

ration of the reference solution might lead to erroneous results. Analytical data obtained under carefully controlled conditions provide the information on which a critical evaluation of the method may be based.

Analytical Results. Analytical results, obtained under conditions designed to show the contrast between the two methods, are presented in Table VI. After a reading of the test solution against the perchloric reference was obtained, the reference cell was emptied and refilled, using the test solution after treating it with 2 drops of sodium nitrite solution. Another reading was taken immediately. Any discrepancy between the data must be related to the difference between the two reference solutions.

In all cases where precision data are given, ten determinations were made; all values were retained. Standard deviation was calculated as $\sigma = \sqrt{\frac{\sum D^2}{n-1}}$.

The data for the first four samples indicate good agreement between the two methods. However, in the analysis of the tungsten steels, 50b and 153, the results are as much as 2 to 3% higher when based on the nitrite reference. This indicates that the sodium nitrite has a bleaching effect on colored ions, or complexes, in addition to the permanganate ions.

Summary. It would be difficult to prove that the perchloric reference method is right, and the nitrite method is wrong. However, theoretical considerations favor the former, because

it is more likely that nitrite goes beyond the reduction of permanganate ions than that perchloric acid produces complexes whose spectral quality changes with periodate treatment.

The nitrite reference method appears to be satisfactory for the analysis of the types of alloys studied, with the possible exception of the tungsten steels. The 1 to 2 minutes saved per determination is important in the routine control laboratory, perhaps more important than the 2 to 3% error which may be involved in the analysis of tungsten steels.

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RECEIVED for review March 22, 1952. Accepted October 13, 1952. Presented in part at the Second Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 1951.

Spectrophotometric Determination of Thorium in Monazite Sands

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The objective sought in this investigation was the development of a rapid and accurate method of determining thorium in monazite sands. The procedure adopted involves fusing the sand with potassium bifluoride and separating the insoluble rare earth and thorium fluorides by centrifuging, dissolving these fluorides in a saturated solution of aluminum nitrate, extracting the thorium into mesityl oxide followed by stripping it from this solvent with water, and concluding the determination by a spectrophotometric analysis of the resulting thorium solution using the disodium salt of 2-(2-

hydroxy-3,6-disulfo-1-naphthylazo)benzenearsonic acid as the color-forming reagent. Seven different monazite sands were analyzed using this method. The results obtained were checked against those reported by the various laboratories which supplied the samples. The average difference between the reported values and those found using this procedure was $\pm 0.14\%$ thorium. The average precision obtained was $\pm 0.03\%$. This method has the advantages of greater speed and fewer separations than the commonly used methods for determining thorium in monazite sands. Satisfactory accuracy is retained.

DURING the past decade the analytical chemistry of thorium has received considerable attention. Because of its limited supply, particular emphasis has been placed on the determination of thorium in its ores. Monazite sand is the preponderant thorium ore; consequently this paper will deal exclusively with a proposed scheme of analysis for thorium in this material.

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 (36) outlines three methods that have proved successful in his work. Rodden and Warf (37) have made an ex-

tensive 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, Schweitzer, 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 (49), and treatment with hydrofluoric acid (9). Fusion with potassium hydrogen fluoride (36) has proved 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, 13-

15, 18-21, 28-30, 32, 41, 43, 44, 46-49, 51). Other precipitation methods investigated recently use selenious acid (2), iodic acid (45), potassium iodate (51), ammonia (3) at a controlled pH, and radioactive pyrophosphate (26) in which the activity of the excess pyrophosphate in the filtrate is measured.

The use of mesityl oxide to extract thorium selectively (9, 22) has been suggested. Very recent work (12, 33, 50) indicates that ion-exchange and chromatographic techniques are also useful for this separation.

Preliminary separation of thorium from the rare earths is not necessary in certain titrimetric procedures (5, 25, 39, 40) for thorium. When small amounts of thorium are involved or when speed is desired, it is often advantageous to conclude the analysis spectrophotometrically (7, 16, 17, 31, 34, 42). The rare earths interfere in most of these latter methods and a preliminary separation is required.

The aim of this particular project has been to develop a method for the determination of thorium in monazite sands which will be both rapid and accurate. Levine and Grimaldi (22), Kronstadt and Eberle (16), and Rodden (37, p. 193) have developed methods which appear to approach this goal. The procedure proposed in this report further simplifies this determination without any significant loss of accuracy. The mesityl oxide extraction of Grimaldi and Levine (22) has been modified and combined with the spectrophotometric method of Thomason *et al.* (42) in the procedure to be proposed here. The method is outlined as follows:

The sand is decomposed by a potassium hydrogen fluoride fusion, the insoluble fluorides containing all of the rare earths and thorium are digested in dilute hydrofluoric acid, and are finally separated by centrifugal action.

These fluorides are dissolved in a saturated aluminum nitrate solution acidified with nitric acid.

The thorium is separated from this latter solution by extraction into mesityl oxide. The thorium is then stripped from the solvent with water.

Appropriate aliquots of this aqueous solution are reacted with the sodium salt of 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid to produce the colored complex ion which is the basis for the spectrophotometric determination.

MATERIALS AND APPARATUS USED

Thorium. A 0.45 *M* thorium nitrate tetrahydrate solution which was 2 *M* in calcium nitrate and 3 *M* in nitric acid was extracted twice with an equal volume of methyl isobutyl ketone which had been saturated by shaking with an equal volume of 4 *N* nitric acid for 5 to 10 minutes. The thorium was removed from the solvent by shaking with an equal volume of water. It was then precipitated from this aqueous solution as the oxalate and ignited to the oxide at 500° C. It was spectrographically free of significant quantities of rare earths and all common cations. Appropriate amounts of this oxide were then dissolved to make the stock solutions which were standardized by an oxalate precipitation.

Sodium Salt of 2-(2-Hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic Acid (Thorin). Naming the compound as a benzene arsonic acid derivative instead of the substituted naphthol, 1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, was considered preferable because of the analytical selectivity of the arsonic acid group. The common name Thorin is suggested here since the more commonly used terminology, thoron, is easily confused with the daughter product in the thorium decay scheme. This compound was prepared in this laboratory according to the procedure of Margerum *et al.* (23). The product is marketed commercially by: Fine Organics, Inc., 211 East 19th St., New York 3, N. Y.; Smith-New York Co., Inc., Freeport, L. I., N. Y. (under the name Naphtharson); and The British Drug House, Ltd., Poole, England.

Mesityl Oxide. The purified product (No. 582) of Distillation Products Industries was found to be satisfactory.

Other Chemicals. All other chemicals used were reagent grade except for the potassium hydrogen fluoride which was the technical grade product of the City Chemical Co., New York, N. Y.

Equipment. All volumetric ware used was the standard Pyrex brand volumetric ware of the Corning Glass Works. Because this volumetric ware is manufactured to class A capacity tolerances further calibration was considered to be unnecessary. All pH measurements were made with a Beckman Model G pH meter.

The absorbance measurements were made on a Beckman Model DU spectrophotometer. For centrifugal separations an International clinical centrifuge with 50-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 8.5 ml. of water was taken and to this were added 1.5 ml. of concentrated nitric acid and 19 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 I. Thorium Recovery in the Extraction and Conformance to Beer's Law^a

ThO ₂ , Mg./200 ml.	Absorbance, A (Extracted)	Absorbance, A (Unextracted)
0.4	0.128	0.127
0.8	0.255	0.254
1.2	0.382	0.379
1.6	0.507	0.505
2.0	0.632	0.630

^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 mμ 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 of 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-

Table II. Effect of pH on the Reaction between Thorium and Reagent

pH	A	pH	A	pH	A
0.38	0.388	0.58	0.388	0.78	0.387
0.48	0.388	0.71	0.388	0.92	0.388
0.49	0.391	0.71	0.387	1.02	0.386
0.57	0.389	0.71	0.386	1.18	0.383
				1.38	0.384

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 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^a

Soln. No.	0.1% Thorin, Ml.	A	pH
1	10	0.633	0.98
2	15	0.656	1.02
3	20	0.647	0.98
4	25	0.639	0.98
5	30	0.631	0.98

^a 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 was used as the source of thorium. Table III contains the data. The thorium concentration represented by these aliquots was 2.035 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 place over a low flame to drive off any moisture. Gradually 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 3 to 5 minutes and no longer. Excessive heating may result in partial conversion of some of the thorium to a highly refractory oxide. Transfer the cooled melt to 300-ml. platinum dishes with the aid of approximately 100 ml. of hot water. (Note: smaller platinum dishes may be used if these larger ones are not available; the 300-ml. size is recommended for convenience only). Add 20 ml. of 48% hydrofluoric acid and digest under infrared heating lamps (or on a steam bath) for 30 minutes. Pulverize the melt and allow to cool.

Separation and Solution of the Fluorides. Transfer the fluorides to 50-ml. Lusteroid centrifuge tubes and separate at the full speed of the centrifuge for 5 to 10 minutes. Carefully pour off the supernatant liquid. After the last of the soluble fluorides has been discarded, wash the insoluble ones with dilute hydrofluoric acid. This may be done by nearly filling the tube with water and adding a few milliliters of 48% hydrofluoric acid. Transfer these fluorides to a 150-ml. beaker containing 19 grams of aluminum nitrate enneahydrate and 2.5 ml. of nitric acid, using a minimum amount of water for the transfer. Place on a hot plate. As the mixture is warmed, the fluorides will dissolve through the formation of the stable fluoaluminate ion. Reduce the volume to 20 ml. by evaporation and allow to cool.

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. separatory funnel. Measure 20 ml. of mesityl oxide (boiling point, 128° to 130°C.) into the beaker, swirl, and add to the separatory funnel. Shake for 20 seconds. Drain off the aqueous phase into a second separatory funnel. (Frequently 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. Since nitric acid will oxidize the reagent, further addition of the acid is not recommended. The exact nature of this effect is not known; however, it does not appear to affect the results in any way.) Add 10 ml. of solvent to the second separatory 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. Again shake for 20 seconds and discard the aqueous phase. Repeat this operation twice more. Strip the thorium 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 solvent turns brown during the extraction apparently because of some oxidation by nitric acid. Occasionally this effect will cause a yellow tinge in the strip solution. 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 solutions.

Spectrophotometric Determination of Thorium. Usually the analyst will have only the roughest estimation of the thorium assay 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 suggested as a first approximation. Pipet 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.

A solution 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, with the wave length set at 545 mμ, and 1-cm. cuvettes, 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 concentration of 2 mg. of thorium per 200 ml. Because of some variation in the purity of the Thorin, the analyst should

Table IV. Results

Sample No. ^a	ThO ₂ Found, %	ThO ₂ Reported, %	Difference	No. of Analyses
NBL 8412	6.39 ± 0.02	6.05	+0.34	5
NBS 2601	9.53 ± 0.03	9.65	-0.12	3
Florida	4.86 ± 0.02	4.9	...	2
Idaho	3.89 ± 0.02	3.8	...	4
AN 516032	3.52 ± 0.05	3.60	+0.08	4
AN 4236	9.20 ± 0.02	9.19	+0.01	3
SMI 187	6.37 ± 0.01	6.54	-0.17	4

^a First two sands were obtained from New Brunswick, the next two from Lindsay Chemical, and the last three from the Bureau of Mines.

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. From the slope of the best straight line through these points one can relate the absorbance with the thorium content. If the absorbance is plotted as the ordinate and milligrams of thorium per 200 ml. as the abscissa, the milligrams of thorium per 200 ml. corresponding to 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, Ill. 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 2601 which was a National Bureau of Standards sample issued by the New Brunswick Laboratory.

With the exception of NBL 8412, 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 exploratory work has been done on nonmonazite thorium-containing ores and the method cannot be recommended for these ores without further investigations. It has been definitely established that some modification is necessary if the procedure is to be used with black sands.

ACKNOWLEDGMENT

The authors wish to express their appreciation to C. J. Rodden of the New Brunswick laboratory of the Atomic Energy Commission, Howard E. Kremers of Lindsay Chemical Co., and Reuben Kronstadt of the U. S. Bureau of Mines for providing the monazite sands used in this work.

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Received for review September 17, 1952. Accepted November 28, 1952. Work performed in the Ames Laboratory of the Atomic Energy Commission. Contribution 211 from the Institute for Atomic Research.