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SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM IN THORIUM

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SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM IN THORIUM

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ABSTRACT

At a controlled high acidity, zirconium (0.005 to 0.350 per cent) is determined in thorium metal using sodium alizarin sulfonate without prior removal of thorium. Acetone and heat accelerate the rate of color development and increase the stability of the color. Small amounts of iron and other metals normally present in thorium do not interfere.

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I. INTRODUCTION

An investigation of new techniques for the purification of thorium presented a need for a method for the determination of small percentages of zirconium in thorium.

A number of organic reagents have been studied and recommended for the direct colorimetric determination of zirconium. These include p-dimethylamino-azophenylarsonic acid[1], alizarin[2,3], alizarin red S[4-8], purpurin[2,3], quinalizarin[2,3], thoron[9], and chloranilic acid.[10,11] In their present form the methods are either time consuming or require the removal of thorium if present in large amounts.

Alizarin red S (sodium salt of 1, 2-dihydroxyanthraquinone-3-sulfonic acid) showed the most promise, since the colors ordinarily produced by interfering metals (other than hafnium) are vitiated in strong mineral acid solution. The various contributory factors were studied in order to obtain the maximum absorbance due to the zirconium-alizarin red S lake under conditions that result in minimum interferences from other sources.

II. EXPERIMENTAL

A. APPARATUS

1. Beckman Model G pH meter using calomel reference electrode.
2. Beckman Model DU spectrophotometer with 1-centimeter cuvettes.
3. Water bath maintained at 70° to 90° C.

B. SOLUTIONS

1. Standard Zirconium - Dissolve 35.33 grams cp $ZrOCl_2 \; 8H_2O$ in an aqueous hydrochloric acid solution (pH 1.2) and dilute to 1 liter with the same (pH 1.2) solution. Standardize, using the p-bromomandelic acid method [12]. This solution contains 10 mg zirconium per ml. Prepare solutions containing 0.100 mg per ml and 0.010 mg per ml by properly diluting the stock solution with the hydrochloric acid solution (pH 1. 2).

2. Standard Thorium - Dissolve and fume 29.74 gm of $Th(NO_3)_4 \cdot 4H_2O$ with 150 ml concentrated perchloric acid. Dilute to 1 liter with water. Be sure that the pH is approximately 1. The solution contains 25 mg thorium per ml. Analyze by precipitating the thorium as oxalate and weighing the oxide.[13]

3. Reagent - Dissolve 500 mg alizarin red S (National Aniline Division, Allied Chemical and Dye Corp., New York) in 2:3 hydrochloric acid and dilute to 1 liter with the same solution. Let stand for two days and filter through Whatman No. 40 filter paper. Solution is stable for at least one month.

4. Sample-diluting and Wash Solution - Prepare a hydrochloric acid-water solution having a pH of 0.70.

5. Sample Preparation Reagents - Perchloric acid, cp, concentrated.
Nitric acid, cp, concentrated.
Hydrofluoric acid, cp, 2 per cent in water.
Hydrochloric acid, cp, 1:1 with water.

C. SAMPLE PREPARATION

Weigh metal or compound containing 0.800 gm thorium into a platinum dish. Add 10 ml of concentrated nitric acid (or hydrochloric acid) and a few drops of 2 per cent hydrofluoric acid. Warm to initiate the reaction and remove from the heat. If the reaction becomes too vigorous, it may be moderated by the addition of water. When the reaction subsides and solution is complete, add 5 ml concentrated perchloric acid. Evaporate to near dryness and cool. Add 2 ml nitric acid and 5 ml perchloric acid and again evaporate to near dryness. Dissolve the residue in 5 ml (1:1) hydrochloric acid with heat. Transfer to a 100-ml volumetric flask and adjust to volume with water.

D. ANALYTICAL PROCEDURE

Transfer a 25-ml aliquot (200 mg sample) to a 50-ml beaker. Add 4 ml of acetone and adjust the volume to 32 ± 2 ml with water. Adjust the pH of the sample to 0.70 using (1:1) hydrochloric acid solution and water.

Pipette 10 ml of alizarin red S reagent into a 50-ml volumetric flask and then transfer the sample to the flask. Use the pH 0.70 wash solution for all rinsings and any volume adjustments. Heat in the hot-water bath for 10 to 30 minutes to develop the zirconium color. Cool to room temperature.

Using water as reference, read the absorbance at 540 $m\mu$ within 3 hrs after the start of heating. Absorbance readings are made using 1-centimeter cuvettes in a Beckman Model DU spectrophotometer. Obtain zirconium concentration from a standard absorbance-versus-zirconium-content curve prepared by using the same reagents and the standard solution of zirconium and thorium (Fig. 1).

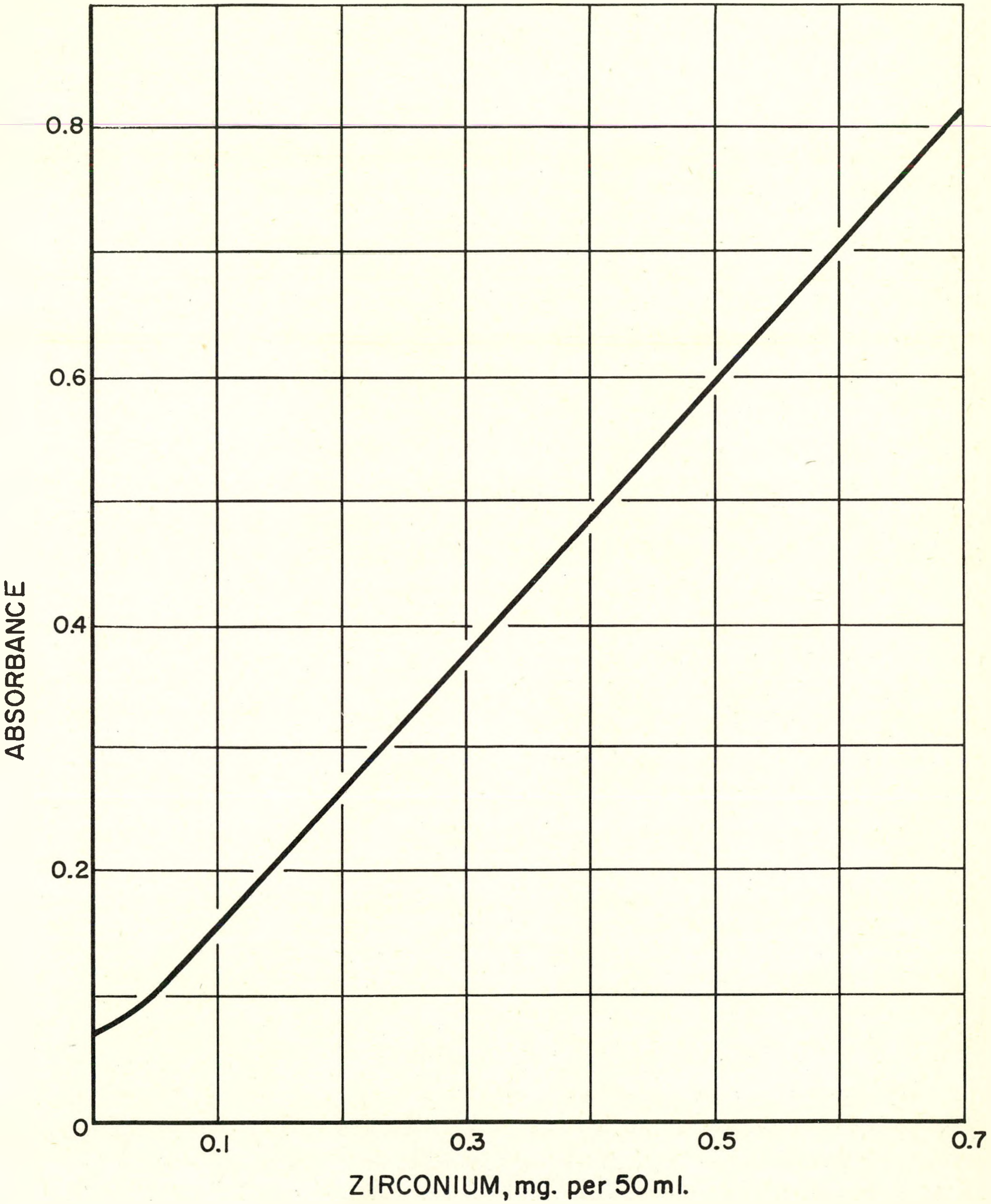

Fig. 1. Standard Curve for Determination of Zirconium in 200 Milligrams of Thorium

If the zirconium content is high, use a smaller aliquot and add the amount of thorium necessary to provide a total of 200 mg per sample.

III. RESULTS

Using the recommended procedure on 200-mg samples of thorium metal, it is possible to determine 0.005 to 0.350 per cent zirconium in a 50-ml volume solution. The standard curve is linear from 0.050 to 0.700 mg zirconium, but curves slightly at the lower zirconium contents (Fig. 1). The entire curve is reproducible. Larger percentages of zirconium may be determined by using smaller samples and adding standard thorium to provide the necessary 200-mg total.

Compounds and solutions may be analyzed if the thorium content is known within 10 per cent, if the thorium and zirconium content can be made soluble in water, and if the interfering complex-forming ions are removable.

Tables I and II illustrate the reproducibility and applicability of the method as shown by two series of thorium-zirconium melts obtained from zone-melting experiments. Similiar reproducibility has been obtained from several other experiments.

A thorium sample reported to be 0.03 per cent in zirconium (spectrographic analysis) was found to contain 0.031, 0.031, 0.033 per cent zirconium. Two other thorium samples contained 0.021, 0.024, 0.024, 0.025 per cent and 0.027, 0.028, 0.028, 0.028 per cent zirconium respectively.

IV. DISCUSSION

Preliminary investigations showed that the absorbance of a solution containing alizarin red S, zirconium, and large concentrations of thorium is dependent upon the wavelength, conditions of color development, concentration of alizarin red S, acidity, and thorium content as well as the zirconium concentration. The effect of each variable was investigated in order to decrease the sensitivity of the method to all factors except zirconium content.

TABLE I

ANALYSIS OF A ZONE-MELTING RUN

ZIRCONIUM IN THORIUM

Sample Number	Zirconium (Per Cent)	Standard Deviation[14] s_w
End	0.092, 0.093, 0.093	0.001
1	0.106, 0.106	
2	0.150, 0.155, 0.155	0.001
3	0.062, 0.066	
4	0.079, 0.079, 0.080	0.001
5	0.068, 0.069	
6	0.074, 0.075, 0.077	0.002
7	0.081, 0.082, 0.083	0.001
8	0.089, 0.089, 0.090	0.001
9	0.079, 0.079, 0.079, 0.081	0.002
10	0.005, 0.005	
Thorium (unalloyed)	0.000, 0.000	

TABLE II

ANALYSIS OF A ZONE-MELTING RUN

ZIRCONIUM AND MOLYBDENUM IN THORIUM

Sample Number	Zirconium* (Per Cent)	Molybdenum[15] (Per Cent)
1	0.068, 0.069	0.06
2	0.085, 0.086	0.02
3	0.088, 0.089	0.09
4	0.096, 0.096	0.25
5	0.095, 0.096	0.07
6	0.096, 0.096	0.04
7	0.077, 0.081	0.03
8	0.079, 0.080	0.03
9	0.086, 0.086	0.09
10	0.085, 0.086	0.04
11	0.082, 0.084	0.10
12	0.106, 0.106	0.15

* Corrected for molybdenum content from data obtained in interference study.

A. WAVELENGTH

Green[4] showed that the effect of varying the necessary excess of alizarin red S on the absorbance of the zirconium-alizarin red S lake was least at 540 mμ under the conditions of his experiments. At 540 mμ and at low pH, the absorbance caused by the excess alizarin red S is negligible and that resulting from the thorium-alizarin red S compound decreases appreciably. The absorbance ascribed entirely to the zirconium compound is at a maximum in the region 520 to 530 mμ and is only slightly lower at 540 mμ (Fig. 2).

B. CONDITIONS OF COLOR DEVELOPMENT

It has been shown[4] that high ion-content of the system decreases both the rate of color development and the stability of the zirconium alizarin red S lake. Color development by preliminary (temporary) decrease in acidity[4, 5, 6] is negated by the presence of thorium. Under the usual conditions for the determination of zirconium in aqueous solution, the high thorium content causes clouding of the mixture before the zirconium-alizarin red S color has fully developed.

Of the stablizing agents investigated, carbitol (monethyl ether of diethylene glycol) prolonged the period of stability but decreased the rate of color development and the overall sensitivity of the method. An alizarin red S-carbitol reagent was usable only during the second and third day after preparation.

Acetone and heat increase the rate of color development, having little or no adverse effect on the sensitivity of the system, and produce a color which is stable for several hours. Variation of the acetone content causes no significant change in the color intensity. Four to 10 per cent of acetone by volume is recommended to prevent precipitation.

C. REAGENT CONCENTRATION

Since the reaction of zirconium and alizarin red S attains equilibrium[8], a large excess of the reagent is desirable. Some of the excess is used by the thorium. Too high a concentration of the reagent, particularly in the presence of much thorium, favors the precipitation of the system, as manifested by a general cloudiness. Five mg of alizarin red S per 50 ml of final solution is a convenient reagent concentration.

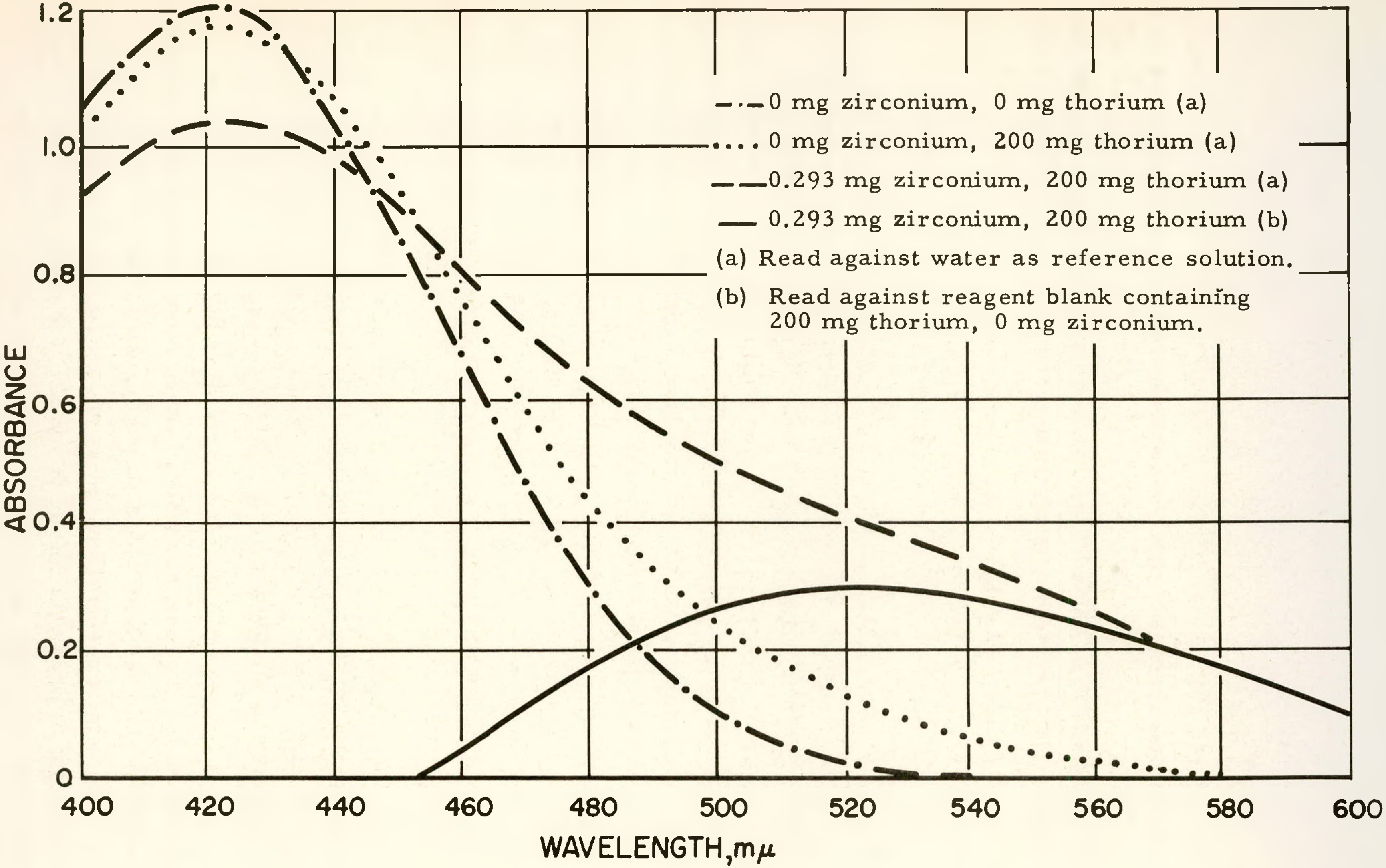

Fig. 2. Absorbance Spectra of Alizarin Red S Complexes

D. ACIDITY CONTROL

At measurable pH, the absorbance of the alizarin red S-zirconium-thorium system is so sensitive to acid content that reproducible results are not easily obtained. Simple additions of acid to systems of varying original acid content are unreliable, even though the sensitivity decreases at the higher acidities. Consequently the sample solution should be adjusted to some reproducible pH at less volume and then the final acidity should be obtained by the addition of a prescribed amount of acid. Reproducible acid conditions are readily obtained by the addition of 10 ml of alizarin red (2:3) hydrochloric acid reagent solution to 40 ml of prepared test samples which originally are adjusted to pH 0.70. All rinsings and volume adjustments are made with a solution of pH 0.70. A variation of ±0.20 in the original pH adjustment results in an absorbance variation of ±0.005 units.

E. THORIUM CONTENT

The effects of the presence of large amounts of thorium in previously reported alizarin red S methods for zirconium include the tendency to cause precipitation at their recommended pH values, delay in color development, and high absorbance caused by the thorium-alizarin red S combination. The conditions recommended in this report eliminate the first two effects and minimize the third. The absorbance attributed to the thorium-alizarin red S is accounted for in the standard curve obtained by using 200 mg thorium with each synthetic standard. A variation of as much as 10 per cent (20 mg) thorium causes less than 2 per cent error in results in the region 0.3 to 0.4 mg zirconium. The error is only slightly higher for the lower zirconium contents.

F. DIVERSE IONS

Alpha-hydroxy carboxylic acids, inorganic fluorides, and sulfates which form stable complexes with zirconium interfere. The first two may be removed by repeated treatment with nitric and perchloric acids. The effect of sulfate may be eliminated by the addition of calcium, not barium.[7]

Table III indicates the effect of a number of diverse ions that might interfere and might be present in thorium solutions. Other ions, specifically reported to cause no interference at lower acid concentrations, do not interfere at the acidity used here, except in concentrations great enough to increase the ion-concentration to the point of precipitation or delay of color development. Nitrates, equivalent to the thorium present, decrease the rate of color development. Under

TABLE III

EFFECT OF DIVERSE IONS ON THE DETERMINATION OF ZIRCONIUM IN THE PRESENCE OF 200 MILLIGRAMS OF THORIUM

Diverse Ion (Milligrams)	Zirconium Added (Micrograms)	Zirconium Found (Micrograms)
5, Al	200	200
1, Be	176	175, 177
10, U	176	175, 176
1, Ni	176	176, 176
5, Fe	176	174, 180
10, Fe	176	177, 183
1, Ce	280	280, 280
5, Ce	200	182
0.04, Mo	222	222
0.08, Mo	222	222
0.20, Mo	222	225
0.50, Mo	222	227
H_2SO_4*	176	0
$HClO_4$*	176	174

*1/2 ml acid included before pH adjustment.

the present conditions, no reduction of iron content is necessary for the quantities investigated. No attempt was made to account for the presence of hafnium in any samples or standards. When present[2], this element undoubtedly causes an increase in absorbance.

SUMMARY

The colorimetric determination of zirconium using sodium alizarin sulfonate as reagent has been adapted to tolerate at least 200 mg of thorium. The acidity should be controlled to that of a 40-ml solution having a pH of 0.70 plus 10 ml of (2:3) hydrochloric acid. Acetone and heat are used to develop and stabilize the color.

The thorium content of the final samples should be 200 ±10 mg per 50 ml of final solution corresponding to the content of the solutions used for the standard curve.

The reproducibility of the determination of zirconium (0.01 to 0.70 mg) in thorium (200 mg) is in the range of 0.01 per cent zirconium and the standard deviation is 0.002 per cent. Higher percentages of zirconium may be determined with suitable sample and volume adjustment if the acid concentration is kept constant.

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