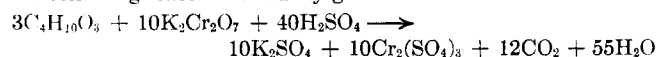


amounts of diglycols are present, it may be necessary to add water to the residue and redistill to remove the aldehydes completely. This process does not appreciably affect the diglycol determination.

The time specified for refluxing with dichromate is about the minimum time but additional refluxing does not alter results.

An unsuccessful attempt was made to remove the iodine compounds by precipitation as metal salts (5, 6), using lead, barium, bismuth, and other metals so that the dichromate could be titrated with sodium thiosulfate.

For the oxidation of diethylene glycol by potassium dichromate, the following reaction is usually given:



By this reaction, factor B should be 0.1082. This factor, as de-

termined by the above method, was 0.1381 which is roughly equivalent to 8 moles of potassium dichromate to 3 moles of diethylene glycol. This factor is reproducible and was used in this work. The reason for this deviation from the theoretical is not known.

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Determination of Microgram Amounts of Thorium

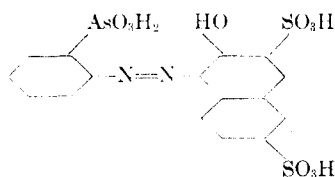
A Colorimetric Method

P. F. THOMASON, M. A. PERRY¹, AND W. M. BYERLY²

Oak Ridge National Laboratory, Oak Ridge, Tenn.

A method for determining thorium in the range 5 to 80 micrograms has been developed, using 1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulfonic acid. Uranium and the rare earths do not interfere in amounts less than 1000 micrograms and interference from iron can be lessened by reduction to the ferrous state.

THE colorimetric determination of thorium on the microgram level has received little consideration in the literature, no doubt because of the absence of characteristic colored complexes of thorium. Survey tests in this laboratory with alizarin and other reagents that are known to complex thorium (1, 10) have not indicated any stable complex that might be used as a basis for a satisfactory colorimetric micromethod. Recently, however, it was reported by Kuznetsov (7) that 1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulfonic acid formed a specific red precipitate with thorium in hydrochloric acid. It was stated that by visual comparison 1 microgram of thorium per milliliter could be detected, and a spot test technique was described.



In view of the need for a rapid micromethod for the determination of small amounts of thorium, the reagent was synthesized and the possibilities of developing a spectrophotometric procedure were investigated. As a result, a method has been developed for the determination of thorium in the range of 5 to 80 micrograms per 10 ml. of final volume. The method consists of the following steps: adjustment of pH, addition of the organic reagent, dilution to volume, and measurement of the optical density in a spectrophotometer versus a reference solution of the reagent.

EXPERIMENTAL

Synthesis of Organic Reagent. The 1-(*o*-arsonophenylazo)-2-

naphthol-3,6-disulfonic acid was synthesized according to directions given by Kuznetsov.

To 2.17 grams of *o*-aminophenylarsonic acid (0.01 molar) dissolved in 40 ml. of water, add 3 ml. of hydrochloric acid (specific gravity 1.12), cool, and diazotize by adding 5.0 ml. of a 2 *N* solution of sodium nitrite. Filter the diazo compound away from the accidental dirt and rapidly mix with a filtered solution of 4.2 grams of the sodium salt of 2,3,6-naphtholsulfonic acid (R salt) and 4 grams of anhydrous sodium carbonate in 40 ml. of water. The mixture immediately becomes red, and after some seconds a precipitate forms. Let stand for 2 to 3 hours, then slowly warm (the precipitate dissolves) and add 14 grams of clean, solid sodium chloride. On cooling, the mass thickens. Filter, squeeze out the liquid, and wash with cold water. Ruby red crystals are produced. A solution in water and dilute acid is orange colored, in alkali is orange-red, in concentrated sulfuric acid is rose colored. It is not soluble in alcohol.

The required *o*-aminophenylarsonic acid was obtained by reducing *o*-nitrophenylarsonic acid by treatment with ferrous sulfate (better ferrous chloride) and sodium hydroxide (2-4). *o*-Nitrophenylarsonic acid is readily prepared by the reaction of Bart by the interaction of diazotized *o*-nitroaniline with an alkaline solution of arsenic trioxide (5, 6, 9).

By analysis the arsenic content of the recrystallized organic reagent was found to be 13.1%. Theoretical is 13.0% for the disodium salt. A more complete and detailed procedure for the synthesis of the organic reagent is to be published by Reed and associates (8).

Materials. Reagent grade chemicals of the common materials were used for testing interferences. Spectrographic analysis of the yttrium nitrate reagent disclosed only the rare earths and calcium as impurities. The zirconyl chloride reagent contained hafnium and traces of iron. No traces of thorium were found in the lanthanum nitrate reagent.

A standard thorium solution was made by dissolving 23.8 grams of chemically pure thorium nitrate tetrahydrate in distilled water and diluting to 1 liter. The thorium nitrate obtained from

¹ Present address, University of Tennessee, Knoxville, Tenn.

² Deceased.

the Lindsay Light and Chemical Company, West Chicago, Ill., gave no spectrographic evidence of yttrium or the rare earths. This solution, which contained approximately 10 mg. of thorium per ml., was standardized by evaporating 10-ml. aliquots to dryness and igniting (to ThO_2) at 1000°C . to a constant weight. Dilutions were made of this solution to obtain a solution containing 10 micrograms of thorium per ml.

Apparatus and Technique. A Beckman Model DU quartz spectrophotometer with 1-cm. path length cells was used for all measurements. All solutions were diluted to a final volume of 10 ml. before being transferred to the absorption cells. The spectral band width ranged from 1.6 to 2.0 $m\mu$ for the spectral absorption curves, Figure 1. A spectral band width of 2.0 $m\mu$ was used to obtain a standard calibration curve.

Absorption Curves. The measurement of the spectral absorption of a water solution of the organic reagent (A, Figure 1) and of a similar solution containing thorium (B, Figure 1) indicated a shift of the absorption band toward longer wave lengths upon the addition of thorium. Water was used as the reference for these measurements. When the solution of reagent plus 67 micrograms of thorium was measured against the solution of reagent (C, Figure 1), the predicted curve indicating a maximum absorption at 545 millimicrons was obtained. The solutions containing 1 ml. of a 0.1% aqueous solution of the reagent were adjusted to a pH of approximately 0.5 with hydrochloric acid in a 10-ml. final volume. The data are plotted in Figure 1.

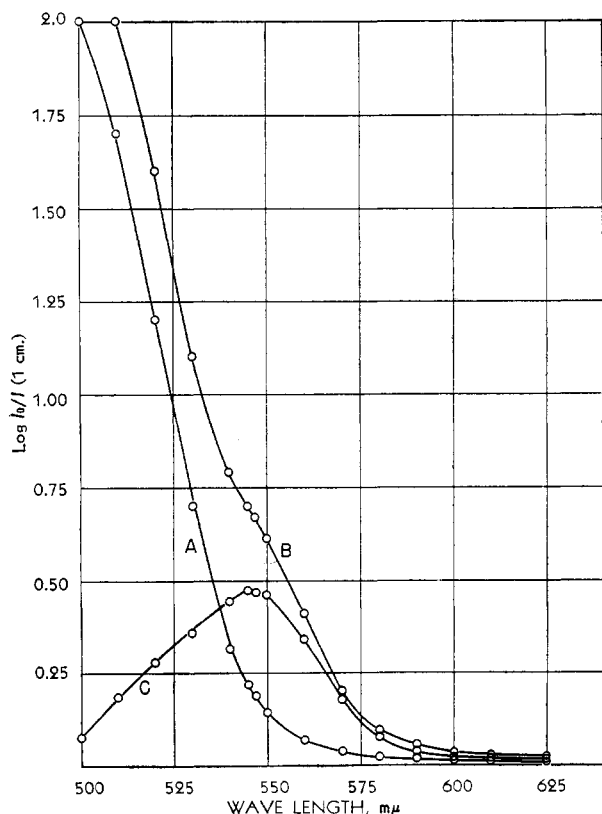


Figure 1. Absorption Spectra of 1-(*o*-Arsonophenylazo)-2-naphthol-3,6-disulfonic Acid

- A. Reagent against water
B. Reagent plus thorium against water
C. Reagent plus thorium against reagent

Effects of Various Amounts of Reagent. The absorption of a series of solutions of pH 0.5, each containing 67 micrograms of thorium but with varying amounts of the organic reagent, was measured to determine a suitable concentration of the reagent. The data plotted in Figure 2 indicate that 1.0 ml. of a solution 0.1% in organic reagent is sufficient to complex at least 70 micrograms of thorium. Experience with later batches of the reagent

indicated differences in purity and moisture content. Therefore, it is recommended that absorption curves be obtained for each batch of reagent to determine the amount required by 80 micrograms of thorium.

Effect of pH. A series of solutions containing thorium and the organic reagent was adjusted to various pH's with hydrochloric acid. Each of these was measured against a pH 0.5 reference solution containing only the reagent. A series of reference solutions containing only the reagent at various pH's was measured against distilled water. Between a pH of 0.2 and 1.0, the absorption remained essentially constant, as indicated in Table I. However, above pH 1.0 the absorption decreased rapidly and approached zero at pH 7.

The data show that in the pH range of 0.3 to 1.0 the maximum error due to variation in pH is about 2%.

Stability of Color. Solutions of thorium and organic reagent show no intensity variation over periods of time up to 24 hours. The colored solution obeys Beer's law, giving a standard curve that is a straight line through the origin with an optical density of 0.53 for 80 micrograms of thorium. When the amount of thorium exceeds 300 micrograms in a 10-ml. volume, a slight turbidity is detected. One milligram, or over, of thorium in a 10-ml. volume will form a red gelatinous precipitate which settles rapidly upon standing.

Interfering Substances. The interference from the UO_2^{++} ion increases with increasing pH as shown in Table II.

The absorption of various cations with the reagent was measured against a reagent reference (Table III).

Table I. Variation of Optical Density with pH

1 Ml. of 0.1% Organic Reagent in Water plus 43 Micrograms of Thorium, Measured vs. Reagent		1 Ml. of 0.1% Organic Reagent Diluted to 10 Ml. with Distilled Water, Measured vs. Water	
pH	Optical density	pH	Optical density
0.20	0.295	0.22	0.220
0.28	0.300	0.30	0.218
0.30	0.303	0.42	0.218
0.49	0.300	0.52	0.220
0.56	0.307	0.65	0.216
0.76	0.310	0.85	0.220
1.05	0.300	1.03	0.218

Table II. Interference of Uranium

(5000 micrograms as UO_2^{++})		
pH	Optical Density	Thorium Equivalent, γ
0.40	0.068	9.5
0.50	0.078	12.0
0.92	0.185	26
1.10	0.342	49
1.45	0.76	>85
1.68	0.94	>85
1.75	1.12	>85

Table III. Absorption of Various Cations

Cation	Amount in 10-Ml. Vol., γ	Optical Density	Thorium Equivalent, γ
U ⁺⁺⁺⁺	20	0.050 ^a	7
U ⁺⁺⁺⁺	40	0.120 ^a	16
U ⁺⁺⁺⁺	80	0.275 ^a	40
Zr	22	0.050	7
Zr	44	0.108	15
Zr	88	0.195	33
Fe ⁺⁺⁺	500	0.058	7
Fe ⁺⁺⁺	1000	0.107	15
Fe ⁺⁺⁺	2000	0.137	20
La	5000	0.125	8
La	10,000	0.252	17
Yttrium	1000	0.102	15
Yttrium	3000	0.305	45
Yttrium	5000	0.520	72
Ti	1000	0.020	2.5
Ti	3000	0.050	9.0
Ti	5000	0.095	14.0
Ce ⁺⁺⁺	1000	0.012	2.0
Ce ⁺⁺⁺	3000	0.040	6.0
Ce ⁺⁺⁺	5000	0.080	12.0
Ce ⁺⁺⁺⁺	1000 (Bleaches reagent completely)		

^a Uranium (IV) complex with reagent seems unstable, as same solutions measured after 2 hours gave optical density of 0.022, 0.080, and 0.195, respectively.

Anions that complex thorium inhibit the formation of the colored complex. Fluorides, oxalates, phosphates, and large amounts of sulfates must be absent or removed.

Analytical Procedure. The following procedure is followed in this laboratory for the analyses of samples which may contain organic material or tetravalent uranium.

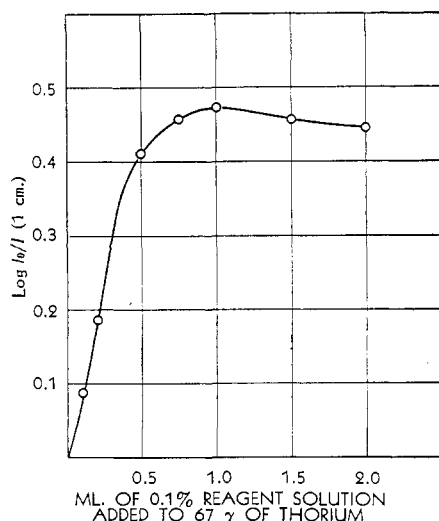


Figure 2. Effect of Various Amounts of Reagent

Each measured against reference containing an equal amount of reagent

Pipet a volume containing 5 to 80 micrograms of thorium into a small beaker. Take to dryness on a hot plate and make one or more evaporations with nitric acid. Add 0.5 ml. of concentrated nitric acid, 0.5 ml. of water, and 1.0 ml. of 70% perchloric acid and evaporate to dryness. Take up in 5 drops of concentrated hydrochloric acid and transfer to a 10-ml. glass-stoppered, volumetric flask.

Add 1.0 ml. of a 0.1% aqueous solution to the organic reagent.

Make up to 10-ml. volume and measure at 545 mμ in a spectrophotometer against a reference solution. The reference solution is made by adding 5 drops of concentrated hydrochloric acid and 1.0 ml. of the organic reagent to a 10-ml. volumetric flask and making up to volume with water.

Elimination of Interferences. Interference from tetravalent uranium and organic compounds that complex thorium are minimized or eliminated by the nitric-perchloric acid step of the procedure. Relatively large amounts of fluoride may be eliminated by carrying the thorium with a hydroxide precipitation of a few milligrams of aluminum.

Synthetic samples containing varying amounts of thorium with 8 mg. of sodium fluoride and 4 mg. of aluminum were analyzed by adding ammonium hydroxide to precipitate the aluminum and thorium, centrifuging, and dissolving the precipitate in dilute hydrochloric acid. The precipitation was repeated three times. The organic reagent was added to the dissolved precipitate, the pH adjusted to 0.5, and the absorption determined in the usual manner. The results are shown in Table IV.

Ferric iron interference can be minimized by reduction to the ferrous state. This can be done by boiling the sample for a few minutes with 1 ml. of 10% hydroxylamine hydrochloride. According to the data shown in Table V, 50 micrograms of thorium can be determined in the presence of 1000 micrograms each of uranium and iron with an error of less than 5% by this procedure.

DISCUSSION

In the course of analyzing several hundred samples for thorium, a number of synthetic samples of known composition have been analyzed simultaneously with the actual samples to test the re-

Table IV. Estimation of Thorium after Separation from Sodium Fluoride

Sample No.	Thorium Present, γ	Thorium Found, γ	Recovery, %
1	10	9.5	95
2	30	28	93
3	50	48	96
4	70	67	96

Table V. Determination of Thorium in Presence of Uranium and Iron

Sample No.	Sample Composition, γ	Thorium Found, γ
1	Th 50 Fe 1000	50
2	Th 50 Fe 2000	50
3	Th 50 U 500 Fe 1000	50
4	Th 50 U 1000 Fe 1000	51

liability of the thorium determination in the presence of other elements. The results of these analyses are shown in Table VI.

This reagent, while not as specific as might be desired, has been very useful for routine analysis of solutions containing relatively large amounts of aluminum and calcium.

SUMMARY

A rapid colorimetric method for the determination of thorium in microgram quantities has been developed. Thorium can be determined in the presence of 20 times its amount of uranium and iron with an error of less than 5%.

Table VI. Analysis of Synthetic Samples

Sample No.	Sample Composition	Thorium Found, γ	Recovery, %
1	55.5	54.0	97
2	49.2	49.0	99
3	12.3	13.8	112
4	49.2	51.0	104
5	49.2	49.8	101
6	37.0	36.0	97
7	49.2	49.2	100
8	49.2	49.0	99
9	49.2	50.0	101

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