Summary.

In the study of the four systems, it has been shown that potassium fluoride and potassium carbonate in the anhydrous form are equally efficient in dehydrating acetone. Potassium fluoride is the more rapid agent of the two, and gives cleaner cut separations. If a large excess of anhydrous calcium chloride is used, the acetone is completely dehydrated. Sodium chloride dehydrates to 85.8% of acetone.

The saturated solution of potassium fluoride will dehydrate to 98%, while the saturated potassium carbonate dehydrates only to 96.5% of acetone. 98.4% acetone can be obtained with a saturated calcium chloride solution.

Neither the fluoride nor the carbonate solutions entail much loss of acetone, practically no acetone being soluble in these saturated solutions, while calcium chloride retains 23% of acetone in the aqueous solution of the chloride. Sodium chloride is the least satisfactory of the four, as it retains over 21% of acetone, and in addition dehydrates only to 85.8%. The viscid nature of the calcium chloride solution is objectionable. The fluoride gives the cleanest and most rapid separation and seems to be the most satisfactory salting out or dehydrating agent for acetone.

This investigation covers the following lines:

1. The isotherms at 20° for the systems water, acetone, and potassium fluoride, water, acetone and potassium carbonate, water, acetone and calcium chloride and water, acetone and sodium chloride are given and thoroughly investigated.
2. Temperature effects in the systems are noted, and while no upper critical solution temperatures were found, the lower critical solution temperatures of a series of solutions are given.
3. A quantitative method is given for the determination of acetone in an aqueous solution, provided a third substance is not present. The effect of the presence of methyl alcohol, when this method is used, is discussed.

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A NEW METHOD FOR THE DETERMINATION OF THORIUM IN MONAZITE SAND.

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The large amount of work published upon the determination of thorium in monazite sand is an indication of the importance of this problem. Several methods have been devised for this determination. The principal ones, up to the year 1910, were the ammonium oxalate method,[1] the

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[1] Glaser, *Chem. Ztg.*, **20**, 612 (1896).

thiosulfate method,[1] the hydrogen peroxide method,[2] the fumaric acid method,[3] and the nitrobenzoic acid method;[4] the thiosulfate method being the one usually employed.

In all of these, as well as in the more recent volumetric molybdate method,[5] it is necessary to precipitate the thorium, and other rare earth elements, as oxalates from the solution of the sand, in order to separate them from the phosphoric acid. This precipitation and the subsequent treatment of the oxalate precipitate, in order to dissolve it and obtain a neutral solution of the rare earth salts, requires considerable time. Potassium trinitride[6] and sebacic acid[7] have also been proposed as reagents for the separation of thorium from the other rare earth elements. A neutral or only slightly acid solution is required, so these methods could not be applied to the analysis of monazite sand without first precipitating with oxalic acid.

The only methods in which the thorium is precipitated from the solution of the sand, in the form of a salt other than the oxalate, are the iodate method[8] of Meyer and Speter and the hypophosphate method[9] of Rosenheim. These are both known as "rapid methods."[10]

The iodate method gives very accurate results. Meyer and Speter have tested the method thoroughly on pure solutions and on a sand which had been analyzed in the laboratory of Dr. Gilbert, of Hamburg, in which laboratory the determinations for the German thorium industry are made.[11] The results compared very well with the result obtained by Dr. Gilbert. Although the reagent used is expensive, this expense is outweighed by the gain in working time. The method requires considerable care to avoid loss in the numerous transfers of the precipitate of thorium iodate from the paper to a beaker.

One cannot judge as to the accuracy of the hypophosphate method, as Rosenheim gives no results, either upon pure solutions or upon sands. The reagent, sodium hypophosphate, cannot now be purchased.

Several years ago we noticed that the pyrophosphates of thorium, ceric

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[1] Hintz u. Weber, *Z. anal. Chem.*, **36**, 27 (1897); Drossbach, *Z. angew. Chem.*, **14**, 655 (1901); Hauser u. Wirth, *Ibid.*, **22**, 484 (1909).

[2] Wyrouboff and Verneuil, *Compt. rend.*, **126**, 340 (1898); *Bull. soc. chim.*, [3] **19**, 219 (1898); Benz, *Z. angew. Chem.*, **15**, 297 (1902).

[3] Metzger, THIS JOURNAL, **24**, 901 (1902).

[4] Neish, *Ibid.*, **26**, 780 (1904).

[5] Metzger and Zons, *J. Ind. Eng. Chem.*, **4**, 493 (1912).

[6] Dennis and Kortright, *Am. Chem. J.*, **16**, 79 (1894); Dennis, THIS JOURNAL, **18**, 947 (1896).

[7] Smith and James, THIS JOURNAL, **34**, 281 (1912).

[8] *Chem. Ztg.*, **34**, 306 (1910).

[9] *Ibid.*, **36**, 821 (1912).

[10] Meyer und Hauser, "Die Analyse der seltenen Erden und der Erdsäuren," page 263.

[11] Meyer u. Speter, *Chem. Ztg.*, **34**, 306 (1910).

cerium, and zirconium are insoluble in dilute acids, while the pyrophosphates of cerous cerium and the other rare earth elements are readily soluble in dilute acids. This difference in the solubility of the pyrophosphates is the basis of the new method for the determination of thorium presented in this paper.

Thorium pyrophosphate has been mentioned very little in the literature. Cleve,[1] in 1874, in a paper on thorium salts, made note of the fact that pyrophosphoric acid, when added to a thorium salt, precipitates $ThP_2O_7.2H_2O$, and that this salt dissolves in an excess of sodium pyrophosphate, forming $Na_4Th(P_2O_7)_2.2H_2O$. The various chemical handbooks and dictionaries give these formulas and refer to the article by Cleve. The striking difference in the solubility of the pyrophosphates in acids has apparently not been noticed.

The normal sodium salt, $Na_4P_2O_7.10H_2O$, is the most convenient pyrophosphate to use for precipitating the thorium. It is inexpensive and is readily obtained. A water solution of this salt is very stable, and there is no appreciable hydrolysis to orthophosphate even after standing for a long time or on heating.

Thorium pyrophosphate dissolves readily on heating with an excess of sodium pyrophosphate. It dissolves with difficulty in a large excess of pyrophosphoric acid and is precipitated from this solution slowly by heating, and rapidly by adding a strong acid and heating. It is soluble also in ammonium carbonate and in alkali oxalate solutions. From solutions of the double pyrophosphate, thorium is completely precipitated by boiling with an excess of sodium hydroxide. It is not precipitated from this solution by ammonium hydroxide or by oxalic acid; if the solution is strongly acidified after adding oxalic acid, a mixture of oxalate and pyrophosphate is precipitated. The addition of a strong acid to the double pyrophosphate breaks it up and causes the precipitation of thorium pyrophosphate.

In order to precipitate thorium completely as the pyrophosphate, the solution must be boiled after adding the sodium pyrophosphate, otherwise 1–2 mg. of thorium will remain in solution. The acidity should be about 0.3 N or equal to 5 cc. of hydrochloric acid (1.19) in 200 cc. of solution. If the acidity is very much too low, some thorium may fail to be precipitated by going into the form of the double pyrophosphate; if too high, the solvent effect of the acid comes into play. The acidity may, however, vary within fairly wide limits without the loss of any thorium. Zirconium is completely precipitated from a solution under the same conditions as thorium.

The pyrophosphates of cerous cerium, praseodymium, neodymium, lanthanum, yttrium, ytterbium, and erbium are soluble in an excess of

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[1] *Bull. soc. chim.*, [2] 21, 116.

sodium pyrophosphate. Freshly precipitated pyrophosphates of each of these metals, equivalent to about 125 mg. of the oxide, when suspended in 100 cc. of water, dissolved readily on the addition of 1–1.5 cc. of dilute hydrochloric acid (1.10). On adding bromine water to the solution of cerous pyrophosphate in dilute hydrochloric acid and heating, a white precipitate of ceric pyrophosphate formed immediately.

Thorium pyrophosphate may be ignited by drying the precipitate, removing it from the paper, burning the paper at as low a temperature as possible, then adding the main body of the precipitate and igniting for about fifteen minutes. Long-continued ignition causes a slight loss of P_2O_5. As is the case in the ignition of other phosphates, it is difficult to burn off all of the carbon. Thorium oxalate is readily changed to the oxide by ignition. Since it is necessary to precipitate as the oxalate at some point in the analysis of monazite sand, in order to remove zirconium (zirconium oxalate being soluble in an excess of oxalic acid) it seemed advisable to precipitate the thorium finally as the oxalate and ignite and weigh the oxide.

It was quite difficult to find a really satisfactory method for changing the pyrophosphate quantitatively to oxalate. The first method tried was to change the pyrophosphate to hydroxide by boiling with sodium hydroxide. Other thorium precipitates, for example the thiosulfate and oxalate, are readily changed to hydroxide in this way. This method was not successful, the transposition not being at all complete. The next method tried was to dissolve the pyrophosphate in an excess of warm sodium pyrophosphate, change the thorium to hydroxide by boiling with sodium hydroxide, filter and wash this precipitate, dissolve it in hydrochloric acid and precipitate the thorium as oxalate. This was not entirely satisfactory, on account of the difficulty in washing out all of the soluble pyrophosphate from the thorium hydroxide. Similar methods applied to the solutions in ammonium carbonate and oxalate were unsatisfactory.

We next tried dissolving the thorium pyrophosphate in concentrated sulfuric acid and oxidizing the filter paper. Instead of the use of sodium nitrate for this purpose, as is customary, we made use of ammonium perchlorate.[1] By the use of concentrated sulfuric acid and a small amount of ammonium perchlorate, a 15 cm. filter paper, containing about 200 mg. of moist thorium pyrophosphate, will be completely destroyed, the pyrophosphoric acid changed to orthoacid, and the thorium brought into solution in about ten minutes. The dry paper, alone, can be destroyed in much less time. Using sodium nitrate, as in the hypophosphate method,

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[1] We are indebted to H. H. Willard for this suggestion. Potassium perchlorate may also be used, but in this case the sulfates dissolve more slowly, probably due to the formation of a double sulfate. The excess of the potassium salt remains largely undissolved.

one or two hours would have been required. The amount of ammonium perchlorate used is small and the reagent is inexpensive. On cooling and adding water to the mixture of concentrated sulfuric acid and thorium sulfate, a clear solution results. To change the thorium completely to an oxalate entirely free from phosphate, it was found best to first change the sulfate to hydroxide by boiling with sodium hydroxide, filter this, dissolve it in hydrochloric acid and precipitate as oxalate. This was found to give much more satisfactory results than neutralizing with ammonium hydroxide, adding acid until the precipitate dissolves and precipitating with oxalic acid, the procedure in the hypophosphate method.

This method was first tested on pure solutions of rare earth salts. Pure thorium nitrate was prepared from the commercial salt by the method of Wyrouboff and Verneuil,[1] consisting of a double precipitation of the thorium by hydrogen peroxide. After dissolving the pure salt in water, the strength of the solution was determined by precipitating the thorium from a measured volume in a dilute acid solution as the oxalate, allowing this to stand over night, then filtering and igniting to the oxide. The cerium, praseodymium, neodymium, and lanthanum salts were the double ammonium nitrates. The sodium pyrophosphate solution was made up by dissolving 25 g. of $Na_4P_2O_7.10H_2O$ in 500 cc. of water. The ammonium perchlorate was the commercial salt purchased from Kahlbaum. As this left a slight residue on dissolving in water, it was purified by one recrystallization.

The completeness of the precipitation of thorium by sodium pyrophosphate is shown by the following experiments:

To 35 cc. of pure thorium nitrate solution, 5 cc. of HCl (1.19) were added and the solution diluted to 200 cc. It was then heated to boiling and 10 cc. of the sodium pyrophosphate solution were dropped in slowly from a pipet with constant stirring. The solution was then gently boiled for five minutes, stirring occasionally to keep the precipitate in suspension. The precipitate was allowed to settle for five or ten minutes and was then filtered[2] and washed with water containing a small amount of hydrochloric acid (one or two drops of acid in 200 cc.). The paper containing the moist precipitate was put into a 125 cc. Soxhlet[3] flask and 15 cc. of sulfuric acid (1.84) and a few crystals of ammonium perchlorate were added. The flask was then covered with a watch glass which was held slightly away from the top of the flask by three small bent glass rods in order to allow escape of gases. The flask was heated gently and the heating continued until a brown solution was obtained. The flame was then removed for a moment and more ammonium perchlorate carefully added. Heating was then resumed. More perchlorate was added if necessary. In a short time the solution became colorless and the carbonaceous matter had been entirely oxidized. The solution was then allowed to cool. The flask was placed in cold water and about 75 cc. of dis-

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[1] *Loc. cit.*

[2] Thorium pyrophosphate offers no difficulty in filtration, the much more bulky orthophosphate, however, is very hard to filter.

[3] A Kjeldahl flask was later found to be preferable, as it eliminates all chance of loss by spattering.

tilled water were slowly added with stirring. In a short time a clear solution resulted. This solution was then poured slowly into a solution of 30 g. of sodium hydroxide in about 125 cc. of water, and the flask was washed out with distilled water, collecting the washings in the sodium hydroxide solution. The solution was stirred and boiled for several minutes to convert the thorium to hydroxide. The hydroxide was filtered on a hardened filter paper, using slight suction. This was washed thoroughly with hot water. The paper containing the thorium hydroxide was then placed in the beaker in which the hydroxide precipitation had been made, and 5 cc. of hydrochloric acid (1.19) were added. This was allowed to remain in contact with the paper for a short time and then the solution was diluted and boiled. The paper was filtered off and washed thoroughly. A solution of 2 g. of oxalic acid was added to the filtrate and this was diluted to about 450 cc. and allowed to stand warm over night. The oxalate was filtered, washed with water containing a trace of hydrochloric acid, and ignited to oxide. The amount of thorium oxide taken was 0.1376 g. The amounts found in three experiments were: (1) 0.1384 g., (2) 0.1374 g., (3) 0.1376 g. The filtrate from the thorium pyrophosphate gave no precipitate on boiling with sodium hydroxide or ammonium hydroxide, or on adding oxalic acid and allowing to stand.

Experiments were then carried out to determine if a quantitative separation of thorium from the other rare earth elements can be obtained by one precipitation with sodium pyrophosphate. The acidity and volume of solution were the same as in the previous experiments:

Experiment 1.—Weight of ThO_2 taken: 0.1376 g.; weight of CeO_2 taken: 0.1235 g.; weight of ThO_2 found: 0.1413 g. Weight of CeO_2 carried down with the thorium was 3.7 mg.

Experiment 2.—Weight of ThO_2 taken: 0.1376 g.; weight of Pr_4O_7 taken; 0.1241 g.; weight of ThO_2 found: 0.1409 g. Weight of Pr_4O_7 carried down with the thorium was 3.3 mg.

Experiment 3.—Weight of ThO_2 taken: 0.1376 g.; weight of Nd_2O_3 taken: 0.1240 g.; weight of ThO_2 found: 0.1392 g. Weight of Nd_2O_3 carried down with the thorium was 1.6 mg.

The oxides in Experiments 2 and 3 were quite strongly colored.

It was seen that a second precipitation of the thorium as pyrophosphate would be necessary in order to remove the small amounts of rare earth salts that are carried down. This reprecipitation was easily accomplished. The sulfate solution of the pyrophosphate precipitate was rinsed into a beaker and ammonium hydroxide added until alkaline. A few drops of methyl orange were added and hydrochloric acid dropped in until a neutral reaction was obtained, then 7.5 cc. of hydrochloric acid (1.19) were added and the solution diluted to 300 cc. The solution was heated to boiling and precipitated with sodium pyrophosphate as before. The pyrophosphate was filtered, washed, and converted to sulfate, hydroxide and oxalate in the manner previously described.

In a number of experiments this method was tried upon thorium salts alone, and a complete recovery of the thorium was made in each case. When tried upon mixtures of thorium and other rare earth salts, the thorium oxide obtained was in all cases entirely pure. The results obtained are shown in Table I.

TABLE I.

ThO_2 taken. Gram.	CeO_2 taken. Gram.	La_2O_3 taken. Gram.	Pr_4O_7 taken. Gram.	Nd_2O_3 taken. Gram.	ThO_2 found. Gram.
0.1376	....	....	....	....	0.1375
0.1376	....	....	....	....	0.1372
0.1376	....	....	....	....	0.1371
0.1376	0.1235	....	....	....	0.1377
0.1376	0.2470	....	....	....	0.1371
0.1376	....	0.1250	....	....	0.1374
0.1376	....	....	0.1241	....	0.1376
0.1376	....	....	0.1241	....	0.1371
0.1376	....	....	....	0.1240	0.1366
0.1376	....	....	....	0.1240	0.1375
0.1376	....	0.1250	0.1241	0.1240	0.1383
0.1376	0.1235	0.1250	0.1241	0.1240	0.1374

This method was then tested upon monazite sand. The best method for the decomposition of the sand seemed to be the one used by Meyer and Speter, taking a 50 g. sample of the unground sand and decomposing it with 100 cc. of concentrated sulfuric acid. The sulfates may then be dissolved in water, filtered, diluted to one liter, and aliquot portions taken for analysis. A 50 cc. portion should be diluted to about 440 cc., in order to obtain the acidity used in the experiments on pure solutions. On precipitating the thorium from this solution with sodium pyrophosphate, a small deposit of ceric pyrophosphate formed on the bottom of the beaker, and this was very difficult to remove. By diluting the solution to 450 cc. and adding 5 cc. of concentrated hydrochloric acid, this did not occur. In carrying out the method in the same manner as on pure solutions, many good results were obtained, but in some cases the results were slightly too high and the final oxide had a faint pink or brown color. This was caused by a trace of rare earth phosphate not dissolving in the hydrochloric acid and thus being carried along with the thorium. This was avoided by precipitating the sulfate solution with sodium hydroxide instead of ammonium hydroxide, filtering and washing the precipitate and dissolving it in the proper amount of acid. This process, of course, involves the use of an additional hydroxide filtration, but as the hydroxide is filtered with suction and the filtration and washing are rapid, but little more time is required than in the other method. An experiment on pure thorium nitrate solution showed that no thorium is lost by this variation in the method; weight of ThO_2 taken was 0.1376 g., weight recovered was 0.1379 g.

In the presence of a large amount of cerium, such as is found in monazite sand, it was found advisable to add a little sulfurous acid solution to reduce any ceric cerium before precipitating the second time as the pyrophosphate.

The complete method as applied to monazite sand is as follows: 50 g.

of the sand are heated to about 250° with 100 cc. of concentrated sulfuric acid in a thick-walled iron dish until complete decomposition is obtained.[1] This will require from 5–8 hours. The dish is kept covered with a watch glass during the heating. The excess of sulfuric acid is not driven off. The mixture is cooled and introduced slowly into about 400 cc. of cold water contained in a large beaker. This beaker is kept surrounded with cold water. The mixture is stirred with a wide spatula and allowed to stand until the sulfates are dissolved. The solution is then filtered through a folded filter paper into a one liter flask, the paper washed, and the filtrate diluted to the mark. Of this solution, 50 cc., equivalent to 2.5 g. of sand, are measured out and placed in an 800 cc. beaker. Five cc. of hydrochloric acid (1.19) are added and the solution is diluted to 450 cc. This is stirred and 15 cc. of sodium pyrophosphate solution (25 g. in 500 cc.) are slowly added. It is then heated to boiling, stirring[2] when near the boiling point, and is boiled gently for five minutes, after which it is allowed to stand for five or ten minutes and is then filtered. The precipitate[3] is washed several times with hot water containing one or two drops of hydrochloric acid in 200 cc. It is next transferred to a 250 cc. Kjeldahl flask, and 15 cc. of sulfuric acid (1.84) and a few crystals of ammonium perchlorate are added. The flask is covered with a watch glass held away from the top of the flask by three bent pieces of glass rod. The mixture is heated until it changes to a clear brown liquid. More perchlorate is then added and heating is continued until the organic matter is all oxidized.[4] The sulfate is always slightly yellow. The mixture is cooled to room temperature. The cover glass and rods are rinsed off into the sodium hydroxide solution used in converting the sulfate to hydroxide. The flask is placed in cold water, and about 100 cc. of distilled water are slowly added with stirring, and the sulfate will soon dissolve.[5] The solution is rinsed into a solution

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[1] This may be determined by placing a small portion of the mass on a watch glass, cooling, adding water and examining the undecomposed mineral fragments with a magnifying glass. The characteristic appearance of undecomposed monazite can be readily recognized.

[2] As a rule, after boiling begins, no attention is required, as the precipitate does not tend to settle.

[3] This precipitate contains about 15 mg. of oxides of rare earth elements other than thorium and zirconium.

[4] The oxidation of the filter paper requires about ten or twelve minutes, and about 1.5 g. of ammonium perchlorate are used. A larger amount of perchlorate is not harmful. Heating should be discontinued promptly when the organic matter has all been oxidized; if heated much longer, the perchloric acid breaks up at a certain point, causing considerable foaming.

[5] In the case of one of our monazites, a small amount of a greenish blue powder failed to dissolve on adding water. This occurred several times. In each case when this happened, the final result was a few one-hundredths of a per cent too low, as the precipitate contained some thorium. The following method easily overcame this

of 30 g. of sodium hydroxide in about 125 cc. of water contained in a 600 cc. beaker. The mixture is stirred and boiled for several minutes, and the hydroxide is then filtered on a hardened paper by aid of suction. It is washed a number of times with hot water. The paper is then placed in the beaker previously used, ten cc. of hydrochloric acid (1.19) are added and allowed to remain in contact with the paper for a short time, about 150 cc. of water are added and the solution is boiled. The paper is filtered off and washed, and the filtrate is diluted to 400 cc. About 3 cc. of saturated sulfurous acid solution are added, the solution is heated to boiling, and the thorium is again precipitated with sodium pyrophosphate; the precipitate is washed and changed to sulfate and hydroxide in the manner just described. This second sulfate is white and always dissolves completely in water. Finally the hydroxide is dissolved in 5 cc. of concentrated hydrochloric acid, the solution is diluted and boiled, the paper is filtered off, and the thorium is precipitated from the filtrate by a solution of 2 g. of oxalic acid. The solution is diluted to about 450 cc., and is allowed to stand warm over night. The oxalate is then filtered, washed with water very faintly acidified with hydrochloric acid, and is ignited to the oxide.

To determine the accuracy of the results, they were compared with those obtained by carefully carrying out the iodate method. The sand is decomposed and the solution made up in the manner previously described. 100 cc., corresponding to a 5 g. sample, are measured out, 50 cc. of concentrated nitric acid added, and the mixture cooled by placing in cold water. A solution of 15 g. of potassium iodate in 50 cc. of concentrated nitric acid and 30 cc. of water is added, this solution having been previously cooled. The mixture is stirred frequently and allowed to stand for one-half hour. It is then filtered.[1] The beaker is rinsed out with a solution of 4 g. of potassium iodate in 100 cc. of dilute nitric acid and 400 cc. of water. The same filter paper is used throughout the analysis. When the solution has all drained through, the precipitate is washed into the beaker with the iodate washing solution. It is stirred with about 100 cc. of this solution and filtered again. Any lumps of precipitate are pressed out with a spatula. The precipitate is now rinsed from the paper into the beaker with hot water. The mixture is heated to boiling, and the precipitate is dissolved by the addition of 30 cc. of concentrated nitric acid. The iodate is reprecipitated by a solution of 4 g. of potassium iodate in a

difficulty: The precipitate was filtered on a small paper, washed a few times, and with the paper put in a small flask. The paper was oxidized and the precipitate brought into solution by heating with 5 cc. of concentrated sulfuric acid and a little ammonium perchlorate. After cooling and diluting with water, the solution was made alkaline with sodium hydroxide and added to the main solution containing the precipitate of thorium hydroxide.

[1] A 15 cm. S. and S. filter paper, No. 589, is recommended.

little hot water and dilute nitric acid, the solution being fully cooled before filtering, After filtering, the precipitate is again transferred to the beaker with the washing solution and is filtered once more. The precipitate is then washed from the paper with water, and the iodate is dissolved in hydrochloric acid with the aid of sulfurous acid.[1] The thorium is precipitated from the boiling solution by ammonium hydroxide, the hydroxide washed with boiling water until free from iodide, dissolved in dilute hydrochloric acid, and precipitated with an excess of oxalic acid. The oxalate is allowed to stand, filtered, washed, and ignited.

Three monazite sands were analyzed by both of these methods, and the results were found to check very closely:

MONAZITE D.		MONAZITE E.		MONAZITE F.	
Pyrophosph. meth.	Iodate meth.	Pyrophosph. meth.	Iodate meth.	Pyrophosph. meth.	Iodate meth.
5.42%	5.43%	5.70%	5.68%	5.32%	5.37%
5.41	5.43	5.70	5.68	5.34	5.34
5.41	5.50[2]	5.68	5.69	5.35	5.32
5.40		5.66	5.64	5.28	5.30
5.41		5.67	..	5.35	5.36
..		..	..	..	5.39
..		..	..	..	5.29

The oxide obtained in the pyrophosphate method was in all cases white. About 200 mg. of this oxide were fused with potassium pyrosulfate, and the melt was dissolved in water and dilute nitric acid. This solution gave no test for phosphate. Another sample of the oxide was dissolved in the same way and tested for cerium by neutralizing the solution, adding an excess of potassium carbonate solution until the soluble potassium thorium carbonate was formed, and then adding a little hydrogen peroxide. No color was obtained.

The pyrophosphate method can be completed in as short a time as either of the two rapid methods. Starting with the filtered sulfuric acid solution of the sand, all of the operations up to the precipitation of the oxalate can be carried out in about seven hours. The short time required and the cheapness of the reagents should make this a useful method for this important determination.

The monazite sands and several of the rare earth salts used in this investigation were furnished us through the courtesy of H. S. Miner of the Welsbach Company.

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[1] We have found it best to heat with dilute hydrochloric acid and add the sulfurous acid a little at a time until just enough has been added to reduce the iodate. If too much is added, the hydroxide filters slowly.

[2] This oxide had a fairly strong pink tinge, while the other oxides were white.