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GRAVIMETRIC METHOD FOR THE DETERMINATION OF THORIUM AND PHOSPHORUS IN THORIUM PHOSPHIDES

by

R. E. Telford and Y. Baskin

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DETERMINATION OF THORIUM AND PHOSPHORUS
IN THORIUM PHOSPHIDES

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ABSTRACT

Thorium was precipitated as the oxalate and ignited to the oxide after dissolving the sample in a $\text{HNO}_3\text{-Br}_2$ solution. Phosphorus was determined in the filtrate by precipitation and weighing as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$.

INTRODUCTION

Thorium phosphide shows promise as a ceramic nuclear fuel material because of its attractive high-temperature properties.⁽¹⁾ It possesses the rock salt-type crystal structure and has a melting point of about 2900°C . Moreover, the compound exhibits complete solid solubility with uranium phosphide, and the intermediate compositions show many interesting properties.⁽¹⁾ This suggests that the binary system ThP-UP may also have considerable potential for nuclear fuel applications.

Thus far, only a few investigations have been reported on thorium phosphides. Strotzer and Biltz⁽⁸⁾ and Meizel⁽⁶⁾ reported on the compound Th_3P_4 and on a subphosphide, $\text{ThP}_{0.7}$, and Wilson⁽⁹⁾ has described the synthesis, crystal chemistry, and stoichiometry of thorium phosphides. These investigations were in agreement that the rock salt structure of thorium phosphide could tolerate a rather high concentration of anion vacancies and that, most generally, ThP was hypostoichiometric. The fact that thorium monophosphide may commonly be hypostoichiometric makes it essential to have an accurate analytical method for determining both thorium and phosphorus. The method described here is a modified version of the one proposed by Wilson.⁽⁹⁾

EXPERIMENTAL

Synthesis

The general procedure for synthesizing thorium phosphide was identical to that used for UP.⁽²⁾ Existence of more than one thorium hydride compound complicated the hydriding and dehydriding steps, as

compared to those for uranium, but the latter steps were the same as with UP. Thorium chips were comminuted by successive hydriding and dehydriding cycles. The active powder was brought in contact with PH_3 gas at temperatures above 550°C to initiate the reaction. A mixture of Th_3P_4 and free thorium resulted from reaction of a stoichiometric amount of PH_3 with thorium. X-ray diffraction photographs of the reacted material showed clear patterns for Th_3P_4 , but none for the metal. The final step consisted of heating the powder in vacuum at $1200\text{--}1300^\circ\text{C}$, to homogenize the material and drive off any excess phosphorus. The resulting powder was dark blue and could be safely handled in air. Most, if not all, of the oxygen present occurred in the secondary ThO_2 phase. This phase produced a weak but clearly identifiable X-ray pattern.

Apparatus

X-ray powder photographs taken with $\text{CuK}\alpha$ ($1.5418\text{\AA}$) radiation were used to identify phases present in the different samples. Thermogravimetric analysis (TGA) was conducted in static air with an Ainsworth, Type RV, semimicrobalance and using a heating rate of $5^\circ\text{C}/\text{min}$.

Dissolution for chemical analysis was made in a 60-ml quartz Kjeldahl flask attached to a 40-cm water-jacketed reflux condenser with a $\text{F } 24/40$ joint.

Reagents

Reagent grade chemicals were used for all tests.

Magnesia Mixture - The mixture was prepared by dissolving 50 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in 500 ml of water, adding 100 g of NH_4Cl and a slight excess of NH_4OH , and stirring until dissolved. After standing overnight and filtering, the solution was made slightly acid with HCl and diluted to one liter.

Oxalate Wash - The wash was prepared by dissolving 25 g of oxalic acid in water, adding 30 ml of HCl , and diluting to one liter.

Standard Solutions

Standard thorium solution was prepared by dissolving approximately 5.0 g of thorium metal in 40 ml of HCl , and evaporating to dryness on a steam bath. Twenty ml of HNO_3 and one ml of 0.5M HF were added, the beaker was covered, and the contents were boiled for about 10 min. The solution was diluted to 200 ml, filtered into a 500-ml volumetric flask, and made to volume. Ten-ml portions were assayed by the oxalate precipitation method.⁽⁵⁾

Standard phosphate solutions were prepared by (a) diluting 2.25 ml of H_3PO_4 to one liter and standardizing by the magnesium phosphate method,⁽⁷⁾ and (b) dissolving 0.4393 g of NBS KH_2PO_4 in water and diluting to 100 ml to give exactly 1.000 mg of phosphorus per milliliter.

Preliminary Studies

Separation of thorium from phosphate by double precipitation of $\text{Th}(\text{IO}_3)_4$ in 6M HNO_3 medium proved to be a long and cumbersome method giving poor results for thorium and complicating the determination of phosphorus because of excessive amounts of salts present.

Some attempt was made to determine thorium by using the anion-exchange method proposed by Fritz and Garralda.⁽³⁾ Thorium is absorbed on Dowex 1 from 6M HNO_3 , and phosphate may be recovered quantitatively in the eluate. Thorium is then stripped from the column with 0.5M HNO_3 , the pH adjusted to 2.0 to 3.0, and the solution titrated with standard 0.05M EDTA. Our results indicate that recovery of thorium from synthetic samples is not quite quantitative. Recoveries of 48.5 mg of thorium using 200 ml of wash were 98.0%, 98.8%, 98.3%, and 98.3%.

Dissolution of Sample

Because of the volatility and loss of phosphine, which is evolved in acid dissolution unless strong oxidizing conditions are maintained, only two satisfactory procedures were found. The first was that of using the modified Carius combustion tube⁽⁴⁾ in which sample and nitric acid are sealed in a heavy walled tube and heated to 300°C overnight. The other method, less involved and somewhat shorter, consisted of refluxing the sample with HNO_3 and liquid Br_2 in a quartz Kjeldahl flask connected to a vertical condenser.

Recommended Procedure for Thorium Determination

Weigh approximately 0.13 g of powdered ThP sample, and transfer to a dry 60-ml Kjeldahl flask. Add 15 ml of HNO_3 , 0.5 ml of bromine, and 1 ml of 0.5M HF. Connect to vertical condenser, and turn on cooling water. Heat gently to boiling, and continue for 15 min. Turn off water, and boil vigorously to volatilize bromine. When no residue of bromine remains in the flask, add 5 ml of water through the condenser tube. Continue the flow of cooling water. Boil until solution is clear and no residue of insoluble ThO_2 remains. This may require as long as an hour. Allow contents of flask to cool, and transfer to a 250-ml beaker. Cover with ribbed watch glass. Evaporate solution on a hot plate to about 5 ml, and continue on a steam bath to about 1 ml or to a moist residue. Add 3 ml of HCl to dissolve residue, and 100 ml of water. Heat to near boiling with frequent stirring to prevent bumping. A faint gelatinous precipitate of $\text{Th}_3(\text{PO}_4)_4$

may appear. Add slowly with stirring 20 ml of hot 10% oxalic acid. Allow to stand overnight. Filter solution through No. 42 Whatman filter paper containing a few milliliters of filter pulp. Transfer precipitate to paper, and wash five or six times with 5 ml of oxalate wash solution. Ignite paper gently in a weighed platinum crucible until carbon has burned off, and then to constant weight at 1100°C. The weight of ThO_2 multiplied by 0.8788 will equal the weight of thorium found.

PHOSPHORUS DETERMINATION

To the filtrate from the thorium determination, add 15 ml of magnesia mixture, and cool in an ice bath. Neutralize with NH_4OH to the yellow color of methyl red, and add an additional 20 ml. Stir vigorously for several minutes until precipitation occurs, and allow solution to stand 4 hr in ice bath or overnight at room temperature. Filter through No. 42 Whatman filter paper, and wash with a total of 25 ml of cold 1M NH_4OH . Discard filtrate and washings. Dissolve precipitate with 50 ml of hot 1M HCl , collecting filtrate in original beaker. Wash with 25 ml of hot water. Add 2 ml of magnesia mixture, dilute to 100 ml, and cool in ice bath. Neutralize with NH_4OH to methyl red color change, and add an additional 5 ml with constant stirring until precipitation occurs. Allow solution to stand 4 hr in ice bath or overnight at room temperature. Filter solution through a 20-ml, medium-porosity, sintered-glass crucible using suction. Transfer precipitate to crucible, and wash with a few ml of cold 1M NH_4OH . Wash precipitate with two 15-ml portions of 95% ethyl alcohol and two 15-ml portions of ethyl ether. Draw air through crucible for 5 min, and wipe dry. Allow crucible to stand 30 min at room temperature, and weigh. Dissolve precipitate with 25 ml of hot 1M HCl , apply suction, and rinse with 25 ml of hot water. Dry the crucible at 110°C for a few minutes and at room temperature for 30 min. Weigh crucible and subtract weight from that of crucible and precipitate. The weight of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ multiplied by 0.1262 is equal to the weight of phosphorus.

Chemical: Discussion and Results

Since standard ThP samples were not available to evaluate the accuracy and precision of the method, reliability was determined by attaining material balance in analyzed samples, and satisfactory recovery of known amounts of thorium and phosphorus from solutions prepared to simulate those of the actual samples. Results obtained for thorium on synthetic samples using the oxalate precipitation method were quite accurate. Wilson⁽⁹⁾ determined phosphate in the filtrate from the thorium precipitation by oxidizing oxalate with KMnO_4 , and adding excess $\text{Zr}(\text{SO}_4)_2$. The precipitate was filtered off and ignited to ZrP_2O_7 . Satisfactory results using this method were not obtained, so the MgNH_4PO_4 precipitation method was investigated.⁽⁷⁾ Originally it was considered desirable to remove oxalate before precipitation. This was best accomplished by

adding 2.5 g of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ per gram of oxalic acid present to the hot solution and boiling for 15 min. Later tests showed that it was unnecessary to remove oxalate if the cold solution was stirred sufficiently and contained about 15% excess NH_4OH . The buffering effect of the oxalate requires the addition of more NH_4OH than would normally be used.

Synthetic mixtures were prepared by pipetting known amounts of thorium and phosphate standards into a 250-ml beaker, evaporating to near dryness, and following the procedure as given above. Results are shown in Table I. For equimolar ratios of thorium to phosphorus, thorium may be determined with an accuracy of 0.1%. For higher phosphorus/thorium ratios of 5 or 10 to one, a slightly lower recovery of thorium is obtained. Phosphorus values were somewhat less accurate and more erratic. An accuracy of 0.5% can be attained. The procedure of obtaining tare weight of crucibles after, rather than before, filtration of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ was found to make no difference in phosphorus results. The usual order may be followed if preferred. With the proposed procedure, a small savings of alcohol and ether is achieved.

TABLE I
Recovery of Thorium and Phosphorus from Synthetic Mixtures

No. of Samples	Taken (mg)		Found (mg)		% Recovery	
	Thorium	Phosphorus	Thorium	Phosphorus	Thorium	Phosphorus
A. After oxidation of oxalate with $(\text{NH}_4)_2\text{S}_2\text{O}_8$						
2	97.6	10.05	97.6	10.14	100	100.9
4	97.6	15.14	97.6	15.25	100	100.7
1	97.6	50.46	96.7	50.60	99.1	100.2
1	97.6	100.92	96.9	101.2	99.3	100.2
2	97.6	10.15	-	10.09 ^(a)		99.4
2	97.6	10.15	-	10.14 ^(b)		99.8
B. Without oxidation of oxalate						
2	97.6	10.15	97.4	-	99.8	
4	97.6	15.14	97.6	15.17	100	100.2
3	-	15.00 ^(c)	-	15.03		100.1

(a) 10 ml of excess NH_4OH used in first precipitation.

(b) 20 ml of excess NH_4OH used in first precipitation.

(c) Standard prepared from NBS- KH_2PO_4 .

Small amounts of oxygen were determined in the ThP by the inert-gas fusion method. Results shown in Table II are average values.

TABLE II
Analysis of Thorium Phosphide Samples

Sample No.	Calcination Temp, °C	No. of Analyses	% Th	% P	% O	P/Th*
ThP-1	1300	3	87.93	11.30	0.29	0.99
ThP-2	1200	4	88.73	10.89	0.33	0.95
ThP-3	1200	2	88.95	10.88	0.40	0.95

*The ratio only applies to the ThP phase and excludes the thorium tied up in ThO_2 .

Thermogravimetric

Oxidation of sample ThP-1 was investigated using the TGA technique, and the results are shown in Figure 1. Based on the weight gain obtained, 27.4%, the phosphorus/thorium ratio of this sample was exactly unity. This assumes complete oxidation of the sample to a mixture of ThO_2 and P_2O_5 , and complete retention of the P_2O_5 in the oxidized sample. Incomplete oxidation or loss of some P_2O_5 would have meant that the original sample had a phosphorus/thorium ratio greater than unity. However, this was ruled out on the basis of X-ray evidence, which showed no trace of Th_3P_4 in the pattern. Thus, the TGA data appear to corroborate the analytical results on ThP-1. The value obtained ($\text{ThP}_{1.00 \pm 0.02}$) was close to that found by chemical analysis ($\text{ThP}_{0.99}$), and the difference was within the range of experimental error.

Fig. 1

Thermogravimetric Analysis
(TGA) Curve for $\text{ThP}_{0.99}$ in
Static Air

chemical analysis ($\text{ThP}_{0.99}$), and the difference was within the range of experimental error.

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