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A NEW SEPARATION OF THORIUM FROM CERIUM, LANTHANUM, AND DIDYMIUM, AND ITS APPLICATION TO THE ANALYSIS OF MONAZITE.¹

BY FLOYD J. METZGER.

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THE marked disagreement, among well-recognized chemists, in the determination of thorium in monazite sand, seemed sufficient to warrant a more careful investigation of the methods now existing for its determination, and it was with this object in view that the following work was undertaken.

By thorium, is meant the element as it was generally understood before the more recent researches of Brauner and Baskerville, which point quite conclusively toward the isolation of a new element from what is now generally called thorium.

REVIEW OF METHODS.

Among the methods proposed for the separation and purification of thorium, the following may be mentioned as the most important.

Bahr² was the first to notice that thorium oxalate was soluble in a hot concentrated solution of ammonium oxalate. Since that

¹ Read at the meeting of the New York Section of the American Chemical Society, June 6, 1902.

² *Ann. Chem. (Liebig)*, **132**, 231 (1864).

time numerous investigators, namely, R. Bunsen,¹ C. Glaser,² Hintz and Weber³ and others, have attempted to perfect the separation and have found that a complete separation of thorium from the other rare earths, in the form of oxalates, cannot be made by one extraction with a hot concentrated solution of ammonium oxalate, but that the operation has to be repeated several times.

The separation of thorium from the other rare earths by using sodium thiosulphate was first proposed by Chydenius⁴ and later worked by Hermann,⁵ Drossbach,⁶ Hintz and Weber,⁷ and others.

The separation is based on the fact that thorium is precipitated from a neutral or slightly acid solution, by sodium thiosulphate, while cerium and the other rare earths remain in solution.

As was pointed out by Chydenius⁴ and also Glaser,² the precipitation is not complete in one operation, but by reprecipitating the filtrate with ammonia, converting this into the chloride and reprecipitating with sodium thiosulphate (repeating as long as a precipitate is obtained with sodium thiosulphate), a complete separation is obtained.

Hintz and Weber¹⁰ say the separation works best in dilute solutions and in the presence of two or three drops of dilute hydrochloric acid and give this method preference.

Cleve¹¹ was the first to show that thorium could be precipitated by hydrogen peroxide from a sulphate solution, and that the precipitate had the composition represented by the formula $\text{Th}_4\text{O}_7\text{SO}_4$.

Boisbaudran¹² also used hydrogen peroxide as a precipitant about the same time.

Wyrouboff and Verneuil¹³ carried the investigation a little farther and showed that an analogous precipitate of thorium could be obtained from a solution of the nitrate (*i. e.*, $\text{Th}_4\text{O}_7\text{N}_2\text{O}_5$) and

¹ Pogg. Ann., **155**, 380 (1875).

² Ztschr. anal. Chem., **36**, 213 (1897).

³ Ibid., **36**, 27 (1897).

⁴ Pogg. Ann., **119**, 46.

⁵ J. prakt. Chem., **93**, 106.

⁶ Ztschr. angew. Chem., (1901), p. 655.

⁷ Ztschr. anal. Chem., **36**, 676 (1897); Ibid., **35**, 525.

⁸ Loc. cit.

⁹ Chem. Ztg., **20**, 612 (1896).

¹⁰ Loc. cit.

¹¹ Bull. Soc. Chim., **43**, 53 (1885).

¹² Compt. rend., **100**, 605.

¹³ Ibid., **126**, 340 (1898).

that it gave a complete separation of thorium from the other rare earths.

Kosmann¹ separated the greater part of the didymium salt from the crude material, as sulphate. Then he separated thorium from cerium, lanthanum and didymium by successive treatment of the acid solution with hydrogen peroxide solution, an acid-ammonium citrate solution, and ammonia. A precipitate of aluminum phosphate and thorium hydroxide was formed which was afterwards separated by oxalic acid.

Various other methods which are well worth mentioning are: Urbain² used acetylacetonate of sodium. Chavastelon³ separated thorium by means of sodium sulphite. Boisbaudran⁴ precipitated thorium, after reducing the cerium, with cuprous oxide. Dennis⁵ used potassium nitride. Delafontaine⁶ separated thorium from zirconium by fusion with potassium acid fluoride and leaching out the double potassium-zirconium fluoride with hot water. Muthmann and Baur⁷ employed potassium chromate. Kersten⁸ based a method upon the difference in solubility of the oxides in hydrochloric acid. Nilson⁹ precipitated the hydrated sulphate of thorium.

Undoubtedly the best method which has yet been published for the complete analysis of monazite is that of Glaser.¹⁰

Benz,¹¹ in a recent article, makes a very careful study of the methods now employed for the analysis of monazite (the ammonium oxalate, thiosulphate and hydrogen peroxide methods) and gives a good comparison of their accuracy.

He finds that one digestion of the mixed oxalates with even a large excess of ammonium oxalate is insufficient to bring into solution all the thorium; on the contrary he finds that only about one-half the thorium is dissolved, and that after repeated digestions considerable cerium is brought into solution.

¹ *Chem. Centrbl.*, (1897), Part 1, 837.

² *Bull. Soc. Chim.*, **15**, 347 (1896).

³ *Chem. Centrbl.*, **1**, 876 (1900).

⁴ *Chem. News*, **50**, 201 (1884); also *Compt. rend.*, **99**, 525 (1884).

⁵ *Am. Chem. J.*, **16**, 79 (1894); also *This Journal*, **18**, 947 (1896).

⁶ *Chem. News*, **75**, 230 (1897).

⁷ *Ber. d. chem. Ges.*, **332**, 2028 (1900).

⁸ *Pogg. Ann.*, **47**, 385 (1839).

⁹ *Ber. d. chem. Ges.*, (1882), p. 2521; *Ibid.*, (1887), p. 1666.

¹⁰ *This Journal*, **18**, 789 (1896).

¹¹ *Ztschr. angew. Chem.* (1902), p. 297.

With the thiosulphate method he gets very good results after three or four precipitations, and obtains the thoria almost without a trace of cerium. This, however, has the disadvantage of being extremely long.

Hydrogen peroxide, as he shows, precipitates thorium completely from a neutral solution, or from a solution very faintly acid with nitric acid. It also separates thorium from cerium and lanthanum by one reprecipitation.

EXPERIMENTAL.

VARIOUS PRECIPITANTS TRIED.

As very few weak organic acids have hitherto been employed for the separation of thorium from its associated rare earths, the following were tried:

Maleic Acid.—Aqueous solutions of maleic acid with thorium, cerium, lanthanum and didymium give no precipitate hot or cold. Solutions of cerium, lanthanum and didymium in 50 per cent. alcohol, give nothing hot or cold. A solution of thorium in 50 per cent. alcohol, gives no precipitate in the cold, but on heating, a partial precipitation results.

Cinnamic Acid produces at least a partial precipitation of thorium from 20 per cent. alcoholic solutions. The precipitate cannot be filtered (runs through) and for this reason the completeness of the precipitation was not determined. Cerium, lanthanum and didymium give nothing under the same conditions.

Picric Acid and thorium, in alcoholic solutions, give a partial precipitation of thorium. Cerium, lanthanum and didymium give no precipitate under these conditions.

Phthalic Acid in aqueous solution with cerium, lanthanum and didymium gives nothing cold or hot. Thorium, however, in aqueous solution with phthalic acid gives a partial precipitation on heating. From alcoholic solutions a heavy curdy precipitate results on heating, and is approximately half complete. Cerium, lanthanum and didymium, in alcoholic solutions with phthalic acid give no precipitate.

Fumaric Acid.—Aqueous solutions, hot or cold, give nothing with cerium, lanthanum or didymium. Thorium and fumaric acid in aqueous solutions give a precipitate in the cold, which forms slowly, but on applying heat the precipitate forms rapidly

(white, flocculent) , settles out nicely, and is almost complete. From solution in 95 per cent. alcohol, fumaric acid precipitates thorium quantitatively even in the cold. Cerium and fumaric acid in 95 per cent. alcohol give no precipitate in the cold, but, on heating, a small fraction of the cerium is thrown down. Lanthanum and didymium in 95 per cent. alcohol give nothing cold or hot. From solutions in 40 per cent. alcohol, fumaric acid gives a quantitative precipitation of thorium on heating; lanthanum and didymium under the same conditions give nothing. Cerium in 40 per cent. alcohol gives, with fumaric acid, nothing cold or hot, unless the cerium solution is quite strong, when a very small fraction is precipitated.

Ammonium Fumarate precipitates thorium, cerium, lanthanum and didymium from aqueous solutions, insoluble in excess, soluble in mineral acids.

Among the amido and amino compounds tried were:

Urea gave nothing.

Thiourea gave nothing.

Acetamide gave nothing.

Semicarbazine gave nothing.

Succinimide gives no precipitation of cerium, but gives a partial precipitation of thorium from alcoholic solutions.

Diethylamine precipitates thorium, cerium, lanthanum and didymium.

THE QUANTITATIVE PRECIPITATION OF THORIUM BY FUMARIC ACID.

From the experiments given on a preceding page it was now evident that thorium could be precipitated quantitatively from alcoholic solutions, leaving cerium, lanthanum and didymium in solution. It was desirable to know the smallest quantity of alcohol necessary to effect this precipitation, and still leave the cerium, lanthanum and didymium in solution. This strength was reached when the solution contained 40 per cent. of alcohol.

The following results will show the completeness of the precipitation from the various strengths of solution:

Alcohol. Per cent.	Volume. cc.	ThO ₂ .	
		Taken.	Found.
15	150	0.1568	0.1508
35	150	0.1568	0.1551
40	200	0.1961	0.1962
40	150	0.1568	0.1561
40	120	0.1176	0.1176
40	120	0.2007	0.2003
40	100	0.1004	0.1006
40	120	0.1176	0.1179
40	200	0.1961	0.1962

SEPARATION OF THORIUM FROM CERIUM, LANTHANUM AND
DIDYMIUM.

The salts used for the experiments were the best nitrates that could be purchased, and the thorium nitrate was purified according to the method suggested by Wyruboff and Verneuil¹ which is as follows:

Eighty-three grams of the nitrate, corresponding approximately to 39 grams of thoria, were dissolved in 8 liters of water. The solution was divided equally in twelve beakers and precipitated with hydrogen peroxide (10 cc. hydrogen dioxide for every 0.5 gram thorium dioxide). The solutions were then heated to 85° C. and allowed to settle. The precipitates were washed a dozen times by decantation with hot water, and then transferred to a large Büchner funnel, and the washing continued until the filtrate gave no precipitate with ammonia. The precipitate was then transferred to a large porcelain evaporating dish and 150 cc. of concentrated nitric acid added; heat was applied and the whole went into solution readily. The solution was evaporated to dryness, taken up in water, diluted to 8 liters, and the process repeated. The filtrate from the hydrogen peroxide precipitation was treated with ammonia and hydrogen peroxide, giving a brown precipitate of cerium trioxide. This precipitate of cerium peroxide was examined for lanthanum and didymium, but none could be detected.

A stock solution was made of this purified thorium nitrate and standardized very carefully by precipitation with oxalic acid. This was the thorium used for the experiments. A cold saturated solution of fumaric acid in 40 per cent. alcohol (containing approximately 0.1 gram per 10 cc.) was used as the precipitant.

¹ *Compt. rend.*, **126**, 4, 340 (1898).

METHOD OF ANALYSIS.

Make the solution of the neutral nitrate 40 per cent. alcohol (volume about 150-175 cc. with 0.1 to 0.2 gram thorium dioxide and about the same amount of admixed oxides), then add 12 to 15 cc. of fumaric acid solution (about 0.10 gram per 10 cc.) for each 0.1 gram thorium dioxide and heat to boiling (75° to 80° C.); allow to stand a few minutes until the precipitate settles, then filter (while still hot) through a long stem funnel, or by suction. Wash the precipitate four or five times with hot 40 per cent. alcohol, then put paper and precipitate into a platinum crucible, ignite, and weigh as thorium dioxide. A number of analyses were made in this way using mixtures of thorium with cerium, lanthanum and didymium and it was found that the thorium invariably carried with it an appreciable quantity of the impurity which could not be washed out, nor could it be prevented by the addition of such salts as ammonium chloride, ammonium nitrate, etc.

A few results will show the extent to which these impurities are carried down.

CeO ₂ .	La ₂ O ₃ .	Di ₂ O ₃ .	Fumaric acid. cc.	Volume. cc.	ThO ₂ .	
					Taken.	Found.
0.2000	25	150	0.1725	0.1730
0.2000	25	150	0.1961	0.1982
.....	0.2000	25	150	0.1921	0.1941
.....	0.2000	25	150	0.1961	0.1990
.....	0.2000	25	150	0.1882	0.1907
.....	0.2000	25	150	0.1961	0.1978
.....	0.2000	25	150	0.1961	0.1992
.....	0.2000	25	150	0.1961	0.1972
.....	0.2000	25	150	0.1882	0.1901
.....	0.2000	25	150	0.1961	0.1979

Reprecipitation was next tried, and gave very satisfactory results. For this reprecipitation it is only necessary to dissolve the precipitate of thorium fumarate (formed by the first precipitation) off the filter in hot dilute hydrochloric acid—or better, place the paper and precipitate back into the beaker, add a little dilute hydrochloric acid, heat, then filter off the paper—and evaporate to dryness on a water-bath. During the process of this evaporation some of the salt adheres to the sides of the beaker, but this is easily obviated by shaking the beaker occasionally and washing down with a few drops of water from a wash-bottle.

When the residue is free from acid (better add a few cubic centimeters of water and evaporate a second time), add about 50 cc. water (leaving the beaker on the water-bath) and stir the residue loose from the bottom with a rubber-capped stirring rod; some carbonaceous matter from the fumaric acid, partly decomposed, and also some fumaric acid and a trace of thorium fumarate will remain insoluble at this point, but need not be regarded. Add alcohol sufficient to make the solution 40 per cent., dilute to the proper volume with 40 per cent. alcohol, add a little fumaric acid (8 to 10 cc.) and precipitate as before; wash, ignite and weigh.

Hydrochloric acid was used instead of nitric for the solution of the thorium fumarate, for the reason that nitric acid formed, on evaporation, a deposit which was practically insoluble in water.

The following results will show the accuracy of the separation:

CeO ₂ .	La ₂ O ₃ .	Di ₂ O ₃ .	Fumaric acid. cc.	Volume. cc.	ThO ₂ .	
					Taken.	Found.
0.2000	25	150	0.1961	0.1966
0.2000	25	150	0.1961	0.1957
.....	0.2000	25	150	0.1961	0.1964
.....	0.2000	25	150	0.1961	0.1959
.....	0.2000	25	150	0.1961	0.1965
.....	0.2000	25	150	0.1968	0.1965

Mixtures of thorium, cerium, lanthanum and didymium were then made in the proportions in which they are usually found in monazite sand, and analyzed the same as above with these results:

CeO ₂ .	La ₂ O ₃ .	Di ₂ O ₃ .	Fumaric acid. cc.	Volume. cc.	ThO ₂ .	
					Taken.	Found.
0.283	0.133	0.157	10	175	0.0557	0.0558
0.283	0.133	0.157	25	200	0.0572	0.0571
0.283	0.133	0.157	10	175	0.0572	0.0574
0.283	0.133	0.157	10	175	0.0557	0.0558
0.566	0.266	0.314	15	350	0.1115	0.1114
0.566	0.266	0.314	15	350	0.1129	0.1132

Mixtures containing equal amounts of thorium, cerium, lanthanum and didymium, and mixtures containing thorium in excess were then analyzed as follows:

CeO ₂ .	Ta ₂ O ₅ .	Di ₂ N ₂ .	Fumaric acid. cc.	Volume. cc.	ThO ₂ .	
					Taken.	Found.
0.1000	0.1000	0.1000	10	120	0.0995	0.0990
0.1000	0.1000	0.1000	10	120	0.1003	0.0995
0.1000	0.1000	0.1000	25	130	0.1529	0.1523

CeO ₂ .	La ₂ O ₃ .	Di ₂ O ₃ .	Fumaric acid. cc.	Volume. cc.	ThO ₂ .	
					Taken.	Found.
0.1000	0.1000	0.1000	40	150	0.2007	0.2002
0.1000	0.1000	0.1000	40	150	0.2015	0.2010
0.1000	0.1000	0.1000	60	150	0.3011	0.3005
0.1000	0.1000	0.1000	60	150	0.3019	0.3023
0.0500	0.0500	0.0500	25	200	0.1961	0.1963
0.0500	0.0500	0.0500	25	200	0.1968	0.1969
0.0250	0.0250	0.0250	25	200	0.1976	0.1971
0.0250	0.0250	0.0250	25	200	0.1991	0.1985

EFFECT OF SALTS WITH ACETIC RADICALS ON THE PRECIPITATION OF
THORIUM BY FUMARIC ACID.

A very peculiar effect is noticed when an acetate is added to a solution of the rare earths (cerium, lanthanum, didymium, etc.), which has already had added to it some fumaric acid. The results are these:

Take a solution of cerium (lanthanum or didymium) in 40 per cent. alcohol and add to it a solution of fumaric acid; nothing results. If now, one or two drops of ammonium acetate is added to this mixture of cerium and fumaric acid, the cerium is precipitated completely. Then if to this solution containing the precipitate an excess of ammonium acetate is added, the whole redissolves and leaves a clear solution. Cerium (lanthanum or didymium) is not precipitated by ammonium acetate alone. Ammonium fumarate precipitates cerium (lanthanum or didymium) insoluble in excess of precipitant. Add to cerium (lanthanum or didymium) dissolved in 40 per cent. alcohol, fumaric acid, and then one or two drops of acetic acid, and nothing results; but then by adding to this one or two drops of ammonium acetate, the cerium is thrown down quantitatively as before. Thorium differs from cerium, lanthanum and didymium in that the precipitate formed by fumaric acid is only partially soluble in an excess of ammonium acetate. Sodium acetate has the same effect as ammonium acetate.

The exact reaction in the above experiments has not yet been studied, but it is quite evident that salts of acetic acid must be avoided in the separation of thorium from cerium, lanthanum and didymium by fumaric acid.

THE EFFECT OF OTHER METALS ON THE SEPARATION.

It was very desirable to know the effect of other metals on the

precipitation of thorium by fumaric acid, so all the metals available were tried. The solutions in all cases (where such solutions could be obtained) were made in 40 per cent. alcohol and the fumaric acid added. The following salts were tried:

CuSO_4 ; AgNO_3 ; AuCl_3 (acid); MgCl_2 ; CaCl_2 ; $\text{Sr}(\text{NO}_3)_2$; BaCl_2 ; ZnSO_4 ; CdCl_2 ; $\text{Hg}_2(\text{NO}_3)_2$; $\text{Hg}(\text{NO}_3)_2$; HgCl_2 ; H_3BO_3 ; $\text{Na}_2\text{B}_4\text{O}_7$; Al_2Cl_6 ; SnCl_4 (acid); SnCl_2 (acid); $\text{Pb}(\text{NO}_3)_2$; MnCl_2 ; Na_2HPO_4 ; As_2O_3 (slightly sol.); Sb (tartar emetic); $\text{Bi}(\text{NO}_3)_3$ (slightly sol.); $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$; VOCl_2 ; Na_2WO_4 ; Fe_2Cl_6 ; FeSO_4 ; CoCl_2 ; NiCl_2 ; H_2PtCl_6 .

Of the above-named salts, AgNO_3 , $\text{Hg}_2(\text{NO}_3)_2$, and $\text{Hg}(\text{NO}_3)_2$ were the only ones which gave any precipitation. The precipitation of mercurous nitrate appears quantitative as well as the precipitation of mercuric nitrate, while mercuric chloride gives no precipitate whatever. The precipitation of silver nitrate is only a partial one.

Among the rare earths obtainable were yttrium, samarium, gadolinium, erbium and zirconium, which, dissolved in 40 per cent. alcohol, gave with fumaric acid:

Yttrium gives no precipitate cold or hot. Samarium gives no precipitate cold or hot. Gadolinium gives no precipitate cold or hot. Erbium gives a very slight precipitate in the cold, which seems to increase somewhat on heating. Only a very small fraction, however, is thrown down. Zirconium gives a quantitative precipitation on heating.

THE COMPOSITION OF THE PRECIPITATE FORMED BY THORIUM AND FUMARIC ACID.

To determine the composition of the thorium fumarate, a quantity of pure salt was prepared by precipitating the purified thorium solution with fumaric acid, washing very thoroughly with 40 per cent. alcohol and drying. The salt was first dried at 105° C. in an air-bath, and then to determine the point at which the salt was decomposed, the temperature was gradually raised, causing a gradual loss in weight until at 202° to 205° C. it became practically constant and no indications of decomposition were evident even at 245° to 247° C. This dried salt, however, reabsorbed moisture to a considerable extent when exposed to the air.

In order to obtain concordant results, the water was first driven

off at 105° C., collected, and weighed as atmospheric moisture. For this purpose a large tin can, provided with a thermometer, was placed upon the combustion furnace, and the tube passed through in the reverse position. Air was passed through the tube and the temperature maintained at 105° for four hours; the absorption tube was weighed, the can removed and the combustion made in a current of oxygen. The water obtained in this was calculated as water of composition. The residue left in the boat should be thoria, and was weighed as such.

A number of combustions made in the above manner gave no constant results for hydrogen, while the thorium-carbon ratio was practically 1 : 4 as is seen from these results:

	ThO ₂ .	CO ₂ .	Ratio.
I.....	0.1319	0.0883	1 : 4.01
II.....	0.1606	0.1086	1 : 4.05

The above ratios were calculated from the thoria just after removal from the furnace. After the combustion had been completed and the boat (containing the thoria) weighed, it was placed in a platinum tube and heated with a blast-lamp for ten or fifteen minutes. White fumes were given off, and the thoria decreased in weight to the extent of several milligrams. These fumes do not condense, but if made to pass through alcohol they are partially absorbed, and from this solution a very slight precipitate can be thrown down with ammonia. The losses were:

0.1606 gram thoria lost on ignition 0.0039 gram.

0.1147 gram thoria lost on ignition 0.0036 gram.

0.1403 gram thoria lost on ignition 0.0053 gram.

0.1641 gram thoria lost on ignition 0.0054 gram.

Being under the impression that this loss was incurred by the coprecipitation (by fumaric acid) with thorium, of some compound, which on ignition with the blast yielded a volatile oxide, it was thought advisable to prepare a quantity of thorium fumarate from thorium which had been precipitated with fumaric acid and thoroughly ignited. This was done in the following way: The pure thorium solution was precipitated in the usual way with fumaric acid, and ignited for a period of one and one-half hours in the strongest heat that could be obtained from a blast-lamp. The thoria was again brought back into solution after many evaporations with concentrated sulphuric acid, precipitated with ammonia,

filtered, redissolved in nitric acid, evaporated to dryness, taken up in water and reprecipitated with fumaric acid, thoroughly washed, and dried.

Combustions were then made on this compound as before:

	ThO ₂ .	CO ₂ .	Ratio.	Loss on ignition.
I.....	0.1870	0.1270	1 : 4.07	0.0066
II.....	0.2434	0.0073

The same white fumes were driven off on ignition with the blast, causing a corresponding decrease in the weight of thorium left after combustion.

To learn whether the white fumes were a carbon-containing compound or not, the platinum tube was connected to the combustion furnace and then heated with a blast. No increase in weight was obtained in the soda-lime tube, showing the absence of carbon, but an increase, slightly greater than the loss in weight of thorium, was found in the water-absorption tube (pumice and sulphuric acid).

To find out whether the fumaric acid employed was pure and free from any non-volatile substance, several portions were burned at a gentle heat in a Bunsen flame; no residue was left. A combustion of the acid was also made giving:

	Calculated.	Found.
H	3.44	3.42
C.....	41.38	41.302

The fumaric acid was pure, and the white fumes obtained by the ignition of the thorium fumarate are as yet unaccounted for. These white fumes, however, will be made the subject of a separate investigation. The only conclusion to be drawn from the above work is that the thorium and fumaric acid react molecule for molecule. It is not supposed that the unsaturated valences in the fumaric acid play any part in the reaction, but rather that fumaric acid is of just the proper strength to throw out the very feebly basic thorium.

MONAZITE ANALYSES.

To test the application of the fumaric acid to the analysis of monazite sand, three samples were procured: two Brazil sands, and one from North Carolina,¹ and to check the results obtained,

¹ It was through the kindness of Professor Baskerville that we secured this sample of North Carolina sand.

two of the best known methods, the thiosulphate and ammonium oxalate separations, together with a third,—a combination of the thiosulphate and oxalate—were employed.

A description of the methods used is as follows:

Ammonium Oxalate Separation.—About 1 gram of the sand, ground to an impalpable powder, was weighed out into a platinum vessel, covered over with 15 to 20 cc. concentrated sulphuric acid, and evaporated on an asbestos board until fumes were no longer driven off. More sulphuric acid was added, and this repeated several times until the conversion of the phosphates into sulphates was complete.

This mass was then projected in very small quantities into about 700 cc. water at 0° C. with constant agitation (the temperature was not allowed to rise above 2° C.). This was allowed to stand several hours with frequent stirring, was filtered and washed.¹ The filtrate was then nearly neutralized with dilute ammonia (1:20) and 50 cc. of a cold saturated solution of oxalic acid added (for each gram of ore taken), stirred well, and allowed to stand. After the heavy white precipitate had settled completely, the solution was filtered, washed, and the precipitate washed into a 400 cc. beaker, using a cold saturated solution of ammonium oxalate for the purpose. After making the volume of ammonium oxalate equal to about 50 cc. the beaker was placed on a water-bath, covered with a watch-glass, and digested for one and one-half hours with occasional stirring. This was then diluted to 300 cc. and allowed to stand over night, filtered (filtrate A), and washed. The residue was again subjected to the treatment with ammonium oxalate, etc., etc., and filtered (filtrate B).

Filtrates A and B were combined and precipitated by a large excess of ammonia, heated to boiling, filtered, and the thorium hydroxide dissolved off the filter in hot dilute nitric acid; evaporated to dryness, the residue taken up in water and precipitated with oxalic acid. This precipitate of thorium oxalate, which still contained some impurity, was again treated with ammonium oxalate as before (one treatment), precipitated with an excess of ammonia, converted into the oxalate, ignited and weighed as thorium dioxide.

¹ Preliminary experiments showed that no metals precipitable by hydrogen sulphide were present, so this part of the process was omitted.

Thiosulphate Method.—The mineral was decomposed and brought into solution as before, and precipitated with oxalic acid. The precipitate of oxalates was washed into a beaker and treated with a strong solution of caustic potash (about 25 cc.) : heated to boiling (this converts the oxalates into hydroxides which are then quite soluble in acids), diluted, and filtered; washed thoroughly and dissolved off the filter in hot dilute hydrochloric acid (1:1); evaporated to dryness to free from acid, taken up in 75 to 100 cc. water and 15 cc. of a saturated solution of sodium thiosulphate added, and heated to boiling (this precipitates nearly all the thorium together with a trace of impurity and considerable sulphur); filtered (precipitate A), and the filter set aside for subsequent filtration. The filtrate was precipitated by an excess of ammonia, filtered, washed, dissolved in hydrochloric acid, evaporated to dryness, taken up in water and reprecipitated with thiosulphate as before. This was filtered through the paper containing precipitate A. The precipitation with thiosulphate was repeated, in the successive filtrates, as long as a precipitate was obtained (usually a third precipitation extracts the thorium completely).

The combined precipitates of thorium thiosulphate were washed completely, then dried and ignited. The ignited mass was fused several times with potassium bisulphate, taken up in water and a few drops of hydrochloric acid, and precipitated with oxalic acid. These oxalates were converted into the hydroxides as before, dissolved in hydrochloric acid, evaporated to dryness, taken up in water and reprecipitated with sodium thiosulphate; filtered, washed, dried and ignited. This was again fused with bisulphate, dissolved in water and a few drops of hydrochloric acid, and precipitated with oxalic acid; filtered, washed, ignited and weighed.

It was necessary to fuse the thoria several times with bisulphate to get it all into solution.

Combination Method.—Inasmuch as the methods just described are very lengthy and involve very troublesome processes, such as the repeated digestion of a large bulk of oxalates with ammonium oxalate or the repeated fusions necessary in the thiosulphate method, it was found very convenient to make a combination of the two. Another point, well worth mentioning, and shortening the process greatly, is the conversion of the thorium thiosulphate

back into the nitrate without ignition and repeated fusions. This is very easily and quickly done by washing the precipitate of thorium thiosulphate into a beaker with water, adding 20 to 25 cc. of a strong solution of caustic potash and heating to boiling. The thorium is converted completely into the hydroxide, while at the same time any free sulphur is dissolved by the caustic potash. The mass then is simply brought to boiling, diluted, filtered, washed, and dissolved off the filter in dilute nitric acid.

As has been noticed, the same reagent (caustic potash) serves for the conversion of the oxalates into hydroxides which are then easily converted into the nitrates.

The combination method is as follows :

Decompose the mineral as usual and precipitate the rare earths as oxalates ; filter, and wash the oxalates into a beaker ; add 20 to 25 cc. of a strong solution of caustic potash and heat to boiling ; dilute, filter and wash. Dissolve the hydroxides off the filter with hot dilute hydrochloric acid (1:1) and evaporate to dryness on a water-bath. Take up with water and add 25 to 30 cc. of a saturated solution of sodium thiosulphate ; heat to boiling, filter and wash (precipitate A) and set the filter aside for subsequent filtration. Precipitate the filtrate with an excess of ammonia, filter, wash, dissolve off the filter with hot dilute hydrochloric acid and evaporate to dryness. Take up with water and reprecipitate with thiosulphate as before. Filter this precipitate through the paper containing precipitate A. Wash, then wash into a beaker and add 20 to 25 cc. of a strong solution of caustic potash and heat to boiling. Dilute, filter and wash. Then dissolve off the filter in warm dilute nitric acid and evaporate to dryness. Redissolve in water and precipitate with oxalic acid ; filter, wash, and rinse into a beaker using a cold saturated solution of ammonium oxalate for the purpose (about 100 cc.)¹ Digest this on a water-bath for one and one-half hours (covered with a watch-glass), dilute to 300 cc. and allow to stand over night. (The undissolved residue of cerium, lanthanum, didymium, etc., is so slight that it need not be re-treated.) Filter and precipitate the thorium from the filtrate with a large excess of ammonia. Filter, dissolve in dilute nitric acid, evaporate to dryness, take up in water and precipitate the

¹ By this process the oxalate to be digested with ammonium oxalate is almost pure thorium oxalate and goes into solution very easily. Usually only the faintest residue of impurities remains after one digestion.

thorium from this with oxalic acid. Filter, wash, ignite and weigh.

The above method gives very satisfactory results and yields a white oxide of thorium.

Fumaric Acid Method.—The three methods just described are very long and tedious. In many instances the solutions must be allowed to stand over night, and the precipitations repeated several times to insure a complete separation. The minimum time required to execute any one of these methods is from five to six days.

The method about to be described has the great advantage of being extremely short, requiring only about one and one-half days after the decomposition of the mineral, and gives accurate results. The method is as follows: Decompose about 1 gram of mineral as before and precipitate the oxalates; wash, then rinse into a beaker and add 20 to 25 cc. of a strong solution of caustic potash; heat to boiling, dilute, filter and wash. Dissolve off the filter in warm dilute nitric acid (1:1) and evaporate to dryness on a water-bath. Take up in 50 cc. water, then add alcohol and water in such proportions as to make the solution 40 per cent. alcohol (dilution = about 200 cc.). Then add 20 to 25 cc. of fumaric acid (0.1 gram per 10 cc.) and heat to boiling. Filter, while still hot, through a long-stem funnel (or by suction), wash several times with hot 40 per cent. alcohol, then return precipitate and paper to the beaker and add 25 to 30 cc. of dilute hydrochloric acid (1:1); heat to boiling, dilute a very little (keep down the volume as much as possible), and filter off the paper. Wash the paper several times, then evaporate to dryness on a water-bath, shaking from time to time and washing with a few drops of water to prevent the residue from clinging to the sides of the beaker. Add about 50 cc. water (while still on the water-bath) and stir the residue loose from the bottom with a rubber-capped rod. (The carbonaceous matter from the partly decomposed fumaric acid, etc., does not interfere.) Add alcohol and water to make the solution 40 per cent. (dilution about 150 cc.), then add about 10 cc. fumaric acid and heat to boiling. Filter through a long-stem funnel, wash with hot 40 per cent. alcohol, ignite (without previous drying) in a platinum crucible, and weigh the thorium dioxide. In this method hydrogen sulphide need not be passed through the solution before precipita-

tion with oxalic acid, for, as has been shown on a preceding page, none of the metals precipitable by hydrogen sulphide interfere.

A comparison of the analyses of the three samples of sand, made by the methods described is given in the following table: Results are given in percentages of thorium.

METHODS.

	Fumaric.	Oxalate.	Thiosulphate.	Combination.
Brazil (a)	{ 2.41	2.77	2.11	2.48
	{ 2.55	2.03
N. Carolina...	{ 3.95	4.03
	{ 4.02	3.76
	{ 3.92
Brazil (b).....	{ 2.51	2.42
	{ 2.47	2.56

CONCLUSIONS.

1. A saturated solution of fumaric acid in 40 per cent. alcohol precipitates thorium completely from neutral solutions, to which 40 per cent. of their volume of alcohol has been added, while under these conditions the only other metals that give precipitation are zirconium, erbium, silver, and mercury.

2. This precipitation serves as an accurate and rapid separation of thorium from the other earths in monazite, and by its use the thorium can be determined in about one-third the time required by the methods now in use and with equal if not greater accuracy.

3. As the thorium-carbon ratio in thorium fumarate is 1:4, thorium and fumaric acid react molecule for molecule.

4. By the aid of a blast-lamp, white vapors are driven off from the thorium left in the boat after the combustion of thorium fumarate in a stream of oxygen (a fact as yet not explained).

5. Rare-earth oxalates and thorium thiosulphate are completely converted into the hydroxides by heating to boiling in a strong solution of potassium hydroxide, giving a convenient method for the conversion of those salts into the nitrates.

This investigation was carried out under the direction of Professor Edmund H. Miller and I wish here to express my most sincere thanks to him for his kind interest and encouragement in the work, and for the valuable assistance rendered.