10·10

It was found that 10·00 mg. thorium can be separated with a fair degree of accuracy from a five-fold excess of ceric salts and ten-fold excess of cerite earths. The results become somewhat erroneous, however, if the quantity of ceric salts is more than five times the amount of thorium salt.

Separation of thorium from uranium (uranyl salts)

Uranyl salts react with 1-hydroxy-3-methoxy xanthone only at comparatively higher pH and hence do not interfere in the thorium estimation. The results obtained for this separation are given in Table II.

TABLE II

S. No.	ThO_2 (taken as thorium nitrate)	U_3O_8 (taken as uranyl nitrate)	ThO_2 found
	mg.	mg.	mg.
1	50·00	100·00	50·01
2	20·00	100·00	20·02
3	20·00	150·00	21·03
4	20·00	150·00	*20·03
5	20·00	200·00	*20·02
6	10·00	100·00	*10·02
7	10·00	200·00	*10·12

* Double precipitation employed.

A single precipitation with 1-hydroxy-3-methoxy xanthone can separate uranium as much as nearly five to six times the amount of thorium. For separating larger quantities of uranium, the precipitate obtained was heated with concentrated nitric acid to decompose the organic matter. Most of the acid was slowly evaporated off and the solution was again restored to pH 2·8–3·2 and thorium was reprecipitated. With the double precipitation a fifteen-fold excess of uranium could be separated from as little as 20·0 mg. of thorium.

SUMMARY

1-Hydroxy-3-methoxy xanthone forms a complex ThL_4 in aqueous alcoholic solution at pH 2·6–4·0 and it can be precipitated with water, dried

and ignited to yield thorium dioxide. This provides a satisfactory method of estimation of the metal in the presence of a large excess of cerite earths and ceric salts since these are not precipitated by this reagent and also in the presence of uranium which gets precipitated only at higher pH. The method can be used for separation also.

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