Determination of thorium by Organic bases

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Jefferson[1] and Hartwell[2] reported the use of various amines and organic bases for the quantitative estimation of thorium in presence of rare earths. Further work by Atanasiu[3] and Schiotz[4] and Ismail and Hartwood[5] showed that pyridine, quinoline and hexamine are effective for the separation of thorium from cerium earths. An investigation along these lines seemed to promise well because it was considered that among the numerous hitherto uninvestigated organic bases, suitable precipitants might be found for the quantitative determination of thorium and its separation from rare earths and other familar congeners. Series of trial experiments were therefore carried out using *o*-tolidine, dianisidine, *p*-phenylenediamine, *o*-anisidine and *o*-phenetidine as precipitants for thorium. The present communication reports results obtained with the above bases and shows that *o*-anisidine and *o*-phenetidine afford a quantitative separation of thorium from trivalent rare earths.

Experimental

The organic bases used as precipitants were of Merck's reagent grade quality and were purified by repeated recrystallisation or/and distillation. An aqueous thorium chloride (or nitrate) solution was prepared and its thorium content was determined by *m*-nitrobenzoic[6] and sebacic acids.[7] In the case of *o*-tolidine, dianisidine and *p*-phenylenediamine the following procedure was adopted for precipitating the corresponding thorium complex.

To an aliquot quantity (10 ml.) of the thorium solution about 20–30 ml. of alcohol was added and the solution was heated to 90° C. A saturated alcoholic solution of the base was now run in a thin stream with constant stirring till the precipitation was complete, followed by about 5–10 ml. of alcohol. The contents were boiled for a couple of minutes. The precipitate was allowed to settle for an hour, filtered through Whatman 40, washed with cold alcohol, dried and ignited to ThO_2. For obtaining reproducible and accurate results, it is necessary to add the precipitant to an almost boiling hot solution of thorium salt containing an equivalent volume of alcohol and also to continue boiling at least for a few minutes after the complete precipitation of the thorium complex.

A representative group of results is given in Table I.

Since cerium and other trivalent rare earths are also precipitated by the above organic bases under the above experimental conditions, whose adaptability in quantitative analysis is restricted only to the determination of thorium in its aqueous solution.

Series of experiments carried out with *o*-phenetidine and *o*-anisidine, however, showed that these ammines could be used for the precipitation of thorium and its separation from trivalent rare earths e. g. Ce, La, Y and Er.

To a known volume of the thorium solution mixed with varying quantities of the above trivalent salt solutions and an equal portion of alcohol, an alcoholic solution of *o*-phenetidine or *o*-anisidine was added. The

TABLE I

Expt No.	Wt. of ThO_2 (g.) *m*-nitrobenzoic acid (a)	Wt. of ThO_2 (g.)			Difference		
		o-tolidine (b)	dianisidine (c)	*p*-phenylenediamine (d)	a∼b	a∼c	a∼d
1	0.0640	0.0640	0.0638	0.0641	. .	0.0002	0.0001
2	0.0922	0.0919	0.0923	0.0923	0.0003	0.0001	0.0001
3	0.1152	0.1148	0.1149	0.1153	0.0004	0.0003	0.0001
4	0.1164	0.1164	0.1165	0.1165	. .	0.0001	0.0001
5	0.1378	0.1379	0.1376	0.1378	0.0001	0.0002	. .
6	0.1390	0.1392	0.1388	0.1390	0.0002	0.0002	. .

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[1] A.M. Jefferson, *J. Amer. Chem. Soc.*, **24**, 540 (1902).

[2] B.L. Hartwell, ibid. **25**, 1128 (1903).

[3] I.A. Atanasiu, *Ber.*, **60B**, 2507 (1927).

[4] A.B. Schiotz, *Tids. Kemi. Farm. Terapi.*, **14**, 270 (1917).

[5] A.M. Ismail, and H.F. Harwood, *Analyst*, **62**, 185 (1937).

[6] A.C. Neish, *Chem. News*, **90**, 196, 201 (1904).

[7] T.C. Smith and C. James, *J. Amer. Chem. Soc.*, **34**, 281 (1912).

precipitate appeared gradually and was complete in about 20–30 minutes. It was kept aside for six hours, filtered through Whatman 40, washed initially with cold alcohol and then repeatedly with hot 50% alcohol. The precipitate was dissolved in a minimum quantity of dilute 2N-HCl, the solution diluted further to about 50 ml. and thorium reprecipitated. This was washed finally with alcohol, dried and ignited to constant weight as ThO_2.

TABLE II

Expt No.	Wt. of ThO_2 (g.) *m*-nitrobenzoic acid (a)	Wt. of X_2O_3 (g.) added	Wt. of ThO_2 (g.) *o*-phenetidine (b)	*o*-anisidine (c)	Difference a∼b	a∼c
1	0.0640	0.0580	0.0642	0.0644	0.0002	0.0004
2	0.0922	0.0886	0.0926	0.0924	0.0004	0.0002
3	0.1152	0.1022	0.1150	0.1154	0.0002	0.0004
4	0.1164	0.1162	0.1166	0.1166	0.0002	0.0002
5	0.1378	0.1162	0.1376	0.1380	0.0002	0.0002
6	0.1390	0.1228	0.1394	0.1390	0.0004	. .

X = Ce, La, Y or Er

Results in Table II show that the double precipitation effects a quantitative separation of thorium from the trivalent rare earths used in the present investigation. The interference of other familiar congeners of thorium in its determination by the above precipitants is under investigation.

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Summary

Quantitative estimation of thorium by precipitating it from aqueous thorium chloride (or nitrate) solution by *o*-tolidine, dianisidine, *p*-phenylenediamine, *o*-anisidine and *o*-phenetidine has been studied. The precipitated complex is ignited to constant weight and determined gravimetrically as ThO_2.

The use of *o*-anisidine and *o*-phenetidine for the separation of thorium from trivalent cerium has been suggested.

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