

CHEMISTRY OF THORIUM. PART I. RAPID DETERMINATION OF THORIUM IN MONAZITE SAND

BY NIHAR KUMAR DUTT

A rapid method for the quantitative determination of thorium in monazite sand has been developed. Thermometric titration method of Dutoit and Grobet has been used for the purpose. Thorium has been determined thermometrically by titration with a solution of sodium pyrophosphate in acid solution. After adjustment of the concentration of acid, the method has been found applicable to the determination of thorium directly in the solution obtained by the decomposition of monazite sand.

Exact and rapid methods for the quantitative determination of thorium are of interest because of the growing importance of the element in the production of catalysts and alloys and in the investigation of nuclear phenomena. For a rapid determination, recourse must be taken to methods which are applicable to strongly acid solutions, since in such cases, prior removal of phosphoric acid is unnecessary. Only a few methods are available for the purpose. Perhaps the most highly recommended procedure is the iodate method of Meyer and Spater (*Chem. Ztg.*, 1910, 34, 306) depending upon the insolubility of thorium iodate in solutions containing excess of iodate and up to 40% of nitric acid by volume. In its usual form, the method has yielded good results, particularly in the analysis of monazite sand, no doubt, but it is costly. The composition of the thorium compound has been shown by Moeller and Fritz (*Anal. Chem.*, 1948, 20, 1055) to be the simple iodate of thorium $\text{Th}(\text{IO}_3)_4$ and not the double iodate as suggested by Chernikhov and Uspenskaya (*Zavodskaya Lab.*, 1940, 9, 276). This procedure has been adopted by the former workers (M and F) for the titrimetric determination of thorium through the iodometric estimation of the iodate content of the precipitate thereby making it much more rapid. Mention may also be made of the hypophosphate method of Rosenheim in strongly acid solutions (*Chem. Ztg.*, 1912, 36, 821). For rough determinations, he recommended ignition of the hypophosphate to weighable pyrophosphate, but lack of constancy in composition of the ignition product requires decomposition of the precipitated compound with either caustic alkali or a mixture of sulphuric and fuming nitric acids, followed by precipitation as oxalate for accurate results. Of the methods available the cheapest seems to be the pyrophosphate method of Carney and Campbell (*J. Amer. Chem. Soc.*, 1914, 36, 1134) but it is rather tedious. The method consists in precipitating thorium with sodium pyrophosphate from boiling solutions in 0.3*N* hydrochloric acid. In this case also a second pyrophosphate precipitation and ultimate precipitation with oxalic acid are necessary to yield pure thorium materials. Insufficient acid is said to prevent complete precipitation through the formation of soluble $\text{Na}_4\text{Th}(\text{P}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$. A radioactive procedure of estimation of thorium in monazite has been developed by Moeller and Schweitzer (*Anal. Chem.*, 1948, 20, 1201) following the method of Carney and Campbell (*loc. cit.*) and using a measured excess of standard sodium pyrophosphate solution containing a known activity of radioactive phosphorus (P^{32}) and determining the excess by measurement of its radioactivity.

None of the methods described are easy, simple or quick. In searching for a rapid method of estimating thorium in presence of phosphoric acid and rare earths, thermometric titration method has been tried. The method is originally due to Dutoit and Grobet (*J. chim. phys.*, 1924, 19, 324, 331). It has been used by numerous workers in recent days for volumetric estimations (cf. Dean and Watts, *J. Amer. Chem. Soc.*, 1924, 46, 855; Newcomer, *ibid.*, 1925,

47, 64; Meyer and Fisch, *Z. anal. Chem.*, 1929, 76, 418; Paris and Robert, *Bull. soc. chim.*, 1943, 224; 1945, 16, 538). The successful application of this method for the estimation of thorium forms the subject matter of the present communication. Titrations with both potassium iodate and sodium pyrophosphate have been tried; that with hypophosphate is in progress. Experiments with iodate proved unsuccessful, probably due to the fact that the thorium compound formed only in presence of a large excess of potassium iodate. It has been found, however, that sodium pyrophosphate can be employed with much success. This method has also been found applicable to the determination of thorium directly in monazite sand after adjusting the acid concentration. The optimum acid concentration has been found to be in the neighbourhood of 1.0 *N*, somewhat higher than that recommended by Carney and Campbell. This is essential for the success of the process. It is probable that at room temperature, the double salt, that is formed, is not broken up into simple thorium compound by dilute acid although it does so on boiling. The method gives results comparable with those obtained by accepted procedures and is much more rapid.

EXPERIMENTAL

The sample of thorium nitrate used was supplied by E. Merck and Co., and sodium pyrophosphate was supplied by Merck and Co., U.S.A. Thorium nitrate solution was standardised by precipitation with oxalic acid and subsequent ignition to dioxide. Sodium pyrophosphate solution was standardised as magnesium pyrophosphate after conversion into orthophosphate by boiling with concentrated nitric acid.

Thermometric Titration

The experimental arrangement was the same as that used by the present author (this *Journal*, 1945, 22, 4).

TABLE I

Pure thorium solution: Effect of acid conc. on the position of the break.

Thorium soln. = 0.0803 *M*. Pyrophosphate soln. = 0.208 *M*. Thorium soln. taken = 20 c.c.
= 8.10 c.c. of the above pyrophosphate solution.

No.	Acid conc.	Position of the break in c.c. of pyrophosphate used.	Ref.
1	0.4 <i>N</i>	7.20	Fig. 1, <i>a</i>
2	0.6	7.50	
3	0.8	8.00	Fig. 1, <i>b</i>
4	1.0	8.10	Fig. 1, <i>c</i>
5	1.2	8.20	
6	1.5	7.80	Fig. 1, <i>d</i>

Thorium in presence of Cerium.—As in monazite the ratio $\text{ThO}_2 : \text{R}_2\text{O}_3$ is never below 1 : 6, experiments were not carried with artificial mixtures below this ratio.

The original thorium solution (20 c.c.) was taken and to this solid cerium (being taken as a representative element of the rare earths) nitrate was added to get the desired ratio.

TABLE II

No.	$\frac{\text{CeO}_2}{\text{ThO}_2}$	Acidity=1.0—1.2 <i>N</i> .	Pyrophosphate
			soln. required.
1	4		8.10 c.c.
2	8		8.20
3	10		8.20
4	12		8.25
5	15		8.50

Results show that thorium can be accurately determined in presence of cerium earths when the ratio is as high as 1 : 10, but for ratios higher than 10 some contaminations occur giving higher results.

FIG. 1

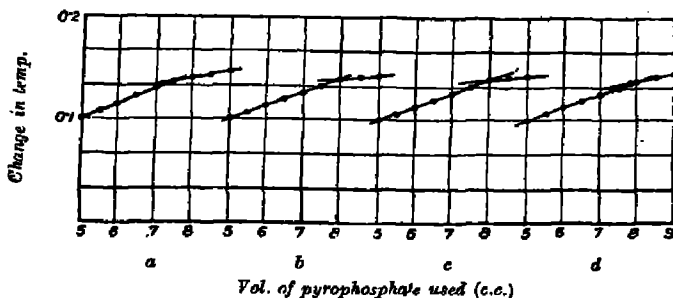
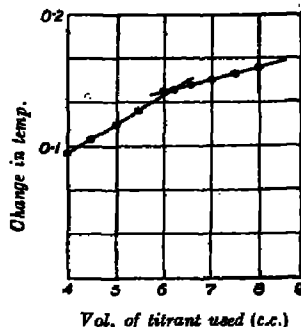


FIG. 2



Thorium in Monazite Sand.—Monazite sand (50 g.) was decomposed with 100 c.c. of H_2SO_4 (conc.), cooled, dissolved in ice-cold water, filtered and diluted to one litre. The solution was then analysed for ThO_2 -content by two methods, hydrogen peroxide method of Benz (*Z. angew. Chem.*, 1902, 15, 297) and pyrophosphate method of Carney and Campbell (*loc. cit.*).

Determination of ThO_2 in the above solution by Thermometric Method.—The solution (50 c.c.) was taken in the inner Dewar flask. To this were added 60 c.c. of water and 2 c.c. of HCl. Sodium pyrophosphate solution was added from the burette. For an aliquot of 100 c.c. solution, volumes of water and acid were doubled. Results are shown in the following table; for comparison results obtained by other methods are given side by side

TABLE III

Strength of monazite sand soln. with respect to the ThO_2 content = 0.0136 *M*
Strength of pyrophosphate used = 0.1151 *M*.

No.	Vol. of soln. taken	Vol. of $\text{Na}_4\text{P}_2\text{O}_7$ soln. reqd.		Percentage of ThO_2 by			Ref
		Calc.	Found.	Thermometric method.	Carney and Campbell's method.	H_2O_2 method.	
1.	50 c.c.	6.2 c.c.	6.2 c.c.	7.2	7.2	7.16	Fig. 2
2.	50	6.2	6.1	7.1			
3.	100	12.4	12.3	7.1			
4.	100	12.4	12.3	7.1			