THE HYPOPHOSPHATE METHOD FOR THE VOLUMETRIC DETERMINATION OF THORIUM

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THE HYPOPHOSPHATE METHOD
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By

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INTRODUCTION

The use of hypophosphate for the quantitative estimation of thorium was first proposed by Kauffman (11) in 1899. He found that thorium formed a white amorphous precipitate when sodium hypophosphate or hypophosphoric acid was added to a thorium solution. The precipitated thorium hypophosphate was insoluble in water, acids and alkalis. This procedure was carried out in strongly acid solution and was important in the separation of thorium from the rare earths and for its quantitative gravimetric estimation. It is assumed that the precipitate was ignited to the pyrophosphate or converted to the oxalate and then ignited to the oxide as the final weighing form.

Rosenheim (24) was also successful in using hypophosphate for the determination of thorium. He dissolved the precipitated thorium hypophosphate in sulfuric acid, changed to the chloride, converted to the oxalate and ignited to the oxide. The method is described in detail by Meyer and Hauser (15). Koss (12) found that thorium could be separated from the cerium earths in 6% hydrochloric acid solution by hypophosphate precipitation. Hecht (9) also used hypophosphate to separate thorium from the rare earths. The Rosenheim method as modified by Wirth (30) was used to decompose the hypophosphate and the final weighing form was the oxide.

Since the precipitation of thorium was quantitative in strongly acid solution and a reasonable separation from the rare earths was possible, it was believed that a rapid volumetric method for the determination of thorium utilizing hypophosphate as the precipitating agent, would be feasible. The oxidation of hypophosphate with dichromate in strongly acid solution was investigated by Chulski (7). He found that the oxidation of hypophosphate by excess potassium dichromate in 12N sulfuric acid was quantitative.

The initial investigation on the volumetric determination of thorium by oxidation of thorium hypophosphate was begun by Paine (20). Thorium hypophosphate was precipitated from a 10% hydrochloric acid solution with a 10% excess of disodium dihydrogen hypophosphate reagent. Paine found that the precipitate contained a thorium to phosphorus ratio of 1 to 2.271 instead of a ratio of 1 to 2. The amount of excess hypophosphate must be calculated on this basis. The precipitate was washed free of chloride and hypophosphate with 250 ml. of 1% sulfuric acid. The choice of a proper acid concentration of the wash solution was investigated and Paine found that the precipitate was soluble in 5% sulfuric acid causing low results.

The thorium hypophosphate was oxidized with an excess of standard dichromate in 12N sulfuric acid. An excess of standard ferrous sulfate was added and the excess back titrated with standard dichromate using diphenylamine sodium sulfonate as a redox indicator. It was found that a thick asbestos suspension facilitated the filtration of the gelatinous precipitate. The asbestos blank was determined and this value was subtracted from the final volume of standard dichromate used.

An empirical factor was found to be necessary and it was suggested that the apparent equivalent weight of thorium oxide, 118.4, be used instead of the normal equivalent weight, 132.1.

The purpose of this investigation is to continue the study begun by Paine, to extend the method by studying the effect of interfering ions, and ultimately to apply the method to the determination of thorium in monazite sands.

HISTORICAL

The chief source of thorium at the present time is monazite sand, a phosphate of cerium earths with varying amounts of thorium as an accessory constituent. The deposits in Brazil and Travancore are the principle source of supply. Thorium also occurs as a rare silicate, $ThSiO_4$, thorite and thoranite, a mineral containing rare earths associated with uranium (10). Thorium was principally used in the preparation of incandescent gas mantles but recently has been used in the manufacture of photocells, X-ray targets, glow tubes, alloys for jet engines, and as a catalyst in the preparation of aldehydes and ketones (14).

Thorium normally exists in a single valency state of plus four, however, under special conditions unstable lower valency states have been prepared (1). Because of its similarities in ionic charge and ionic size, thorium resembles the elements of Group IV-A, and cerium IV. The fact that thorium is less basic than the trivalent rare earths makes possible the separation of thorium from the rare earths by controlled hydrolysis methods.

The literature prior to 1948 has been extensively reviewed by Moeller, Schweitzer and Starr (18), therefore, the historical will be limited to a literature survey since that time.

Since the thorium ion is colorless, colorimetric methods are relatively few. The methods depend on the formation of colored derivatives or of compounds from which a color may be developed. An indirect colorimetric method has been proposed by Rider and Mellon (21) in which thorium oxalate is precipitated with an excess of oxalic acid at a pH of 0.7-3.2. The excess oxalate is reacted with potassium permanganate. The unreduced permanganate gives the colored system. This method presupposes a separation of thorium from the rare earths. Ions which react with oxalate or reducing agents which destroy the permanganate color interfere. Murthy and Raghavarao (19) have used sodium alizarin sulphonate (alizarin red-S) to determine thorium colorimetrically. This method has been applied to monazite sand only after the removal of zirconium, titanium and cerium. The use of 1-(o-arsenophenylazo)-2-Naphthol-3,6 disulfonic acid has been suggested by Thomason, Perry and Byerly (25) as a rapid colorimetric method. The interferences are so numerous that the method is not practical. Iodine liberation, when thorium iodate is treated with hypophosphorous acid in the presence of sulfuric acid, has been used by Williams (29) as a basis for a colorimetric method.

Gravimetric procedures for the determination of thorium have received the greatest amount of attention. As a rule gravimetric methods are involved and require a great number of operations. An example of this is the hexamine method of Ismail and Harwood as published by the New Brunswick Laboratory (22). There are seventy-three separate operations in the analysis which ends with an oxalate precipitation followed by ignition to the oxide as the final weighing form. This is typical of most gravimetric procedures.

Volumetric methods for the determination of thorium have received little attention. Banks and Diehl (2) have determined thorium by an oxidimetric method based on the precipitation of thorium as the normal molybdate followed by reduction and titration of the molybdenum equivalent to the thorium. An electrometric method is described in which the thorium is titrated with ammonium paramolybdate in 7% acetic acid solution using a 0.1N calomel-molybdenum wire electrode system. Moeller and Fritz (16) have described the use of iodate for the volumetric determination of thorium. Thorium iodate is precipitated from a strong nitric acid solution and the thorium estimated by iodometric determination of the iodate content of the precipitate. This is a refinement of the method of Chernikhov and Uspenskaya (6) and has the disadvantages of loss due to hydrolysis and difficulty in removing the adsorbed iodate. Moeller and Schweitzer (17) have published a radiometric method in which the thorium is precipitated with an excess of standard pyrophosphate containing a known activity of radioactive phosphorus (P^{32}). The amount of excess pyrophosphate is determined by its radioactivity. Ytterium earths cause high results and a preliminary separation is recommended. The use of thorium periodate has been suggested by Venkataramanick and Raghavarao (26) as a volumetric method. Thorium periodate is precipitated from a hot neutral solution with potassium periodate. The gelatinous precipitate is dried and dissolved in hydrochloric acid. A slight excess of potassium iodide is added and the liberated iodine titrated with standard thiosulphate.

A recent method employing high frequency titrimetry has been investigated by Blaedel and Malmstadt (3). Oxalic acid is used in an indirect titration of thorium. Small amounts of titanium and zirconium may be tolerated but the method can not be used in the presence of rare earths and ions which complex or precipitate oxalate.

EXPERIMENTAL

A. Reagents

Standard Disodium Dihydrogen Hypophosphate Solution

Disodium dihydrogen hypophosphate was prepared by the oxidation of red phosphorus with sodium chlorite solution according to the directions of Leininger and Chulski (13). Exactly 7.8535 grams of the air dried reagent was dissolved in water and diluted to one liter to give a 0.05N solution with respect to the oxidation of hypophosphate to phosphate. Because the compound was difficult to dry to the exact state of hydration, $Na_2H_2P_2O_6 \cdot 6H_2O$, the solution was standardized with standard potassium dichromate.

Standard Potassium Dichromate Solution

Baker's primary standard grade potassium dichromate was ground to a fine powder and dried in an oven at 140° C. for four hours. The crystals were cooled in a desiccator for thirty minutes and the correct amount was weighed out to give a 0.15N standard redox solution.

Standard Ferrous Sulfate Solution

A 0.15N ferrous sulfate solution was prepared by dissolving approximately the correct amount of ferrous ammonium sulfate in six liters of 1M sulfuric acid solution. The solution was standardized daily against the standard dichromate.

Diphenylamine Sodium Sulfonate Indicator

Exactly 0.32 grams of barium diphenylamine sulfonate was dissolved in 100 ml. of water and 0.5 grams of sodium sulfate was added. The solution was filtered by decantation from the precipitated barium sulfate. An indicator blank of 0.05 ml. was subtracted from the amount of dichromate used (28).

Asbestos Suspension

Approximately 50 grams of Baker's acid washed asbestos were weighed into a Buechner funnel and washed with concentrated hydrochloric acid and concentrated nitric acid. The asbestos was washed free of acid with water and transferred to a one liter beaker. It was allowed to digest overnight on the steam bath in a dichromate-sulfuric acid solution. The asbestos was then filtered and washed a number of times with large quantities of distilled water. It was finally diluted to a thick suspension with two liters of distilled water. Fifty ml. of this suspension were digested for three hours on a steam bath with exactly 25 ml. of standard dichromate in 12N sulfuric acid. The solution was cooled and diluted to 250 ml. Eighteen ml. of 85% orthophosphoric acid were added. A measured excess of standard ferrous sulfate was added and the excess back titrated with standard dichromate using diphenylamine sodium sulfonate as the redox indicator. The amount of dichromate used constitutes the asbestos blank.

The asbestos blank was not a constant one but varied considerably for each preparation. The asbestos absorbs dichromate into its pores and this is only partially removed during the washing with distilled water. The same lot of asbestos was used throughout this study and the blanks ranged from 0.16 ml. to 0.33 ml.

Standard Thorium Nitrate Solution

A standard thorium nitrate solution prepared by Paine (20) was used throughout this study. An approximately 0.05M thorium nitrate solution was prepared from Baker's thorium nitrate crystals and distilled water. The thorium content was determined by the gravimetric potassium iodate method as described by Bonardi (4) and checked by precipitation of thorium oxalate. The oxalate was ignited to the oxide and weighed. The solution was found to contain 0.3046 grams of thorium oxide in 24.92 ml. (calibrated pipet).

B. Factors Influencing the Apparent Milliequivalent Weight

1. Acidity of Medium and Wash Solution

It has been shown that an empirical factor is necessary in this method (20). The apparent equivalent weight of thorium oxide must be used in place of the normal equivalent weight. The formula, ThP_2O_6, would require an equivalent weight for the thorium dioxide of 132.0. The apparent equivalent weight is obtained by dividing the grams of thorium dioxide present by the number of equivalents of dichromate used in the oxidation of hypophosphate to phosphate. The change in oxidation number is one for each phosphorus atom.

The general procedure followed was to precipitate thorium hypophosphate from an acid solution. The precipitate was filtered through a Gooch crucible and washed with a dilute acid solution. The precipitated hypophosphate was transferred to the original container and oxidized with an excess of standard dichromate. A measured amount of standard ferrous sulfate was added and the excess back titrated with standard dichromate using diphenylamine sodium sulfonate as the redox indicator.

The initial problem was to study the effect of the wash solution on the solubility of the precipitated thorium hypophosphate. Precipitation was carried out in a 10% hydrochloric acid solution as suggested by Hecht (9). The following were mixed in a 250 ml. centrifuge bottle:

25 ml. of standard thorium nitrate solution
18 ml. of concentrated hydrochloric acid
5 ml. of 3% hydrogen peroxide
50 ml. of distilled water
50 ml. of asbestos suspension

The solution is heated in a boiling water bath and a 10% excess of standard disodium dihydrogen hypophosphate, based on the ratio of thorium to phosphorus of 1:2.3 (20), is added. The hypophosphate is added slowly from a buret and the hot solution is stirred constantly during the addition. The precipitate is allowed to digest several minutes. The solution is then centrifuged for thirty minutes and filtered through a Gooch crucible fitted with an asbestos mat. The precipitate is washed with 250 ml. of a 1% sulfuric acid solution which effectively removes the chloride and the excess hypophosphate. The precipitate and the asbestos mat is transferred with a nickel spatula to the original bottle and the crucible is rinsed thoroughly with 50 ml. of hot water. Exactly 25 ml. of 0.15N potassium dichromate and enough concentrated sulfuric acid to make the solution 12N (35 ml.) are added. The solution is heated in a boiling water bath for two hours with constant stirring. Adjustable electric stirrers were used. After the precipitate has been completely oxidized, the contents are cooled and transferred to a 500 ml. Erlenmeyer flask. The solution is diluted to 250 ml. and 18 ml. of 85% orthophosphoric acid are added. A measured excess of standard ferrous sulfate, exactly 25 ml., is added and the excess is back titrated with 0.15N dichromate. The asbestos blank and the indicator blank are subtracted from the volume of potassium dichromate used. The results are recorded in Table I.

Willard and Gordon (27) have shown that 70% perchloric acid has several advantages over sulfuric acid in the decomposition of monazite sand. It was, therefore, decided to determine the effect of precipitating

TABLE I

EFFECT OF ACIDS ON SOLUBILITY

Wt. ThC$_2$ Present g.	Acidity by Volume	Wash Solution	Apparent Meq. Wt.
0.3048	10% HCl (12M)	250 ml. 1% $HClO_4$	0.1043 0.1051 0.1043 0.1047
			Av.0.1048
0.3048	10% HCl (12M)	150 ml. 1% H_2SO_4	0.1084 0.1091 0.1091
			Av.0.1088
0.3048	10% $HCLO_4$ (70%)	150 ml. 1% $HCLO_4$	0.1016 0.1016 0.1026 0.1023
			Av.0.1020
0.3048	10% $HCLO_4$ (70%)	150 ml. 1% $HCLO_4$ Saturated ThP_2O_6	0.1012 0.1023 0.1012 0.1016
			Av.0.1016

thorium hypophosphate from a perchloric acid solution and washing with dilute perchloric acid. Perchloric acid does not interfere in the oxidation of hypophosphate and the washing period would require less time than if hydrochloric acid was used. The volume of wash solution necessary to remove the excess hypophosphate was reduced to 150 ml. which also saved time. The time required to carry out the precipitation and washing was two hours when a perchloric acid medium (10% by volume of 70% perchloric acid) and a 1% perchloric acid wash solution was used.

Saturating the wash solution with thorium hypophosphate has only a slight effect on reducing the solubility. This is an indication that there is not only a solubility effect to take into consideration but also the possibility of loss due to dispersion.

These solubility studies show that a perchloric acid system was most satisfactory in reducing the solubility of the precipitate and effectively removing the excess hypophosphate.

2. Effect of Varying Amounts of Thorium on the Milliequivalent Weight

In order to establish the lower limit of applicability, a study of the effect of varying the amounts of thorium on the apparent milliequivalent weight was carried out. The results are listed in Table II. In each instance the precipitating medium was 10% perchloric acid and 150 ml. of 1% perchloric acid were used as the wash solution. It will be noted that a two-fold dilution had little effect on the factor, however, a four-fold dilution produced inconsistent results. The range should be kept between 0.15 and 0.3 grams of thorium oxide for accurate

TABLE II

EFFECT OF VARYING AMOUNTS OF THORIUM

Wt. ThO_2 Present g.		Apparent Meq. Wt.
0.0731		0.0973
0.0733	Four fold excess of	0.0973
0.0737	$Na_2H_2P_2O_6$	0.0958
0.0741		0.0988
		Av. 0.0973
0.1455		0.1020
0.1477	Two fold excess of	0.1025
0.1466	$Na_2H_2P_2O_6$	0.1017
		Av. 0.1021
0.3048		0.0999
0.3048	Two fold excess of	0.1009
0.3048	$Na_2H_2P_2O_6$	0.1012
0.3048		0.1002
		Av. 0.1005

results. The upper limit could be higher than 0.3 grams but a larger amount of precipitate is difficult to filter and wash free of excess hypophosphate.

3. Effect of Cerium on the Milliequivalent Weight

Since the major interference to be expected is from cerium, the effect of varying amounts of cerium on the apparent milliequivalent weight of thorium oxide was investigated.

To a hot solution containing:

25 ml. of standard thorium nitrate
15 ml. of 3% hydrogen peroxide
15 ml. of 70% perchloric acid
35 ml. of distilled water
50 ml. of asbestos suspension
10 grams of primary standard grade ammonium hexanitrate cerate (gives 3.0 grams of CeO_2)

a 10% excess of 0.05M disodium dihydrogen hypophosphate was added. The solution was allowed to stand for several minutes then centrifuged until the supernatent liquid was clear. The solution was filtered through a Gooch crucible fitted with an asbestos mat. The precipitate was washed with 150 ml. of a 1% perchloric acid solution. The gelatinous mass was transferred to the original bottle and the crucible was rinsed with hot water. The volume at this point was 50 ml. The solution was made 12N with respect to sulfuric acid by adding 35 ml. of concentrated sulfuric acid and exactly 25 ml. of 0.15N potassium dichromate was pipetted into the bottle. The mixture was heated in a boiling water bath with constant stirring for two hours. At the end of this time, the solution was cooled and transferred to a 500 ml. Erlenmeyer flask. The green solution was diluted to 250 ml. and exactly 25 ml. of standard ferrous sulfate were added. Eighteen ml. of 85% orthophosphoric acid is added and the excess ferrous sulfate was back titrated with standard dichromate to the diphenylamine sodium sulfonate end point. The indicator and asbestos blanks were subtracted from the volume of dichromate used. The results of varying cerium content are shown in Table III. There appeared to be no serious interference from cerium even when there was ten times as much cerium as thorium. The 3% hydorgen peroxide was effective in reducing the ceric to cerous ion which does not interfere.

4. Effect of Acidity in the Presence of Interferences

It is known that the trivalent elements such as the rare earths do not form hypophosphates which are insoluble in strong acid solutions. In order to ascertain the optimum acidity for the precipitation of thorium in the presence of rare earths ions, thorium hypophosphate was precipitated in the presence of a fixed amount of cerium with varying acid concentrations. The thorium was precipitated in the same manner previously described and oxidized in the usual way. The acidity was the only variable. The results are tabulated in Table IV.

The initial acidities ranged from 10% to 5% but after addition of the 10% excess of disodium dihydrogen hypophosphate reagent the acidities fell in a range of 6.5% to 3.0%. Results were consistant when the acidity was in the higher range. This was in line with the findings of Koss (12) who showed that inconsistencies resulted when the acidity fell below 6% hydrochloric acid by volume, especially in the presence of such

TABLE III

EFFECT OF CERIUM

Wt. ThO_2 Present g.	Acidity by Volume	Wt. CeO_2 Present g.	Apparent Meq. Wt.
0.3048	10% $HClO_4$	3.0	0.0994
			0.0994
			0.0996
			0.0993
			Av. 0.0994
0.3051	10% $HClO_4$	2.5	0.0993
			0.0994
			0.0990
			0.0993
			Av. 0.0992
0.3048	10% $HClO_4$	2.0	0.1018
			0.1016
			0.1011
			0.1011
			Av. 0.1014

TABLE IV

VARYING ACIDITY IN THE PRESENCE OF CERIUM

Wt. ThO_2 Present g.	Initial Acidity	Final Acidity	Wash Solution	Apparent Meq. Wt.
0.3048	10% $HClO_4$ by volume	6.5%	150 ml. 1% $HClO_4$	0.0994
				0.0994
				0.0996
				0.0993
				Av. 0.0994
0.3048	7.5% $HClO_4$ by volume	4.9%	150 ml. 1% $HClO_4$	0.0992
				0.0983
				0.0983
				0.0983
				Av. 0.0985
0.3048	5.0% $HClO_4$ by volume	3.0%	150 ml. 1% $HClO_4$	0.0899
				0.0951
				0.0804
				0.0980
				Av. 0.0908

interferences as cerium. Best results were obtained when the initial acidity was 10%.

5. Effect of Thorium-Cerium Ratio on the Factor

The results shown in Tables III and IV indicate that the apparent milliequivalent weight of thorium can be reproduced in the presence of cerium when the cerium to thorium ratio is 10:1 if precipitation is made from a 10% perchloric acid solution. It was necessary to determine if this ratio was consistent when the quantities of both thorium and cerium were changed but the ratio maintained at 10 to 1. The precipitation and oxidation procedures followed were the same used in the previous studies with one exception, 2 ml. of 30% hydrogen peroxide was used in place of 3% in order to keep down the volume of reducing agent necessary. The results show that when the cerium to thorium ratio is kept within the range 8-10:1 consistent results can be obtained, however, when the cerium content is changed considerably, the apparent milliequivalent weight changes appreciably.

C. Determination of Thorium in Monazite Sand

A sample of Brazilian monazite sand was obtained through the courtesy of the Lindsay Light and Chemical Company of West Chicago, Illinois. The sample as received was ground to a fine powder, minus 200 mesh, and was analyzed by the peroxide-double oxalate-hexamine method (5). This method is used by the company as an umpire method when results of the highest accuracy are desired. The exact percentage of

TABLE V

EFFECT OF THORIUM-CERIUM RATIO

Wt. ThO_2 Present g.	Wt. CeO_2 Present g.	Apparent Meq. Wt.
0.3051	3.0	0.0994
		0.0996
		0.0994
		0.0993
		Av. 0.0994
0.2002	2.0	0.0996
0.1988		0.0993
0.2002		0.0998
0.1993		0.0994
		Av. 0.0995
0.1990	3.0	0.0961
0.1995		0.0976
0.1992		0.0960
		Av. 0.0966

thorium oxide was not known until the investigation was completed.

It was hoped that the hypophosphate method could be applied directly to the monazite sand without prior separation of the interfering elements. A 2.5 gram sample of monazite sand was decomposed in a platinum dish with 20 ml. of 70% perchloric acid according to the directions of Willard and Gordon (27). The mixture was boiled for 1.5 hours. The contents of the dish were cooled somewhat and 30 ml. of water were added followed by 2 grams of hydrazine dihydrochloride. The solution was heated on a steam bath for one hour. At this point the solution was clear. Three grams of Celite filter-aid were added and the solution was filtered through a Whatman No. 41 paper. The residue was washed several times with 1-3 perchloric acid, one part 70% perchloric acid and three parts water. The filtrate was evaporated on the steam bath to a volume of about 50 ml. Five ml. of 3% hydrogen peroxide and 50 ml. of asbestos suspension were added. The solution was heated in a boiling water bath for several minutes. The solution formed a solid gel which indicated that the phosphates must be removed prior to the precipitation of the hypophosphate.

In order to separate the thorium from the phosphorus and the rare earths, an attempt was made to precipitate thorium from a sulfuric acid solution as a peroxysulfate with hydrogen peroxide (23). A 10 gram sample of monazite sand was decomposed with 25 ml. of concentrated sulfuric acid. The mixture was heated in a platinum dish for one hour. The mixture was cooled and poured into a beaker containing crushed ice. The contents were poured into a 250 ml. volumetric flask and diluted to volume. The solution was filtered through a Whatman No. 42 paper and the first 20 ml. of filtrate was discarded. The remainder was collected in a dry 250 ml. volumetric flask. A 25 ml. sample was pipetted into a 400 ml. beaker and the acidity was adjusted to 1N with respect to sulfuric acid. Thirty ml. of 30% hydrogen peroxide were added. The solution was heated for a short time between 55° and 60° C. and then cooled to room temperature. No precipitate was observed. The acidity was adjusted to a pH of 2.5 with ammonium hydroxide and a gelatinous precipitate resulted. This precipitate proved to be a thorium and rare earth phosphate. Further information of the exact conditions necessary to carry out the quantitative precipitation of the peroxysulfate were not available because the material has not been declassified by the Atomic Energy Commission. This approach was, therefore, abandoned.

The only solution to the troublesome interference of phosphorus was an oxalate separation. This separates thorium and the rare earths from phosphorus as well as zirconium and titanium.

A 50 gram sample of monazite was weighed into a 1000 ml. Erlenmeyer flask and 200 ml. of 70% perchloric acid were added (27). The mixture was boiled vigorously for 1.5 hours. The contents were cooled, 50 ml. of 70% perchloric acid and 300 ml. of water were added with constant rotation. Eighteen grams of hydrazine dihydrochloride were added slowly with vigorous shaking. The contents were warmed on a steam bath for one hour to remove gaseous decomposition products. The solution became clear but there was still a residue probably consisting of rutile, quartz, silica and zircon.

The flask was cooled with tap water and 3 grams of Celite filter-aid were added. The solution was agitated in order to distribute the filter-aid well. The solution was filtered through a medium porosity filter paper using a platinum cone for support. The filter paper was removed and macerated with a few ml. of perchloric acid. It was then filtered and the filtrate was added to the main solution. This was repeated several times. The combined filtrates were diluted with perchloric acid, 1-3, to 1000 ml. in a volumetric flask. A 50 ml. sample was pipetted into a 600 ml. beaker. Concentrated ammonium hydroxide was added with mechanical stirring to the appearance of a permanent turbidity. Ten ml. of concentrated hydrochloric acid were added and the solution was allowed to stand 5 minutes with constant stirring. One hundred ml. of water were added followed by 12 grams of methyl oxalate. The solution was warmed gently (70°-85° C.) for thirty minutes. After the thirty minute warming period, a hot solution of 8 grams of oxalic acid in 280 ml. of water was added. The contents were heated for an additional thirty minutes.

The solution was cooled to room temperature, filtered through a Watman No. 41 paper and washed with 2% oxalic acid containing 40 ml. of concentrated hydrochloric acid per liter. The filter paper with the thorium and rare earth oxalates was decomposed by evaporating with 20 ml. of concentrated nitric acid and 10 ml. of 70% perchloric to fumes of the latter. The solution is now freed of phosphates.

The thorium hypophosphate was precipitated from a hot 10% perchloric acid solution containing 2 ml. of 30% hydrogen peroxide and 50 ml. of asbestos suspension, with a 10% excess of standard hypophosphate reagent (based on the assumption of 7% thorium oxide in the monazite sample). The precipitated hypophosphate was centrifuged, filtered through a Gooch crucible and washed with 150 ml. of 1% perchloric acid. The precipitate was transferred to the original bottle and exactly 25 ml. of 1.15N potassium dichromate is added. The solution is made 12N with respect to sulfuric acid by adding 35 ml. of concentrated sulfuric acid. The mixture is heated in a boiling water bath for two hours with constant stirring. When the hypophosphate is completely oxidized, the solution is transferred to a 500 ml. Erlenmeyer flask. The solution is diluted to 250 ml. with water. Exactly 25 ml. of standard ferrous sulfate and 18 ml. of orthophosphoric acid are added. The excess ferrous sulfate is back titrated with standard dichromate using diphenylamine sodium sulfonate as the redox indicator. The asbestos and indicator blanks are subtracted from the volume of dichromate used.

The thorium oxide is calculated by multiplying the total number of milliequivalents of dichromate used by the apparent milliequivalent weight of thorium oxide (0.0995, Table IV) and dividing by the sample weight. Results on many samples were consistently high and the cause was finally attributed to the incomplete decomposition of the oxalate. A qualitative test on the decomposition of pure oxalic acid with perchloric and nitric acids revealed that the oxalic acid was not entirely oxidized. This would allow some thorium to precipitate as the oxalate which would cause high results. A subsequent run using concentrated potassium permanganate to aid in the decomposition of the oxalates proved unfruitful since in the acid solution cerous ion was preferentially oxidized to the ceric state. Because of high results, it was assumed that the oxalates were not completely decomposed. The only solution to the oxalate decomposition was ignition to the oxide.

Individual 2.5 gram samples of monazite sand were weighed into 250 ml. Erlenmeyer flasks containing 5 ml. of concentrated nitric acid and 30 ml. of 70% perchloric acid (8). The mixture was boiled vigorously for 1.5 hours. The flasks were cooled with tap water, 10 ml. of water and 5 ml. of 3% hydrogen peroxide were added. The flasks were heated for several minutes to clarify the solutions. They were then cooled and the contents filtered through a Whatman No. 41 paper. The residues were washed with 1-3 nitric acid. The filtrates were evaporated to dense white fumes in a 600 ml. beaker. The solutions were cooled and 50 ml. of water were added followed by 5 ml. of 3% hydrogen peroxide. The beakers were warmed until the solutions became clear. One hundred ml. of water were added and enough ammonium hydroxide to give a permanent turbidity. The solutions were stirred and 10 ml. of concentrated hydrochloric acid were added. The solutions were allowed to stand for ten minutes.

To the hot solutions, 12 grams of methyl oxalate were added and the solutions were heated gently between 70° and 85° C. The heating was continued for thirty minutes after which a hot solution containing 8 grams of oxalic acid in 200 ml. of water was added. The solutions were kept warm for an additional thirty minutes.

The solutions were allowed to cool to room temperature and the oxalates were filtered through Whatman No. 42 filter paper. The oxalates were washed by decantation with a 2% oxalic acid solution containing 40 ml. of concentrated hydrochloric acid per liter. The oxalates were transferred to platinum crucibles and ignited to the oxides. The oxides were dissolved in 15 ml. of concentrated hydrochloric acid containing a small crystal of potassium iodide (5). The crucibles were rinsed with hot water. The solutions were heated on a hot plate until the oxides completely dissolved. After dissolution, 10 ml. of 70% perchloric acid were added and the solutions heated until the perchloric acid began to fume.

The perchloric acid solutions were transferred to 250 ml. centrifuge bottles and the beakers were rinsed with water. The volume at this point was 50 ml. Fifty ml. of asbestos suspension and 2 ml. of 30% hydrogen peroxide were added. The solutions were heated in a boiling water bath to remove the excess peroxide. A 10% excess of hypophosphate reagent is added with constant stirring. The precipitate was allowed to digest several minutes. The bottles were then placed in the centrifuge for thirty minutes. The solution is filtered through a Gooch crucible fitted with an asbestos mat and washed with 150 ml. of 1% perchloric. The mat is transferred to the original bottle and the crucible is rinsed with 50 ml. of hot water. Exactly 25 ml. of 0.15N potassium dichromate and 35 ml. of concentrated sulfuric acid are added to the aqueous mixture. The solutions are heated for two hours in a boiling water bath with mechanical stirring. The bottles were cooled and the solutions transferred to 500 ml. Erlenmeyer flasks. The suspension was diluted to 250 ml. and 18 ml. of 85% orthophosphoric acid were added. A measured excess, 25 ml. of standard ferrous sulfate was added and the excess back titrated with standard dichromate using the usual diphenylamine sodium sulfonate end point. The asbestos and indicator blanks are subtracted from the final volume of dichromate used. The amounts of thorium oxide found were calculated and tabulated in Table VI. There was good precision among the samples.

In order to obtain a check to determine if the method would apply when the thorium to cerium ratio was altered, a set of four determinations were made using 2.5 grams samples of monazite sand and a measured amount of standard thorium nitrate solution. If the recovery were complete, the method would be applicable to any thorium containing sand.

The decomposition and precipitation procedures were the same as those described for the previous determinations. A 10 ml. sample of thorium nitrate solution containing 0.1302 grams of thorium oxide was added just prior to the precipitation of the hypophosphate. The oxidation procedure was not altered. Calculations of the amount of thorium recovered show that an error averaging plus 5.5 mg. resulted (Table VII). This is an error of 3%. The error would be smaller and almost negligible if the apparent milliequivalent weight were determined when the thorium to cerium ratio was also changed.

At the completion of this work, the results obtained by the hypophosphate method were checked against the analyzed value for the monazite.

TABLE VI

THORIUM IN MONAZITE SAND

Wt. Monazite Sand Taken g.	Percent ThO_2 Found	Precent ThO_2 Present	Error
2.5	6.66	6.60	+ 0.06
	6.92		+ 0.32
	6.67		+ 0.17
	6.82		+ 0.22
	6.77		+ 0.17
	6.77		+ 0.17
	6.59		+ 0.01
	6.60		+ 0.00
	6.60		+ 0.00
	6.56		+ 0.04
	6.63		+ 0.03
	6.55		+ 0.05
	6.60		+ 0.00
	6.57		+ 0.03
	Av. 6.66		Av. 0.08

TABLE VII

THORIUM RECOVERY

Wt. ThO_2 from Monazite g.	Wt. ThO_2 Added g.	Wt. ThO_2 Recovered g.	Error mg.
0.1650	0.1302	0.1733	+ 8.3
0.1650	0.1302	0.1708	+ 5.8
0.1650	0.1302	0.1693	+ 4.3
0.1650	0.1302	0.1690	+ 4.0
			Av. 5.5

DISCUSSION AND CONCLUSION

The hypophosphate method for the volumetric determination of thorium has been shown to give fairly accurate results. It has the advantages of being relatively rapid and involves only one separation. The oxalate precipitation efficiently removes phosphorus, zirconium, and titanium. The acid concentration of the original solution should be kept between 6.5% and 10% perchloric acid by volume. There is no interference from cerium at this acidity in the presence of hydrogen peroxide.

The lower limit of thorium oxide which can be present to give satisfactory results should be in the vicinity of 0.15 gram. The upper limit would be fixed by the amount of precipitate which could be handled efficiently. Large amounts of precipitate would be difficult to filter and wash free of excess hypophosphate.

The asbestos suspension is essential for the rapid filtration of the gelatinous precipitate. A blank should be determined on each new preparation of asbestos. The blanks will vary but low blanks can be obtained if the asbestos is washed sufficiently with large quantities of distilled water prior to dilution. The asbestos absorbs dichromate and is removed only after many washings.

The fact that an empirical factor is necessary is somewhat of a disadvantage. The apparent milliequivalent weight should be determined for the thorium to cerium ratio suspected in the sample. It has been shown that when the thorium to cerium ratio is 1:8-10, the apparent milliequivalent weight would have a value of 0.0995 instead of the normal milliequivalent weight of 0.1320. The apparent milliequivalent weight is calculated by dividing the number of grams of thorium oxide by the total number of milliequivalents of dichromate used. In the oxidation of hypophosphate to phosphate, the change in oxidation number is one for each phosphorus atom.

The wash solution should be slightly acid. A 150 ml. of 1% perchloric acid were found to be sufficient to remove the excess hypophosphate and to reduce the solubility of the precipitate.

The filtration process can be done in a minimum amount of time if the precipitate is not allowed to go to dryness before the addition of more wash solution. Once the precipitate has been drawn to dryness, the pores of the asbestos mat become filled and the filtration requires twice as much time. By washing many times with small volumes, the excess hypophosphate can be removed and the filtration can be completed in less than one hour.

The determination of thorium in monazite sand using this method has been shown to be accurate and reproducible. The decomposition of the sand was most efficient when the sample was boiled with concentrated nitric acid and 70% perchloric acid. Only a slight insoluble residue remained. A few ml. of 30% hydrogen peroxide was capable of reducing ceric cerium to cerous which does not interfere. All the precautions cited previously should be observed when monazite sand is being analyzed. The entire analysis can be completed in less than ten hours.

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