and set the beaker in a warm place. When reduced, filter and titrate the iron with standard potassium permanganate. More zinc is used for bauxites high in iron.

METHOD FOR IRON DETERMINATION, USING A LARGER QUANTITY OF BAUXITE. (APPLICABLE TO PUREST ORES).

Place a half gram of the finely powdered ore in a large platinum crucible and add three cc. of twenty-five per cent. sulphuric acid and five cc. of hydrochloric acid, and evaporate very slowly to fumes; drive off the excess of sulphuric acid by heat, boil out the residue with water and add ten cc. of dilute sulphuric acid. Remove the crucible and reduce with zinc, as above, and titrate.

Water and Organic Matter.—Ignite three-tenths gram, cautiously at first and finally very strongly in a covered crucible. The loss of weight equals water and organic matter.

ESTIMATION OF THORIA. CHEMICAL ANALYSIS OF MONAZITE SAND.

By Charles Glaser.

Received July 9, 1896.

SINCE the introduction of the Auer-Welsbach light, the commercial importance of monazite sand has grown greatly, and chemists are now asked to determine the percentage of true monazite, and especially that of thoria, in samples of the sand. This has heretofore been accomplished indirectly ; the quantities of iron, titanium and silica were determined and the remainder of the material calculated as monazite. A sample treated in this manner gave the following results :

	Per cent.
Iron oxide	3.50
Titanic acid	4.67
Silica	6.40
Monazite, by difference	85.43
	100.00

The sample contained 18.38 per cent. phosphoric acid, which calculated as cerium phosphate (factor 3.32) equals 61.10 per cent.

From analyses printed in Dana's Mineralogy, it was inferred that after elimination of rutile and silica, the remainder would be found to consist chiefly of phosphates of the cerium group, but this is not true.

For the determination of the actual composition of the monazite sand in question, it was decided to attempt an estimation of each of its components, by means of methods to be found in the available literature. As chief sources of information, Graham-Otto's Chemistry and Crookes' Select Methods in Chemical Analysis were used; due regard was also given to the work which has appeared in the chemical journals of recent years. I was not able, however, to make an exhaustive examination of the literature.

It became evident that no reliable method could be worked out until examination had been made of all the work which had been done in the field, and it seemed necessary to investigate the whole question. In the following statements of preliminary experiments a large portion of analytical data has been omitted, because otherwise this paper would have been bulky. Only the outlines of a general plan of procedure will therefore be given.

So far as possible, it was my intention to examine all the methods proposed for estimation of thoria, but in one notable instance this could not be done. In Volume XVI of the *American Chemical Journal*, L. M. Dennis and F. L. Kortright describe a method for estimation of thoria by means of potassium hydronitride, KN_3. An attempt to work by the method proved a failure in my hands, partly because of a mishap while preparing the reagent, only enough of which was saved for a single qualitative reaction; but chiefly because Mr. Dennis declined, when requested, to give me further information. He replied that he was not then at liberty to detail his experience, "as the potassium hydronitride process is more than an analytical one. It is a commercial process for the preparation of pure thoria, which is, I think, unequalled by any of the methods employed by the Welsbach chemists, Shapleigh included. Some of them have tried to use the method and have failed. I think I know why they failed. But I do not think it quite fair for them to ask me to help them out of their difficulties."

Although the publication was made in a scientific journal, it seems to have been but a partial statement. For which reason criticism is invited and the value of the work is thrown somewhat in doubt. No further attempt was made to follow it out.

By means of fusion with alkali carbonates, an attempt was made to separate monazite sand into two parts. According to Wöhler all titanic acid ought to become soluble provided the fusion is made at a sufficiently high temperature. Therefore a blowpipe was used. In later work I employed the highest temperatures afforded by a muffle, and for as many as two hours. But at no time was more than a fraction of the titanic acid rendered soluble in water. Moreover, Wöhler's directions to pour the fusion upon an iron plate, and afterwards to powder it, are not practicable because of loss likely to ensue. It was found best to let the fusion soak in water over night, sometimes even for several days, or until perfect disintegration resulted. But such a procedure may have decreased the solubility of titanic acid in water. Phosphoric acid and alumina (and also silica to a large extent) were completely dissolved out of the fused mass. The portion insoluble in water was rendered soluble by the well known treatment with strong sulphuric acid, and also by fusion with acid potassium sulphate. The solution thus obtained, after being freed from silica, was boiled to separate titanic acid, from four to seven hours during the first experiment. Later, after addition of sodium sulphite, this was accompanied by saturating with hydrogen sulphide, first in the hot and then in the cooled solution. This method is preferable to the first.

After separation of titanic acid and the metals of the fifth group, various methods were tried for separation of thoria from the other earths. It was found that the solution must not be strongly acid when treated with ammonium oxalate for precipitation of thoria and the metals of the cerium group, or traces of thoria will remain in solution. It is best to nearly neutralize with ammonia, and to precipitate in boiling solution.

During the earlier experiments some difficulty was found in keeping in solution all of the zirconia, which is accomplished only by a large excess of the reagent, while yttria and glucina readily form soluble double salts. Under these conditions oxalates of the cerium metals precipitate immediately, while thorium oxalate separates upon cooling. Attempts to separate thorium oxalate from oxalates of the metals of the cerium group by filtration of the hot solution, gave unsatisfactory results. The oxalates will pass through the filter for a long time. Bumping of the liquid made it impracticable to keep it boiling until the entire precipitate became crystalline. But if large quantities of thoria are to be separated from small ones of the other oxalates the method works well.

After the insoluble oxalates were separated by filtration and were washed with water, they were converted into oxides by heating and were redissolved as sulphates. In this strongly concentrated solution, made nearly neutral by ammonia, an attempt was made to separate thoria from the other metals by boiling with sodium hyposulphite. In no instance was a complete separation effected, but such portions as were obtained proved to be quite pure. The single exception was that in which the whole of the cerium was precipitated, for reasons not ascertained. Attempts were made to free thoria from most of the cerium by fractional precipitation with weak ammonia, but no considerable advantage was gained thereby, since repeatedly the second fraction showed traces of thorium.

To determine the solubility or insolubility of the different substances left in the insoluble residue from fusions, such residue was treated with dilute hydrochloric acid both cold and hot. The solution was found to contain all the iron and titanium, the larger part of the silica, and about one-half of the earths present; these consisted of relatively large portions of zirconia and glucina. Thoria seems not to enter into solution, but is left with the remainder of the earths.

An attempt was made to separate thorium oxalate from the mixed precipitated oxalates, by boiling with ammonium oxalate. Such boiling, filtering and crystallizing yielded oxalates, which after ignition, corresponded to 2.29 per cent. of oxides. The earths were, however, of a deep orange color, and contained both cerium and zirconia. The latter was present because an insufficient quantity of ammonium oxalate had been used in the first precipitation. In the oxalates of the cerium metals found insoluble in the above treatment, the presence of thoria could be distinctly proven by means of sodium hyposulphite, for which reason the work proved unsatisfactory.

To facilitate a comparison of the more important reactions of the elements herein studied, the table on the next page has been prepared partly from their known behavior, and partly from the results obtained during this investigation.

With the view of obtaining further knowledge of the behavior of thoria, fragments of Welsbach mantles were subjected to analysis. They weighed 0.6591 gram, which, after ignition, fell to 0.6552 gram. Prolonged treatment with boiling sulphuric acid left a residue of 0.0883 gram, which became soluble in water after fusion with acid potassium sulphate. The solutions thus obtained were examined by the same method, but separately, as follows: After neutralizing with ammonia the greater part of the free acid, the solutions were heated to boiling and hot solution of ammonium oxalate was added.

In solution I a precipitate appeared, but dissolved rapidly upon addition of more of the reagent.

In solution II a slight turbidity appeared, there was no precipitate, and it soon became perfectly clear.

Upon cooling, solution I yielded a moderate quantity of a crystalline deposit, while solution II gave a copious one. Both precipitates were collected on one filter, washed, ignited, and weighed. They yielded 0.1124 grams of thoria.

The filtrate from I gave a copious precipitate with ammonia, while that from II gave only a slight one: both of these were washed on one filter, redissolved in dilute hydrochloric acid, and again precipitated by ammonia. An excess of ammonium carbonate entirely dissolved the precipitate. Potassium hydroxide gave a precipitate not soluble in excess of the precipitant, indicating zirconia, the weight of which was 0.5580 gram. An attempt to purify it from occluded alkali, by again precipitating with ammonia, failed through an accident, in which part of the material was lost. Calculating by difference, the weight of zirconia ought to have been 0.5428 gram. Both precipitates were pure white.

Therefore, this analysis afforded the following composition of the mantles: thoria 17.15 per cent., zirconia 82.85 per cent.

TABLE OF REACTIONS OF THE RARER EARTHS.

	KOH or NaOH	K_2CO_3 or Na_2CO_3.	K_2SO_4 or Na_2SO_4.	$Na_2S_2O_3$.	NH_4OH.	$(NH_4)_2CO_3$.	NH_4Cl.	$(NH_4)_2C_2O_4$.	$NH_4C_2H_3O_2$.
Al_2O_3	Ppt., sol. in excess.	Ppt.	Alums.	Ppt. in boiling almost neutral solution.	Ppt.	Ppt.	Ppt. from solution in NaOH.	No ppt.	Nearly neutral solution boiled gives ppt. of basic salt.
BeO_2	Ppt. sol. in excess. Reppt. when boiled or diluted.	Ppt. with difficulty sol. in large excess and in CO_2.	No ppt., no double salt formed. Sol. with difficulty.	No. ppt.	Ppt. insol. in excess.	Ppt. easily sol. in excess. Ppt. on boiling. Uncertain separation from Al_2O_3.	Hydroxide diss. on prolonged boiling NH_3 escapes.	No ppt., double salt easily sol.	?
ZrO_2	Ppt. insol. in excess.	Ppt. slightly soluble in excess. Ppt. by NH_4OH.	Double salt sol. in hot solution. Ppt. of basic salt on cooling, insol. in HCl.	Ppt. hydroxide mixed with S.	Ppt. insol. in excess.	Ppt. sol. in large excess. Reppt'd. on boiling.	No ppt.	Ppt. sol. in excess.	?
Gadolinite earths.	Ppt. insol. in excess.	Ppt. sol. in excess. After some hours insol. double salt separates (Yt).	Conc. solution ppt. sol. in H_2O or K_2SO_4 (not Yt.) Sept. from thoria and cerites.	?	Ppt. insol. in excess.	Ppt. easily sol. in excess. Ppt. insol. double salt after some hours (Yt).	?	Ppt. red granular powder (Er.) from boiling acid solution.	?
ThO_2	Ppt. insol. in excess.	Ppt. sol. in excess. Turbid on heating, clears on cooling.	Double salt insol. in saturated solution K_2SO_4. Sodium salt much more sol.	Only partial ppt., even on long boiling conc. solution.	Ppt. insol. in excess. ThO_2 ppts. before cerites. Crookes.	Like NH_4OH.	No ppt.	Ppt. nearly insol. in acids. Sol. in excess, hot; ppt. on cooling. HCl ppts.	No ppt. prevents completely ppt'n. by $(NH_4)_2C_2O_4$ Partial ppt. by HCl, complete by excess NH_4OH.
CeO	Ppt. insol. in excess.	Ppt. slightly sol. in excess.	Double salt insol. in K_2SO_4 solution.	No. ppt. (?)	Ppt. insol. in excess.	Like NH_4OH.	No ppt.	Ppt. even in rather acid solution. Slightly sol. in large excess of acid.	Oxalate insol.
Ce_2O_3	Excess gives flesh colored ppt.	Ppt. nearly insol. in excess.		No. ppt.	Like KOH.	Ppt. sol. in large excess. Reppt'd. on boiling.	No ppt.	Like CeO.	Oxalate insol.
La_2O_3	Ppt. insol. in excess.	Ppt. nearly insol. in excess.	Double salt sol. with difficulty.	No. ppt.	Ppt.	White ppt. quite insol. in excess.	No ppt.	Ppt. in neutral or ammoniacal (?) solution.	Oxalate insol.
Di_2O_3	Ppt. insol. in excess.	Ppt. nearly insol. in excess.	Double salt sol. with difficulty.	No. ppt.	Ppt.	Rose colored ppt. quite insol.	No ppt.	Ppt. nearly insol. in oxalic or mineral acids.	Oxalate insol.

The separation of the two earths was effected without difficulty and the thoria was used in the following experiments:

0.0487 gram was weighed, dissolved, and mixed with the solution of cerium metals from a previous experiment. The solution was nearly neutralized with ammonia, heated to boiling, a hot solution of ammonium oxalate added, and the mixture allowed to cool. The precipitate was caught on a filter and washed with cold water, extracted in boiling ammonium oxalate solution, caught on a filter, and washed hot: the filtrate was allowed to cool (precipitate 1). The residue was macerated in a hot solution of ammonium acetate, filtered (residue A), and filtrate examined for thoria, as follows: hydrochloric acid was added to separate thoria as oxalate, which fell in part only and the remainder was obtained by sodium hydroxide (precipitate 2). Both these precipitates afforded but a part of the thoria originally weighed, the greater part being held yet with the cerium metals. The method had failed.

The residue (A) upon the filter was reduced to oxide and dissolved as sulphate. After neutralizing with ammonia, the liquid was heated to boiling, and there was added an excess of ammonium oxalate with some ammonium acetate: after filtering, the filtrate was treated with sodium hydroxide (precipitate 3).

The precipitates, thus obtained in three fractions, were ignited and found to weigh 0.0774 gram, showing that the thoria was very impure. The grayish mass was fused with acid potassium sulphate, and unfortunately, a small fraction of the fused mass was lost. However, from the saved portion a pure thoria, weighing 0.0402 gram. was obtained.

In the next experiment, 0.0343 gram of thoria and 0.1004 gram of impure cerium oxide were dissolved as sulphates, and treated with ammonium oxalate and acetate, as for precipitate 3, next above. By precipitating the filtrate with ammonia there was obtained 0.0360 of impure thoria, which, after purification, weighed 0.0344 gram. Cerium oxide recovered weighed 0.0935 gram.

I desire to call attention to what has been observed frequently during these experiments. If thorium oxalate, held in solution by ammonium acetate, be precipitated by ammonia, the earth so obtained, when washed with the greatest care and redissolved in a mineral acid, cannot from an almost neutral solution be again completely precipitated by ammonium oxalate; even if the earth had been ignited after re-solution. It will also be found that a considerable increase has occurred in its solubility in liquids containing much potassium or ammonium sulphate. When enough thoria has been collected, it is my intention to further examine this peculiar behavior.

SYSTEMATIC METHOD OF ANALYSIS.

From the analytical data given, the following method has been deduced:

It is essential that the mineral be divided to the greatest possible degree. Prolonged powdering in an agate mortar is indispensable. Solution is effected either by prolonged heating with strong sulphuric acid, or by fusion with acid potassium sulphate. In the latter case, the cooled mass is warmed with so much sulphuric acid that the product, after cooling, may be poured from the crucible. The first method takes more time than the second, but it introduces less of the objectionable potassium salts. It is advisable to fuse only those portions which are insoluble in sulphuric acid.

For estimation of silica the sulphuric acid treatment is preferable, in which case it is best to evaporate once on a sand-bath to dryness to render silica insoluble, and then to add fresh sulphuric acid. The resulting mixture should be added slowly to ice cold water, which dissolves the mass excepting silica and tantalic acid, with possibly traces of titanic acid, thoria, and zirconia. After filtering, the residue should be ignited and weighed. Silica is eliminated by repeated treatment with hydrofluoric acid. Any residue remaining should be moistened with sulphuric acid, to convert the fluorides of the earths into sulphates, which, after ignition at a high temperature, are weighed as oxides, and silica determined by the loss in weight. The residue of tantalic acid, with possibly traces of the bodies mentioned above, is treated with sulphuric acid and hydrofluoric acid. Tantalic acid remains insoluble. and may be filtered off and weighed. The matter soluble may be added to the main solution.

The original solution is saturated with hydrogen sulphide, first at boiling and then at the ordinary temperature. Titanic acid is precipitated, together with metals of the fifth group. That sodium sulphite assists in the precipitation of titanic acid has not been verified in my work.

When completely settled, the liquid is filtered and the filtrate boiled to expel hydrogen sulphide. Any free acid may be nearly neutralized with ammonia ; to the boiling liquid is added an excess of a boiling solution of ammonium oxalate, as much as 100 cc. of the cold saturated solution for two grams of monazite sand. The excess necessarily must be large. The mixture is then permitted to cool, best for an entire night. The solution will contain phosphoric acid, the oxides of iron, manganese, aluminum, glucinum, yttrium, zirconium, and calcium. In the precipitate will be found thoria and the oxides of the cerium group.

If the bodies in solution are to be estimated, add ammonia to precipitate the metals as phosphates. Filter and wash thoroughly, preserve the filtrate for estimation of phosphoric acid and alumina. Ignite the precipitate and fuse it with mixed carbonates of potassium and sodium. The fused mass is exhausted with hot water, filtered, and the residue well washed with hot water. The filtrate is added to that containing phosphoric acid and alumina.

The remaining oxides and carbonates are dissolved in sulphuric acid and precipitated with ammonia. Lime is estimated in the filtrate therefrom.

When an attempt is now made to dissolve the precipitated hydroxides on the filter by dilute hydrochloric acid, it sometimes occurs that zirconia in part remains. Therefore it is best, after this operation, to incinerate the filter. Then neutralize the solution with ammonia as far as practicable. Pour this slowly, with constant stirring, into a mixture of ammonium carbonate and ammonium sulphide, prepared as follows : To a solution of ammonium carbonate more than enough to neutralize the free hydrochloric acid above indicated, and to hold in solution the earths to be dealt with, add enough of ammonium sulphide (usually a few cc.) to precipitate the metals of the fourth group. The latter will be precipitated, while zirconia, yttria, and glucinum remain in solution. Iron and manganese may be determined by the usual methods.

If the carbonate solution be boiled for one hour the earths are completely precipitated. They may be caught on a filter and dissolved in hydrochloric acid; or the carbonate solution may be treated directly with that acid, carbon dioxide expelled by boiling, the solution cooled and treated with an excess of sodium hydroxide. Zirconium and yttria are completely precipitated while glucina remains dissolved: to precipitate this, boil the solution one hour.

To separate zirconia from yttria, dissolve the hydroxides in hydrochloric acid, warm, then saturate the solution with sodium sulphate. When cold, zirconia separates in the well-known manner. From the filtrate ammonia separates yttria.

As the earths are apt to occlude alkali salts, it is best to dissolve and again precipitate them (with ammonia) before they are ignited and weighed.

Separation of the precipitated oxalates of thoria and of the cerium group is accomplished as follows: The oxalates are reduced to oxides by ignition, then converted into sulphates, the greater part of the free acid neutralized with ammonia, the solution boiled, and boiling ammonium oxalate added in excess. After a short time (as soon as oxalates of the cerium metals have formed but before the liquid has cooled), a few cc. of solution of ammonium acetate are added. When cold, the entire cerium group is precipitated as oxalates, while thoria remains in solution. After prolonged standing, best over night, the insoluble oxalates are removed by filtration; in the filtrate, precipitate thoria with ammonia in excess, filter, ignite, and weigh.

Separation of cerium from lanthanum and didymium is easily accomplished by the well known method. Pass a current of chlorine through the liquid containing the hydroxides, which have been freshly precipitated by a fixed alkali.

Separation of lanthanum from didymium was not attempted.

An analysis of the monazite sand used in my work, made as indicated in the foregoing notes, gave results as follows :

Titanic acid	4.67
Silica	6.40
Phosphorus pentoxide	18.38
Lead	trace
Alumina	1.62
Lime	1.20
Cerium oxide (CeO)	32.93
Lanthanum and didymium oxides	7.93
Thoria	1.43
Ferric oxide	7.83
Zirconia and yttria	13.98
Glucina	1.25
Tantalic acid	0.66
Not determined	1.72
	100.00

Titanic acid and silica was determined in a separate portion. The determination of tantalic acid was only approximate, since a part of it is dissolved by fusion with acid potassium sulphate, and thus escapes weighing. As several such fusions were made, it is probable that the greater part of the matter "not determined" ought to be reckoned as tantalic acid. The quantity stated was an average of three determinations (minus or plus 0.05) from the residue of repeated fusions.

Through the courtesy of Mr. H. B. C. Nitze, of the Geological Survey of North Carolina, I have received a number of samples of monazite sand mined at various localities in that state. Two of these had been prepared by a new process and were found to be practically free from rutile and garnets. They were excellent material for my methods of analysis, and they gave results as follows :

ANALYSIS OF A COARSE MONAZITE SAND FROM SHELBY, NORTH CAROLINA.

Silica	3.20
Titanic acid	0.61
Cerium metals as CeO	63.80
Phosphorus pentoxide	28.16
Thoria	2.32
Zirconia, glucina, yttria	1.52
Manganese	trace
No iron, alumina, or lime	0.00
	99.61

The color of this sand was honey-yellow.

ANALYSIS OF A FINE MONAZITE SAND FROM BELLEWOOD, NORTH CAROLINA.

Silica	1.45
Titanic acid	1.40
Cerium metals as CeO	59.09
Phosphorus pentoxide	26.05
Thoria	1.19
Zirconia, glucina, yttria	2.68
Tantalic acid	6.39
Iron and manganese oxides	0.65
Alumina	0.15
	99.05

The color of this sand was honey-yellow.

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[CONTRIBUTIONS FROM METALLURGICAL LABORATORY OF THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO.]

THE EFFECT OF AN EXCESS OF REAGENT IN THE PRECIPITATION OF BARIUM SULPHATE.

BY C. W. FOULK.

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"EXCESS of reagent" is a term often used by writers in quantitative chemistry, and the necessity in any given case for adding more of a precipitating reagent than is just sufficient for complete reaction is well known to analysts; but what constitutes such excess, whether it differs for different salts, whether its effect is counteracted by the presence in the solution of other bodies not taking part in the reaction, or whether the effect of such bodies may be counteracted by the addition of a greater amount of precipitant, etc., etc., are questions, the answers to which are difficult to find in chemical literature.

With a view to answer, in part at least, these questions, the following work on the precipitation of barium sulphate was undertaken.

A preliminary experiment, which perhaps is worth noting, was first tried:

A solution of 140 cc. water and five cc. concentrated hydrochloric acid was heated nearly to boiling and 0.1984 gram pure recently ignited barium sulphate was added. This was then stirred up and set aside for one hour, when it was filtered and