Diphenylcarbazone as an Internal Indicator in Volumetric Analysis. III. Volumetric Determination of Thorium by Ammonium Molybdate

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The growing interest in the chemistry of thorium and its compounds has necessitated the development of new and rapid methods of analysis. Of the large number of procedures which have appeared in the literature, practically all are based on the precipitation of thorium in some form from its solution and subsequent gravimetric determination as ThO_2[1,2]. Comparatively few titrimetric methods have been reported for estimating thorium. Among these the iodate method of Chernikhov and Uspenskaya[3] as modified by Moeller and Fritz[4] and the oxidimetric oxalate method of Gooch and Kobayashi[5] are noteworthy. The possibility of precipitating thorium oxinate and titrating the equiv alent of iodine as suggested by Berg[6] has been extensively studied. Iodometric titration of selenious acid liberated from a quantitatively precipitated thorium selenite has been reported from these laboratories[7]. The molybdate procedure of Metzger and Zones[8] which has been modified by Banks and Diehl[9] is found to be applicable to pure thorium or the mixed thorium uranium solution.

Amperometric titration of thorium with ammonium molybdate has recently been studied by Gordon[10], and it is claimed that under the specified conditions, this procedure may be adopted for the estimation of thorium in presence of rare earths and other congeners. Recent observations in these laboratories on the use of diphenylcarbazone as an internal indicator in volumetric analysis showed that on treatment with ammonium molybdate this indicator develops an intense pink colour which is destroyed by the addition of a lead salt solution. The colour change was found to be reversible and formed therefore the basis of the titrimetric determination of molybdenum by using Pb $(NO_3)_2$ as the primary standard[11]. Extension of these observations to the estimation of metals forming stable molybdates suggested itself and a series of experiments were carried out to study the possibility of using the above indicator in the titration of ammonium molybdate with a thorium salt solution. A systematic study of the operative conditions led to the development of a simple and rapid titrimetric method for the estimation of thorium. This has now been described in the present communication.

Experimental

Thorium nitrate (or chloride) solution was obtained by dissolving the pure salt in water; the ThO_2 content of an aliquot portion of the solution was determined by the *m*-nitrobenzoic acid method.

To a known volume of the aqueous thorium solution containing 50–60% alcohol, one ml. of saturated alcoholic solution of diphenylcarbazone was added and the yellow or orange yellow solution was titrated slowly with constant swirling against standard ammonium molybdate. The end point was characterised by a sharp pink flush in the precipitated thorium molybdate. At this point the precipitate tended to coagulate rapidly and the supernatent solution also assumed a pink shade. Since the colour change from pale yellow to pink is completely reversible, any error due to overtitration is rectified easily by running in a known volume of thorium solution and continuing the titration as usual. The accuracy and sharpness of the end point was, however, found to enhance by adopting the following modified procedure: To an aliquot of the thorium solution a measured volume of standard aqueous Pb $(NO_3)_2$ was added followed by an equal volume of ethanol and 0.5 ml. of the indicator. The pink coloured solution was titrated slowly against ammonium molybdate. The colour faded during the initial addition of the molybdate with the simultaneous appearance of a white precipitate. The titration was continued till a sharp pink flush was observed in the precipitate. A blank titration of $Pb(NO_3)_2$ against molybdate using the indicator was carried out under identical experimental conditions. This titre value when subtracted from the total volume

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of molybdate required for the mixed thorium and lead nitrate solution, gave the quantity of molybdate required for the precipitation of thorium as molybdate. Varying quantities of the thorium solution were thus titrated against standard ammonium molybdate. From a knowledge of the ThO_2 content of the solution taken for titration and the molybdenum content of the titrant, the molar ratio Th: Mo corresponding to the end point was calculated. Series of trial experiments showed that within limits of 100–200 mg. of thorium the molar ratio corresponded on the average to 1 : 1.99. It may therefore be inferred that within the specified limits of the above experimental procedure, the titrimetric estimation of thorium may be carried out with reasonable accuracy. This date are returned in Table I.

It has been observed that the sharpness of the end point depends on the quantity of alcohol added initially to the thorium solution. While in the presence of too large a quantity exceeding 70–80% the end point appears prematurely; an excess of molybdate is consumed if the titration is carried out in a purely aqueous media. The overall alcohol content (50–60%) has been determined by a series of trial experiments. For a permanent and sharp end point it is also not desirable to dilute the contents during and/or towards the end of the titration.

The molar ratio Th: Mo=1: 1.99 as observed in the above series of experiments (cf. Table I) is in close agreement with that reported by Gordon.

The amperometric titration method developed by him offers however, a distinct advantage of being applicable to the determination of thorium in presence of other rare earths. This procedure, however, necessitates a rigid control of operative conditions and a special type of apparatus. On the other hand the titrimetric method of Metzger and Zones involves the use of acetic acid- sodium acetate buffer and diphenyl-carbazide as an *external* indicator. It may therefore be pointed out that the present procedure is more rapid, simple and accurate than other titrimetric methods adopted for the determination of thorium.

TABLE I

10 ml. of $Pb(NO_3)_2 \equiv 0.07550$ gm. Pb

Expt. No.	Vol. of Th Cl_4 in ml. (a)	Vol. of Am. Molybdate required in ml. (b)	Wt. of Th in (a)	Wt. of Mo in (b)	Molar Ratio Th: Mo
1.	10.0	9.40	.06489	.05249	1: 1.955
2.	20.0	19.05	.1297	.1064	1: 1.984
3.	42.5	40.60	.1378	.1133	1: 1.987
4.	22.5	21.50	.1460	.1200	1: 1.987
5.	47.5	45.45	.1541	.1269	1: 1.991
6.	25.0	23.95	.1622	.1338	1: 1.995
7.	52.5	50.55	.1703	.1411	1: 2.004
8.	27.5	26.55	.1784	.1483	1: 2.010
9.	57.5	55.50	.1865	.1550	1: 2.009

Summary

A simple volumetric method for the quantitative estimation of thorium as molybdate is described. This is based on the titration of aqueous thorium nitrate (or chloride) solution against standard ammonium molybdate in presence of ethanol by using diphenylcarbazone as the internal indicator. Under specified operative conditions, normal thorium molybdate is precipitated. The indicator behaves reversibly and the accuracy of the method is comparable with those obtained by classical procedures.

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