The problems confronting the analytical chemist in this analysis can be conveniently divided into two classes: (1) the decomposition of the sand and (2) the separation of the thorium from the rare earths. Consequently most of the attention will be focused on these two considerations in the literature review.

A number of excellent reviews (1, 4, 8, 9, 11, 24, 27, 35–38) of the analytical chemistry of thorium have been published. The paper by Bonardi (1) is a very good summary of the better methods of monazite sand analysis prior to 1923, and the pamphlet by Rodden (38) outlines three methods that have proved successful in his work. Rodden and Warf (37) have made an extensive survey of recent work done on the analysis of thorium.

A comprehensive review of the work done before 1948 was the subject of the paper by Moeller, Schwertzer, and Starr (27). Only the work reported since the publication of these latter reviews, and papers of particular significance in the method proposed in this report will be discussed.

The common methods for decomposition of monazite sands are covered in the surveys mentioned above. More recent work has utilized fusion with potassium hydroxide (51), digestion with perchloric acid (33), and treatment with hydrochloric acid (9). Fusion with potassium hydrogen fluoride (36) has proven successful in the method subsequently described.

A number of interesting approaches to the separation of thorium and the rare earths have been presented in recent years. Some of these are new, and others are modifications and improvements of older procedures. The use of organic acids to precipitate thorium selectively has received wide attention (6, 10, 12–
The absorbance measurements were made on a Beckman Model DU spectrophotometer. For centrifugal separations an International clinical centrifuge with 80-ml Lusteroid tubes was used.

**Experimental**

Completeness of Extraction and Conformance to Beer's Law. In order to determine whether the extraction was complete and whether aliquots of the thorium solution, stripped from the solvent after the extraction, could be analyzed directly without further treatment, the following experiment was carried out. Standard stock solution of thorium equivalent to 40 mg of thorium in 50 ml of water was taken and to this were added 1.5 ml of concentrated nitric acid and 15 grams of aluminum nitrate enneahydrate. This solution was then extracted according to the method discussed in the Procedure section. The aqueous thorium extract was diluted to 1 liter to give a solution which should contain 40 micrograms of thorium per milliliter if all the thorium were recovered in the extraction. A second thorium solution having the same concentration as the one just described was prepared by dilution of the standard stock solution. Aliquots of these two solutions were taken to prepare two identical sets of solutions which had varying amounts of thorium in them as shown in Table I.

<table>
<thead>
<tr>
<th>Table I. Thorium Recovery in the Extraction and Conformance to Beer's Lawa</th>
<th>Mg./200 ML.</th>
<th>Absorbance, A (Extracted)</th>
<th>Absorbance, A (Unextracted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ThO₂,</td>
<td>0.124</td>
<td>0.127</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>0.235</td>
<td>0.235</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>0.379</td>
<td>0.379</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>0.563</td>
<td>0.563</td>
<td></td>
</tr>
</tbody>
</table>

a The pH of each solution, 1.00 + 0.04; 20 ml of 0.1% Thorin added to each solution. Total solution volume, 200 ml.

The absorbances of these solutions were measured on the Beckman spectrophotometer at a wave length of 545 μm using 1-cm cells and a slit width of 0.17 mm. The reference solution contained the same amount of reagent at the same pH as the sample solutions. The agreement between the absorbances of the extracted solutions and the standard solutions indicates that the thorium recovery from the extraction is complete. Secondly, it shows that the reaction is not affected by the presence of foreign material introduced during the extraction. This latter conclusion definitely contradicts the findings. Ingles (9) who stated that the thorium must be separated from the aluminum nitrate which contaminates the extract, before reaction with the reagent.

An inspection of these data would indicate a very slight departure from Beer's law at higher concentrations. However, this departure is well within the range of the expected experimental errors and the assumption of a first order dependency between absorbance and thorium concentration seems justified in this concentration range.

Effect of pH. An extracted thorium solution from the analysis of one of the monazite sands was used for the study of the effect of pH on the absorbance of the complex. The concentrations of the thorium and the Thorin remain constant in this series, pH being the only variable. Spectrophotometric measurements were made as previously described. Each reagent reference solution was at the same pH as the sample solution.

This investigation was limited to a particular pH range be-
cause earlier work on the problem in this laboratory as well as elsewhere (42) had shown this to be the optimum range for the reaction. These data prove that the pH dependency of the reaction remains unaltered by any contaminants introduced by the extraction. Also it can be seen that the effects of pH changes are very small over this range. For the subsequent work, a pH of 1 was used. However, any pH value in this range would appear to be suitable.

Stability. Thomason et al. (42) found that solutions of the complex remained stable for 24 hours and this finding has been substantiated in this laboratory. Some nitric acid will be present as a contaminant in the extracted solutions and might slowly oxidize the reagent, resulting in a gradual decrease in the absorbance with time. Studies show that the absorbance remains unaltered over the first few hours and very slowly falls off afterwards. It is advisable to make the spectrophotometric measurements within a 2-hour interval after solution preparation to minimize this source of error. The use of hydrochloric acid to adjust pH would probably lead to a rapid deterioration of the color owing to the strong oxidizing power of the mixture of hydrochloric acid and nitric acids. The stability here refers to the constancy of the absorbance of the sample solutions, using a corresponding reagent solution as the reference.

### Table III. Optimum Amount of Reagent

<table>
<thead>
<tr>
<th>Soln. No.</th>
<th>Thorin, ML</th>
<th>A</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>0.633</td>
<td>0.98</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>0.655</td>
<td>1.02</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>0.647</td>
<td>0.98</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>0.659</td>
<td>0.98</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>0.651</td>
<td>0.98</td>
</tr>
</tbody>
</table>

*Each reference solution for the spectrophotometric measurements contained the same concentration of reagent as the solution with which it was compared.*

**Optimum Amount of Reagent.** The optimum amount of reagent to be used in the reaction over the thorium concentration range indicated in Table I was established in the following manner. Once again one of the thorium solutions extracted from a monazite sand used as the source of thorium. Table III contains the data. The thorium concentration represented by these aliquots was 2.053 mg. of thorium oxide per 200 ml. These data would indicate that the 15-ml. aliquot is the optimum level. However, a 20-ml. aliquot was chosen since the reagent purity is not always reproducible and no significant loss in sensitivity is thus incurred.

**Interferences.** Because all of the common ions are eliminated in this method, a detailed study of interferences in the reaction with Thorin itself is not pertinent to this report. The reader is referred to the work of Thomason et al. (42) for this information. The complete recovery of thorium as evidenced in Table I indicates that the aluminum and nitrate contaminants in the extracted solution do not exhibit any deleterious effects. Levine and Grimaldi (22) presented a rather complete study of those ions which accompany thorium in the extraction process. Several cations that are normally present in monazite sand do so, but they are previously eliminated by the fluoride separation.

Cerous chloride equivalent to 400 mg. of ceria was extracted and the extract was analyzed by the usual spectrophotometric method with no interference indicated. The same results were obtained from 800 mg. of lanthanum oxide, indicating the high efficiency of the separation of thorium from these rare earths. The possibility of interferences from other rare earths seems very remote.

**Procedure**

**Preparation and Decomposition of the Sample.** The samples should be ground to 200 mesh in order to ensure homogeneity of small samples and to increase the efficiency of the fusion. Accurately weigh approximately 0.2-gram samples into 50-ml. platinum crucibles and add 3 grams of technical grade potassium hydrogen fluoride. (Note: potassium hydrogen fluoride is very hygroscopic and the user is cautioned to keep the container tightly sealed at all times when not in use.) Cover the crucible and then place over a low flame or dry off any moisture. Later add 0.63 grams of sodium tetraborate pentahydrate. Increase the temperature until the full heat of the Meker burner is applied. If the full heat is applied directly, excessive spattering occurs. Keep the crucible at a red heat for 10 minutes and then allow to cool. Excessive heating may result in partial conversion of some of the thorium to a highly refractory oxide.

Transfer the cooled melt to 100-ml. platinum dishes with the aid of approximately 100 ml. of nitric acid and 30 ml. of 48% hydrofluoric acid. Transfer the cooled melt to 300-ml. platinum dishes with the aid of approximately 300 ml. of 48% hydrofluoric acid. Transfer these fluorides to a 150-ml. beaker containing 15 grams of aluminum nitrate enneahydrate and 2.5 ml. of nitric acid, using a slight amount of water for the transfer. Place the beaker in a hot plate. As the mixture is warmed, the fluorides will dissolve into the formation of the stable fluoaluminate ion. Reduce the volume to 20 ml. by evaporation.

**Extraction with Mesityl Oxide.** Caution: Carry out the extraction in a hood since excessive inhalation of mesityl oxide may cause serious respiratory difficulties.

Prepare a scrub solution by dissolving 380 grams of aluminum nitrate enneahydrate in 170 ml. of water and 30 ml. of nitric acid and heating. Cool to room temperature before using.

Pour the sample solution from the beaker into a 125-ml. separating funnel. Measure 20 ml. of mesityl oxide (boiling point, 128° to 130°C.) into the beaker, swirl, and add to the separating funnel. Shake for 20 seconds. Drain off the aqueous phase into a second separating funnel. (Freon-11 has a white suspension or emulsion forms at the interface during the extraction. Usually this will not be excessive, but if it is, the effect can usually be minimized by adding an additional 1 ml. of nitric acid.) Add 10 ml. of solvent to the second separating funnel. Shake the system for 20 seconds and discard the aqueous phase.

Combine the solvent with the original portion and add 20 ml. of the scrub solution. After shaking for 20 seconds, shake the aqueous phase. Repeat this operation twice more. Strip the throrium from the solvent by agitation for 20 seconds with 20 ml. of water. Drain the water layer into a 200-ml. volumetric flask and repeat the procedure. Dilute the contents of the flask to volume.

The solution turns brown during the extraction apparently because of some oxidation by nitric acid. Occasionally this effect will cause a yellow tinge in the strip solvent. However, this will not affect the subsequent spectrophotometric work since the color is very slight. This oxidation can be minimized by working with maximum expediency and avoiding the use of warm solvents.

**Spectrophotometric Determination of Thorium.** Usually the analyst will have only the roughest estimation of the thorium by the eye to be expected in the sample. In this case, a fairly reliable first approximation is 5% thorium. For the spectrophotometric work, it is best to take a portion representing 1 to 2 mg. of thorium. For a 0.2-gram sample containing 5% thorium dissolved in 200 ml., a 25-ml. aliquot is sufficient as a first approximation. Pipette the aliquot into a 250-ml. beaker. Dilute to 140 ml. and add 20 ml. of a 0.1% Thorin solution. Adjust the pH with a pH meter to 0.8 ± 0.1 using perchloric acid, and transfer to a 200-ml. volumetric flask. This procedure has been found to give a final pH of 0.9 ± 0.1. The solutions are ready for measurement immediately after dilution and mixing.

Solutions containing the same concentration of reagent at the same pH is used as a reference in the spectrophotometric measurement. Using the Beckman Model DU spectrophotometer, prepare the wave length selected for the slope of the curve, measure the absorbance of the solutions within 2 hours after they are prepared.

**Calculations.** The system conforms to Beer’s law at least up to a 0.2-gram sample containing 5% thorium. Some variation of the purity of the Thorin, the analyst should...
determine the factor for converting absorbance to thorium concentration for his particular reagent. To do this, prepare a series of solutions similar to those in Table I and plot the absorbance against the thorium concentration. For the slope of the best straight line through these points one can relate the absorbance for his particular reagent. To do this, prepare a given absorbance value may be obtained by multiplying that value by the inverse of the slope.

**RESULTS**

A fairly wide variety of monazite sands has been analyzed using this method. These sands were provided by the following laboratories: the New Brunswick Laboratory of the Atomic Energy Commission, New Brunswick, N. J.; U. S. Bureau of Mines, Raleigh, N. C.; and Lindsay Chemical Co., West Chicago, III. The results are tabulated in Table IV. The column labeled "ThO₂ Reported, %" contains the results obtained by the laboratories furnishing the samples with the exception of the sand numbered NBS 201 which was a National Bureau of Standards sample issued by the New Brunswick Laboratory.

With the exception of NBL 5412, these results would seem to be satisfactory. The reason for the disagreement in that sample could not be ascertained.

**DISCUSSION**

The chief advantage of this method is its simplicity and rapidity. This analysis contains a minimum number of separations, and thus reduces the errors due to this factor as well as the time involved. With proper planning and some experience, the entire analysis can be accomplished in about 4 hours. The procedure is readily adaptable to the simultaneous analyses of several samples.

The chief limitation in the method is that its application is restricted, at present, to monazite sands only. Very little examination of the monazite sands used in this work. The results are tabulated in Table IV.

**LITERATURE CITED**

(19) Ibid., pp. 568-72.
(48) Venkataseswarlu, Ch., and Raghava Rao, B. S. V., Ibid., 27, 638-40 (1951).

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