

## CALORIFIC VALUES.

	No. samples tested.	Determined in a Mahler calorime- ter.	Calculated by Du- long's formula.	Calculated by Du- long's formula, but using 8,140 as the value of carbon.
		Calories.	Calories.	Calories.
Limestone coal . . . . .	17	6620	6609	6648
No. 5 coal . . . . .	3	6820	6758	6798
No. 6 coal . . . . .	57	6970	6931	6971
No. 7 coal . . . . .	4	6968	6919	6959
Waterloo coal . . . . .	8	6504	6398	6437
Average . . . . .		6780	6723	6763

Dulong's formula gives results lower than the value as determined in the Mahler calorimeter, especially on the samples highest in moisture and oxygen, the Waterloo coal. By substituting Berthollet's value for amorphous carbon 8,140, the application of the formula gives a very close agreement with the calorimeter results on all of the samples except the Waterloo coal, the average of the results on this being still 1 per cent. low. On the No. 6 coal, which represents the average of 57 samples, the agreement of the calculated and determined value is almost perfect, the value being 6,970 calories as determined and 6,971 calories as calculated.

For some of the Ohio coals, at least, this modification of Dulong's formula gives a calculated calorific value agreeing very closely with the value actually determined, the average difference being within the limits of error of the individual determinations.

The writer again wishes to acknowledge his indebtedness to Professor N. W. Lord for valuable advice and suggestions.

METALLURGICAL LABORATORY,  
OHIO STATE UNIVERSITY,  
COLUMBUS, O.

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## A NEW SEPARATION OF THORIUM FROM CERIUM, LANTHANUM AND DIDYMIUM BY META- NITROBENZOIC ACID.<sup>1</sup>

BY ARTHUR C. NEISH.

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THE work herein described was undertaken with the object of finding a shorter and more satisfactory method for the determination of thorium in monazite sands.

<sup>1</sup> Read at the meeting of the New York Section of the American Chemical Society, May 6, 1904.

The requirements of such a method are first, an accurate separation of thorium from cerium, lanthanum and didymium; second, rapidity and ease of manipulation; third, an inexpensive reagent and one which does not involve the use of alcohol.

It is believed that the method described meets these conditions.

As the analytical methods have been so recently reviewed by Metzger,<sup>1</sup> and a bibliography to the entire literature of thorium recently published by Jöüet, Smithsonian Miscellaneous Collections, No. 1374, the usual historical review of the literature pertaining to the subject is omitted.

#### PREPARATION OF PURE THORIUM NITRATE.

The pure thorium nitrate was made by dissolving 200 grams of chemically pure thorium nitrate, containing a small per cent. of cerium, in water in thirteen beakers each holding about 1,000 cc. To each beaker 150 cc. of hydrogen peroxide (Marchand's medicinal, containing about 4 per cent. hydrogen dioxide) was added (10 cc. for every 0.5 gram thorium oxide). The solutions were heated to 85° C. and allowed to settle. The precipitates were washed by decantation, and at the end of the sixth decantation the filtrate gave no test whatever for cerium on the addition of ammonia. The precipitates were transferred to a large Büchner funnel and the washing continued, stirring the precipitate with a spatula. The precipitate was transferred to a large evaporating dish, and 250 cc. of concentrated nitric acid added, which readily dissolved the precipitate when a little heat was applied. The solution was evaporated to dryness, taken up with water, diluted and divided among the thirteen beakers so that each contained about a liter, and the thorium reprecipitated as before. The precipitate was dissolved in nitric acid and evaporated to dryness, and dried in the air-bath for three days at 115° C. This gave thorium nitrate of the highest purity, containing no free nitric acid.

Sixty grams of this thorium nitrate were dissolved in 7 liters of water, well shaken and divided among several well-stoppered bottles.

#### STANDARDIZING THE THORIUM SOLUTION.

A very accurately standardized burette was used to measure out the thorium nitrate solution; it was connected to the bottle by

<sup>1</sup> This Journal, 24, 901 (1902)

glass tubing so as to facilitate filling without any chance of change due to evaporation or contamination.

Different amounts of thorium solution were run into a number of small beakers and heated to boiling, and a boiling solution of oxalic acid<sup>1</sup> was added, a little at a time with constant stirring. After cooling, the precipitate was filtered and washed with water. If precipitated from cold solutions, the precipitate runs through the paper, but from hot solutions no trouble in filtering is encountered. The paper containing the thorium oxalate was placed in a weighed platinum crucible, gently heated with a Bunsen burner until dry and the paper charred, then the heat was increased and the oxalate changed to oxide; it was next heated by a blast-lamp for fifteen minutes, cooled and weighed.

The following table gives the results:

Th(NO <sub>3</sub> ) <sub>4</sub> cc.	(COOH) <sub>2</sub> cc.	Weight ThO <sub>2</sub> . Gram.	ThO <sub>2</sub> in 1 cc. Gram.
25	20	0.1128	0.004512
25	20	0.1128	0.004512
50	40	0.2256	0.004512
50	40	0.2255	0.004510
50	40	0.2255	0.004510
50	40	0.2255	0.004510

#### PRECIPITANTS TRIED.

Many organic precipitants were tried, mostly weak organic acids, in the hope of finding one that would give a sharp separation, and a precipitate which would filter quickly without the use of alcohol.

The results are briefly as follows:

Gallic acid precipitates thorium quantitatively from a hot alcoholic solution as a flocculent slimy precipitate. Salts of cerium, lanthanum and didymium are not precipitated.

Tannic acid precipitates thorium quantitatively, but cerium, lanthanum and didymium are not precipitated.

Citric acid precipitates all from an acetone solution.

Salicylic acid precipitates thorium. The precipitate is soluble in excess of the reagent.

Oleic acid in a strong alcoholic solution precipitates thorium and cerium. The cerium precipitate is soluble in excess, the thorium insoluble.

<sup>1</sup> Saturated in the cold.

Linoleic acid precipitates all, if insufficient alcohol is present, but with sufficient alcohol the cerium, lanthanum and didymium readily dissolve; the thorium is apparently insoluble.

Paratoluic acid gave a precipitate of thorium but none with cerium, lanthanum and didymium.

Oxyisophthalic acid gave a white, curdy precipitate of thorium in an aqueous solution, almost quantitative; the other three earths gave no precipitate.

Benzoic acid precipitated thorium quantitatively from aqueous solution; the cerium, lanthanum and didymium were not precipitated. This method gives trouble on account of the very slight solubility of benzoic acid in water.

The three nitrobenzoic acids gave white precipitates with a neutral solution of thorium nitrate, while cerium, lanthanum and didymium gave no precipitate. The meta acid, which is the most soluble in water, precipitated the thorium quantitatively. This acid is the principal product of the nitration of benzoic acid, the yield being about 75 per cent.; but as the ortho and para acids as well as benzoic acid act similarly, it is not necessary to use pure metanitrobenzoic acid and the reagent is one readily obtained.

Potassium iodate precipitates all four as heavy white precipitates.

Ammonium vanadate precipitates thorium, lanthanum and didymium as canary-yellow precipitates; the cerium precipitate has an orange color.

Lead acetate in a solution acid with nitric acid produces a white precipitate with thorium, which increases when heated but is incomplete. Cerium, lanthanum and didymium are not precipitated.

Arsenious oxide cream precipitates all four quantitatively in a solution containing sodium acetate.

Sodium tungstate precipitates all four as white precipitates.

#### QUANTITATIVE PRECIPITATION OF THORIUM BY METANITROBENZOIC ACID.

The solution of the precipitant is made by dissolving from 3.5 to 4 grams of the acid in a liter of hot water (about 80° C.). When all is in solution, it is allowed to stand over night when a slight amount will separate out as feathery crystals. The solution is filtered to free it from any crystals and foreign matter.

Thorium nitrate solution was run into a 300 cc. beaker and a solution of the precipitant added very slowly with constant stirring; about 150 cc. gave a liberal excess for 25 cc. of thorium solution equivalent to 0.1128 gram of thorium oxide. This produces a heavy white precipitate which soon collects on standing, more rapidly on heating. The beaker was heated on the water-bath to a temperature between 60° and 80° C. for fifteen minutes. The opalescence disappears and the bulky precipitate settles to the bottom in large flocks, having much the appearance of silver chloride. The solution can either be filtered hot or allowed to cool. The precipitate is washed first by decantation and finally on the filter-paper with a 5 per cent. solution of the precipitant. The precipitate and paper are not dried, for reasons given later, but placed moist in a weighed platinum crucible and carefully heated with the cover off, then, after the paper and volatile matter are driven off, heated with the full flame of a Bunsen burner until white, then covered and ignited for fifteen minutes with the blast-lamp, cooled, and the thorium oxide weighed.

The following table shows that thorium is quantitatively precipitated from a neutral solution of the nitrate by metanitrobenzoic acid:

Th(NO <sub>3</sub> ) <sub>4</sub> cc.	Precipitant. cc.	ThO <sub>2</sub> found. Gram.	ThO <sub>2</sub> taken. Grain.	Error. Gram.
50	300	0.2256	0.2256	-0.0000
25	150	0.1132	0.1128	+0.0004
36	150	0.1630	0.1625	+0.0005

#### SEPARATION OF THORIUM FROM CERIUM, LANTHANUM AND DIDYMIUM.

The next step was to try the separation of thorium from mixtures with cerium, lanthanum and didymium, and then from mixtures of thorium with all three.

As before, known volumes of thorium nitrate solution were placed in beakers; known quantities of cerium, lanthanum and didymium oxides added in the form of nitrates, then an excess of metanitrobenzoic acid was added slowly with constant stirring, the solutions were heated on the water-bath, filtered and washed by decantation with a 5 per cent. solution of the precipitant. The moist precipitate and paper were placed in a weighed platinum crucible, heated and ignited, with the precautions given above, and the thorium oxide weighed.

A separatory funnel with a capacity of 75 cc. was found very convenient, both as a measure of the volume added and for adding the solution slowly while stirring.

The test for cerium in the filtrate by ammonia and hydrogen peroxide is of no use, as the metanitrobenzoic acid itself gives the same color.

The following results will show the efficiency of the separation:

Th(NO <sub>3</sub> ) <sub>4</sub> cc.	Precipi- tant. cc.	Total volume. cc.	Weight CeO <sub>2</sub> . Gram.	Weight Di <sub>2</sub> O <sub>3</sub> . Gram.	Weight La <sub>2</sub> O <sub>3</sub> . Gram.	ThO <sub>2</sub> taken. Gram.	ThO <sub>2</sub> found. Gram.	Error. Gram.
25	150	175	0.1120	.....	.....	0.1128	0.1141	+0.0013
25	150	175	.....	0.1120	.....	0.1128	0.1140	+0.0012
25	150	175	.....	.....	0.1120	0.1128	0.1143	+0.0015
25	150	175	0.1120	0.1120	0.1120	0.1128	0.1199	+0.0071
25	150	175	0.1120	0.1120	0.1120	0.1128	0.1196	+0.0068
25	150	175	0.0560	0.0560	0.0560	0.1128	0.1162	+0.0034

These experiments showed that one precipitation will not separate thorium from an equal weight of cerium, lanthanum or didymium, or from an equal or one-half the amount of all three. A nearly constant amount of each is carried down.

A reprecipitation being necessary, many methods were tried to change the thorium metanitrobenzoate to thorium nitrate. The precipitate is readily soluble in nitric acid, but on evaporating this solution a hard, insoluble skin is left which encloses the impurities, making the second precipitation useless. The precipitate was dissolved off the paper into the precipitation beaker with hot dilute nitric acid (1:5), the paper well washed with hot water, the solution in the beaker diluted to about 150 cc. and 25 cc. of metanitrobenzoic acid added. Then methyl orange was added until the solution became decidedly red, and then dilute ammonia (1:10) run in from a burette very slowly, with constant stirring until the solution turns from deep red to light red or pink. The clear solution, after the addition of some ammonia, becomes opalescent, due to the reprecipitation of thorium metanitrobenzoate, and as more is added the precipitate becomes white and flocculent, increasing as more ammonia is added.

When the precipitate becomes flocculent, the ammonia is added with great care, drop by drop, and the solution thoroughly stirred after every addition.

If the process of neutralization were carried to the yellow tint, the other earths would precipitate.

The addition of ammonia is carried on until the red changes to pink; this marks the neutralization of the mineral acid and the weak acid, metanitrobenzoic, keeps the indicator pink. A very few drops more of ammonia would change the pink to yellow.

The solution of the precipitant changes methyl orange decidedly red only when considerable quantities are added, and then the same depth of color which mineral acids give is not produced. The 25 cc. of metanitrobenzoic acid is sufficient to produce the pink.

At this point, the pink tint, all the thorium should be precipitated, but to insure a complete precipitation 50 cc. more of the precipitant are added, and the beaker heated on the water-bath as before, the solution filtered and the precipitate washed with a 5 per cent. solution of the precipitant and either ignited and weighed or redissolved in nitric acid and the neutralization repeated.

The following table shows the results with three precipitations:

Th(NO <sub>3</sub> ) <sub>4</sub> cc.	Precipi- tant. cc.	Vol- ume. cc.	CeO <sub>2</sub> Grain.	Di <sub>2</sub> O <sub>3</sub> Gram.	La <sub>2</sub> O <sub>3</sub> Gram.	ThO <sub>2</sub> taken. Gram.	ThO <sub>2</sub> found. Gram.	Error. Grain.
25	150	175	0.0560	.....	.....	0.1128	0.1129	+0.0001
25	150	175	.....	0.0560	.....	0.1128	0.1131	+0.0003
25	150	175	.....	.....	0.0560	0.1128	0.1134	+0.0006
50	300	350	0.0560	0.0560	0.0560	0.2256	0.2263	+0.0008
26	150	175	0.1120	.....	.....	0.1175	0.1179	+0.0006
25	150	175	.....	0.1120	.....	0.1128	0.1129	+0.0001
25	150	175	0.1120	0.1120	0.1120	0.1128	0.1135	+0.0007

The above results being satisfactory, the separation was tried on mixtures in the proportions usually found in monazite sands.

The next table shows the results with three precipitations:

Th(NO <sub>3</sub> ) <sub>4</sub> cc.	Precipi- tant. cc.	Vol- ume. cc.	CeO <sub>2</sub> Gram.	Di <sub>2</sub> O <sub>3</sub> Gram.	La <sub>2</sub> O <sub>3</sub> Gram.	ThO <sub>2</sub> taken. Gram.	ThO <sub>2</sub> found. Gram.	Error. Grain.
25	150	175	0.5000	0.3000	0.2500	0.1128	0.1136	+0.0008
25	150	175	0.5000	0.3000	0.2500	0.1128	0.1137	+0.0009
25	150	175	0.5000	0.3000	0.2500	0.1128	0.1140	+0.0012
25	150	175	0.5000	0.3000	0.2500	0.1128	0.1136	+0.0008
25	150	175	0.5000	0.3000	0.2500	0.1128	0.1137	+0.0009
25	150	175	0.5000	0.3000	0.2500	0.1128	0.1136	+0.0008
25	150	175	0.5000	0.3000	0.2500	0.1128	0.1134	+0.0006

It was thought that with greater dilution a closer separation could be obtained with two precipitations.

The following series proves this to be the case:

Th(NO <sub>3</sub> ) <sub>4</sub> cc.	Precipi- tant. cc.	Vol- ume. cc.	CeO <sub>2</sub> . Gram.	Di <sub>2</sub> O <sub>3</sub> . Gram.	La <sub>2</sub> O <sub>3</sub> . Gram.	ThO <sub>2</sub> taken. Gram.	ThO <sub>2</sub> found. Gram.	Error. Gram.
25	150	700	0.5000	0.3000	0.2500	0.1128	0.1126	-0.0002
25	150	700	0.5000	0.3000	0.2500	0.1128	0.1126	-0.0002
25	150	700	0.5000	0.3000	0.2500	0.1128	0.1125	-0.0003
25	150	900	0.5000	0.3000	0.2500	0.1128	0.1132	+0.0004
25	150	700	0.5000	0.3000	0.2500	0.1128	0.1123	-0.0005

The separation was next tried to see if one precipitation would separate thorium from cerium in the proportions in which they are present in Welsbach mantles. Nos. 3 and 4 were reprecipitated, giving slightly low results:

	Th(NO <sub>3</sub> ) <sub>4</sub> cc.	Precipi- tant. cc.	Vol- ume. cc.	CeO <sub>2</sub> . Gram.	ThO <sub>2</sub> taken. Gram.	ThO <sub>2</sub> found. Gram.	Error. Gram.
(1)	25	150	300	0.0011	0.1128	0.1128	±0.0000
(2)	25	150	300	0.0011	0.1128	0.1128	±0.0000
(3)	25	150	300	0.0011	0.1128	0.1126	-0.0002
(4)	25	150	300	0.0011	0.1128	0.1125	-0.0003

THE BEHAVIOR OF OTHER ELEMENTS.

Gluclinum, gadolinium, yttrium, titanium and samarium gave no precipitate, cold or hot.

Zirconium gave a white opalescence and precipitate, which increased on heating.

Erbium gave an immediate white, curdy precipitate in the cold, with little change on heating; the precipitation is quantitative.

The following commoner salts were tried, although none are apt to be present in the analysis of monazite: Calcium chloride barium chloride, magnesium chloride, potassium aluminum sulphate, potassium chromium sulphate, ferrous sulphate, ferric sulphate, zinc sulphate, manganous sulphate, nickel nitrate, cobalt nitrate, bismuth nitrate, silver nitrate, lead nitrate, cadmium nitrate, copper nitrate, arsenious acid, arsenic acid, potassium antimonyl tartrate (tartar emetic), ammonium molybdate, auric chloride, hydrochlorplatinic acid, ammonium tungstate, uranium nitrate, mercurous nitrate, mercuric nitrate, stannous chloride and sodium stannate. With the exception of the last four they gave no precipitate. The precipitates, with mercurous and mercuric nitrates, were very heavy, white and curdy in the cold, but dissolved on heating.



## COMPOSITION OF THE PRECIPITATE.

The precipitate used for the determination of its composition was made by dissolving the pure thorium nitrate in water in a large beaker and precipitating with an excess of metanitrobenzoic acid. The precipitate, after heating on the water-bath, was washed by decantation, then on the filter, a Büchner funnel, with a large amount of water to make the washing complete. The precipitate was transferred in a cake to a glass plate and dried for days in the air-bath at  $115^{\circ}$  C. When thoroughly dried, it was broken and pulverized and again dried for two days, being frequently stirred so as to insure complete drying.

It was assumed that thorium would combine with 4 molecules of the acid as  $\text{Th}(\text{C}_6\text{H}_4\text{NO}_2\text{COO})_4$ .

The percentage composition calculated from this assumption is: Th = 25.93 per cent.; C = 37.46 per cent.; H = 1.79 per cent.; N = 6.26 per cent.; O = 28.54 per cent.

The precipitate gave on analysis: Th = 25.95, 25.97, 26.00 and 26.05 per cent.; C = 37.43, 37.48, 37.32 and 37.12 per cent.; H = 1.85, 1.85, 1.91 and 1.97 per cent.; N = 6.42 and 6.48 per cent.

## PROPERTIES OF THORIUM METANITROBENZOATE.

The precipitate, when dry, presents very peculiar properties; it is snow-white, very light and is electrified. When pressed or touched with a glass rod or a brush it acts like pith balls, being first attracted, then repelled by the rod, so that it is impossible to handle it without loss. Even the transfer of a precipitate to a platinum crucible cannot be accomplished without loss; for this reason, the precipitate is always ignited without previous drying. The thorium metanitrobenzoate is radioactive, giving, after an exposure of five days to an X-ray plate, a faint image, while the thorium oxide, produced from the ignition of the metanitrobenzoate, and the oxide separated from monazite sands by metanitrobenzoic acid, gave about four times the effect.

When thorium metanitrobenzoate is ignited, a large volume of gas is given off which burns with a sooty flame, leaving, after complete ignition, thorium oxide, snow-white and in a very loose condition. This oxide, when placed in a platinum boat inside a platinum combustion tube and strongly heated with two blast-lamps, gave off white fumes, similar to those obtained by Metz-

ger<sup>1</sup> from the oxide obtained by the ignition of thorium fumarate. These fumes were collected in a small glass tube, but disappeared after a few minutes.

Thorium metanitrobenzoate is insoluble in water, it is easily soluble in, and prevented from precipitation by, hydrochloric, nitric sulphuric, and acetic acids. Tartaric acid or tartrates dissolve the precipitate, from which solution the thorium cannot be precipitated either by ammonium hydroxide, potassium hydroxide or oxalic acid. Oxalic acid dissolves the precipitate with the formation of a white, crystalline precipitate of thorium oxalate. Sodium carbonate decomposes the precipitate with the production of a flocculent precipitate, soluble in excess of sodium carbonate. Potassium hydroxide decomposes it with the formation of thorium hydroxide. It is soluble in acetone; alcohol and ether have no solvent effect.

#### MONAZITE ANALYSIS.

The practical application of the precipitation of thorium by metanitrobenzoic acid was applied to the analysis of monazite sands. The results were checked against the two shortest and best methods, the combination method, and the fumaric acid method of Metzger.<sup>2</sup> Five sands were analyzed, three from Brazil and two from North Carolina.

#### FUMARIC ACID METHOD.

Metzger's method was used except for the following modification: The precipitate of thorium fumarate was dissolved in hot, dilute nitric acid (1:5) instead of hydrochloric acid, and instead of evaporating to dryness, which produces a compact residue incompletely soluble in water, the thorium and other contaminating earths were precipitated as hydroxides, with an excess of potassium hydroxide, and the hydroxides filtered off, washed and dissolved in hot, dilute nitric acid (1:5), evaporated to dryness, taken up with 40 per cent. alcohol, and precipitated with fumaric acid, as before; filtered, washed, ignited and weighed as thorium oxide. This modification eliminates any chance of the other earths being enclosed in the insoluble residue on evaporation, and also any possibility of the thorium oxide being contaminated by silica.

<sup>1</sup> This Journal, 24, 901 (1902).

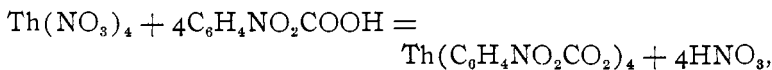
<sup>2</sup> *Loc. cit.*

## METANITROBENZOIC ACID METHOD.

Two grams of the sand were ground to a fine powder and weighed out into a porcelain crucible, about 10 to 15 cc. of concentrated sulphuric acid added and stirred with a small glass rod, which is left in the crucible throughout the digestion. The crucible was placed on a hot plate, heated gradually and stirred cautiously to allow the escape of bubbles of gas, which are only formed at first, and cause loss, if the heating is not done carefully. The heat was increased, or the crucible moved to the hotter part of the plate until a constant cloud of sulphur trioxide was given off. When the excess of acid had evaporated, more acid was added, the contents were stirred with the glass rod and the digestion was continued. As a rule, the digestion lasted all day, since the solution of the sulphates in water was allowed to stand over night, but two results are given where the digestion lasted only three hours, so that longer digestion is unnecessary. At the end of the digestion the phosphates present in the monazite sand were all changed to sulphates; the crucible now contained about 10 cc.; this was well stirred, and, after cooling the crucible in ice water, the mass was allowed to drop from the rod, a drop at a time, with constant stirring into a beaker containing 600 cc. of water cooled to 0°. After all the liquid was added, the crucible itself was placed in the beaker, and the whole allowed to stand, best over night. If it is a refined sand and free from quartz, the residue on the bottom of the beaker should be small, but if there is a flocculent precipitate, it is apt to be hydrated sulphate of thorium. In this case the best thing to do is to start another portion, using greater care in adding the mass to the ice-water and to have enough free acid present to make the mass liquid enough so that when a drop of it is added to the beaker it soon dissolves, leaving a fine white powder instead of sinking to the bottom as a hard lump, as it will do if too little acid is present.

The solution was filtered into a large beaker and heated to boiling. A boiling solution of oxalic acid (saturated in the cold) was added gradually to the solution with constant stirring, a large excess being used in order to make the precipitation complete in presence of so much sulphuric acid, and also to take any zirconium into solution, which would be precipitated by the meta-nitrobenzoic acid; an excess can have no solvent effect whatever

on the thorium present. The solution was allowed to stand and when cool, the white crystalline precipitate, consisting of the oxalates of thorium, cerium, lanthanum and didymium, was filtered and washed with a dilute solution of oxalic acid. It is better to allow the precipitate of the oxalates to stand many hours or, if possible, over night. The precipitate and paper were transferred to the precipitation beaker, 10 to 15 grams of stick potassium hydroxide added, 25 to 50 cc. of water and the whole heated to boiling, washing down any oxalates that were attached to the sides of the beaker. The oxalates were soon changed to hydroxides, having a silky appearance and becoming yellow on account of the oxidation of the cerium. The solution was diluted to about 300 cc., filtered and washed with water until free from alkali. The hydroxides were dissolved into the precipitation beaker with hot dilute nitric acid (1:5). This solution of the nitrates was evaporated to dryness on the water-bath, moistened with water and evaporated until every trace of free nitric acid was driven off; since the precipitate is soluble in dilute nitric acid and as nitric acid is set free in the reaction,



all free nitric acid must be removed from the nitrates.

The nitrates were dissolved in 500 to 600 cc. of water and 150 to 250 cc. of metanitrobenzoic acid solution added slowly with constant stirring, and heated on the water-bath at 60° to 80° until the precipitate has all collected and settled to the bottom. It was then filtered, washed by decantation, using a 5 per cent. solution of the precipitant, then placed on the filter and washed with the same solution. The precipitate was dissolved by hot dilute nitric acid (1:5) into the precipitation beaker, the paper well washed with hot water and diluted to 600 cc.; methyl orange was added until a decided red color was produced, then 25 cc. of metanitrobenzoic acid. This was neutralized with dilute ammonia (1:10) until a pink tint was obtained. This is best done by placing beside the beaker another containing the same volume and amount of acid and indicator, also containing some white powder, such as pulverized quartz, and frequently stirred during the titration to give the same appearance as the contents of the other beaker. As the excess of nitric acid is neutralized, the

thorium reprecipitates as metanitrobenzoate, and the solution changes from a decided red to a pink color, due to the feeble acidity of metanitrobenzoic acid. After the pink tint was obtained, 50 cc. more of metanitrobenzoic acid were added to insure complete precipitation. The beaker was then heated on the water-bath to from 60° to 80°. the precipitate filtered, washed, and the wet precipitate ignited and weighed, after treating for fifteen minutes with the blast-lamp.

In the analysis of monazite some difficulty was experienced in obtaining a white thorium oxide, and also in the process of neutralization, for in making the second precipitation rapidly some experience is required to catch the proper end-point. To obviate this the following modification was used, which, though a little longer, is much easier to carry out, and insures concordant results and a pure white oxide.

After the first precipitate of thorium metanitrobenzoate was dissolved in nitric acid, instead of neutralizing with ammonia, the thorium is precipitated as hydroxide by potassium hydroxide. The potassium hydroxide at first causes a reprecipitation of the flocculent metanitrobenzoate, but a slight excess changes it to hydroxide; this is easily seen by the change from a very voluminous white precipitate to a more compact cream-colored one. The solution was then diluted and filtered through the same paper, washed and dissolved with hot, dilute nitric acid (1:5) into the same beaker, and evaporated to dryness, dissolved in 600 cc. of water and precipitated with metanitrobenzoic acid, and the moist precipitate ignited, and the resultant thorium oxide weighed.

This modification is recommended, as it requires no experience with the use of the indicator, and if the preceding directions are carefully carried out, a snow-white oxide will always be obtained.

## RESULTS ON MONAZITE SANDS.

	Meta-nitrobenzoic.	Modified metanitrobenzoic.	Fumaric.	Combination.
Refined Brazil monazite <sup>1</sup>	5.70	5.70	5.70	5.63
	5.80	5.67	...	...
	5.93	5.65	...	...
	...	5.73	...	...
	...	5.60	...	...

<sup>1</sup> It was through the kindness of Mr. Whitaker, of the Welsbach Light Co., that these samples were obtained.

RESULTS ON MONAZITE SANDS (*continued*).

	Meta-nitrobenzoic.	Modified metanitrobenzoic.	Fumaric.	Combination.
North Carolina monazite	5.48	5.27	5.13	5.39
	5.12	5.26	...	...
	...	5.27	...	...
Brazil monazite	4.89	4.99	4.85	4.90
	4.97	4.98	...	...
	5.04	4.82	...	...
High-grade North Carolina monazite <sup>1</sup>	6.04	6.02	5.89	5.98
	6.15	6.04	...	...
	5.88	5.88	...	...
	...	6.15	...	...
Refined Brazil monazite <sup>1</sup>	...	5.81	5.71	5.97
	...	5.71	...	...

## CONCLUSIONS.

(1) Metanitrobenzoic acid precipitates thorium quantitatively as  $\text{Th}(\text{C}_6\text{H}_4\text{NO}_2\text{CO}_2)_4$  from a neutral solution of the nitrate.

(2) When this precipitation is repeated, it affords a complete separation from cerium, lanthanum and didymium.

(3) This method gives as good results for thorium in monazite as the combination or fumaric acid methods, and has the advantage in that it is much shorter, and offers no difficulties in precipitation or filtration; the precipitant is not expensive and avoids the use of alcohol.

This investigation was carried out under the direction of Professor Edmund H. Miller, and I wish to gratefully acknowledge my indebtedness to him for his kind interest and advice.

QUANTITATIVE CHEMICAL LABORATORY,  
HAVEMEYER HALL, COLUMBIA UNIVERSITY,  
May 1, 1904.

## THE BISMUTHATE METHOD FOR THE DETERMINATION OF MANGANESE.

BY ANDREW A. BLAIR.

Received May 3, 1904.

THIS method was originally proposed by Schneider,<sup>3</sup> and modified first by Reddrop and Ramage,<sup>4</sup> and then by Brearley and Ibbotson.<sup>5</sup>

<sup>1</sup> From the original sample received from Professor Baskerville, not the same as used by Metzger. This Journal, 24, 901 (1902).

<sup>2</sup> The digestion for these lasted three hours.

<sup>3</sup> Ding. poly. J., 269, 224.

<sup>4</sup> Trans. Chem. Soc., 1895, p. 268.

<sup>5</sup> "The Analysis of Steel Works Materials."