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# THE "THORIN" COLORIMETRIC METHOD FOR THORIUM DETERMINATION: EFFECT OF SOME COMMON IONS, AND METHODS FOR OVERCOMING INTERFERENCES



by

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MINES BRANCH
RESEARCH REPORT

R 34

PRICE 25 CENTS

NOVEMBER 26, 1958

Mines Branch Research Report R 34

# THE "THORIN" COLORIMETRIC METHOD FOR THORIUM DETERMINATION: EFFECT OF SOME COMMON IONS, AND METHODS FOR OVERCOMING INTERFERENCES

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## ABSTRACT

The effect of a number of common ions on the Thorin colorimetric method for thorium determination has been investigated. A comparison was carried out on the use of the two reducing agents, ascorbic acid and hydroxylamine hydrochloride, for overcoming the interference of iron and cerium. Molybdenum caused low thorium assays in the presence of ascorbic acid, whereas this effect was not found with hydroxylamine hydrochloride present, or in the absence of a reducing agent. Titanium caused low thorium assays under any conditions tried and a very low tolerance limit must be set for this ion. Zirconium caused high thorium assays under normal conditions, but its effect varied with the form in which it was added, and appeared to be enhanced by the presence of thorium. By using mesotartaric acid as a masking agent for zirconium, approximately 5 mg of zirconium could be tolerated in a final 25 ml volume taken for the colorimetric finish. In the absence of zirconium, mesotartaric acid is not required and a final volume of 250 ml is used.

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(14 text pages, 6 tables)

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# INTRODUCTION

The reagent 1-(o - arsonophenylazo)- 2 - naphthol - 3:6 - disulphonic acid (Thorin reagent) has been extensively applied for the determination of thorium in recent years. After its preparation in 1941 by Kuznetsov[1], the reagent was first used in an analytical method for microgram quantities of thorium, by Thomason et al[2]. Its application to thorium analysis on a wide range of materials is shown by the large number of papers using the procedure (3, 4, 5, 6, 7, 8). Thorin reagent is not completely specific for thorium; consequently, preliminary separation of a number of contaminants is usually carried out.

A number of workers have investigated the effect of various ions on the colorimetric procedure (2, 8, 9), the most thorough work to date being that of Clinch[8]. Nevertheless there are a number of anomalies in the literature. For example, while there appears to be general agreement that zirconium and titanium affect the colorimetric procedure, the extent of this effect, particularly in the case of zirconium, is the subject of considerable disagreement among the different investigators (2, 3, 8, 9), although recently mesotartaric acid has been employed as an effective masking agent for zirconium (10, 11, 12). Furthermore, information is lacking on the effect of molybdenum and vanadium on the colorimetric finish.

In the application of Thorin to thorium analysis, the use of hydroxylamine hydrochloride as a reducing agent for sharply decreasing the effect of iron and cerium has received wide acceptance

(2, 4, 6, 8), and recently ascorbic acid has also been used for this purpose(13), but no data comparing these two reductants have been published.

As a part of a program being carried out here on the development of rapid accurate analytical methods employing the new solvent extraction reagents (aliphatic amines and organic phosphates), it was necessary to assay for thorium in the presence of zirconium, uranium, molybdenum, and varying amounts of sulphate. The purpose of this work, then, was to investigate the effect of these and other ions on the colorimetric finish and to consider ways of eliminating any detrimental effects on thorium assays. At the same time, it was felt also that a comparison of the use of ascorbic acid and hydroxylamine hydrochloride as reductants in the colorimetric procedure, particularly in regard to interactions with interfering metal ions, would be useful.

## REAGENTS

Ascorbic acid solution, 5%:

> Dissolve 5 grams of l-ascorbic acid in distilled water and dilute to 100 ml.

Hydroxylamine hydrochloride solution, 10%:

> Dissolve 10 grams of hydroxylamine hydrochloride in distilled water and dilute to 100 ml.

Thorin reagent, 0.375%:

> Dissolve 3.75 grams of 1-(o-arsonophenylazo) - 2 - naphthol - 3:6 - disulphonic acid (Thorin reagent) in distilled water and dilute to 1000 ml.

Vanadyl sulphate solution:

Dissolve 1 gram of $VO\,SO_4 \cdot 2\,H_2O$ in 100 ml of 1% sulphuric acid. One ml is equivalent to approximately 2.6 mg V.

Ferric sulphate solution:

Dissolve 5 gram of $Fe_2(SO_4)_3 \cdot 6\,H_2O$ in one litre of 0.1% sulphuric acid. One ml is equivalent to approximately 1.1 mg Fe.

Cerous sulphate solution:

Dissolve 1 gram of $Ce(HSO_4)_4$ in 100 ml of water and add a few drops of 29% $H_2O_2$. One ml is calculated to contain approximately 2.6 mg Ce.

Molybdenum solution:

Dissolve 1 gram of $H_2\,Mo\,O_4 \cdot H_2O$ in concentrated sulphuric acid. Evaporate to near dryness. Dissolve in water and make up to 100 ml volume. One ml is calculated to contain approximately 5.3 mg Mo.

Thorium sulphate solution:

Dissolve 5 grams of $Th(SO_4) \cdot 8\,H_2O$ in 500 ml of water. Place in an ice-water bath and stir occasionally to obtain complete solution. Make up to 500 ml. One ml is equivalent to approximately 4.8 mg $ThO_2$. Standardise the solution by carrying out an ammonium hydroxide precipitation on an aliquot containing at least 100 mg of thorium oxide. Ignite the dried precipitate at 1000°C in a platinum crucible.

Zirconium sulphate solution:

Dissolve 5 grams of $Zr\,(SO_4)_2 \cdot 4\,H_2O$ in one litre of distilled water. One ml is equivalent to approximately 1.7 mg $ZrO_2$.

Uranyl sulphate solution:

Dissolve 50 grams of $UO_2\,SO_4 \cdot 3\,H_2O$ in one litre of 10% sulphuric acid. One ml is equivalent to approximately 34 mg $U_3O_8$.

Titanium sulphate solution:

> Dissolve 1 gram Ti O $SO_4$ in concentrated sulphuric acid, fume till just moist, and dissolve in water. Add two or three drops of 29% $H_2O_2$ and make up to 100 ml volume. One ml is equivalent to approximately 5 mg Ti $O_2$.

## PROCEDURE

Evaporate the sample solution containing the thorium and/or contaminating ion to dryness on a hot plate. Add 0.5 ml of concentrated hydrochloric acid per 25 ml final volume, dilute with distilled water, and warm to aid solution of salts. Add 5 ml of 5% ascorbic acid solution or 5 ml of 10% hydroxylamine hydrochloride solution. If the latter is used, boil the solution for 5 minutes. Transfer the cool solution to an appropriately sized volumetric flask and add 1 ml of a 0.375% solution of Thorin reagent per 25 ml final volume. Make the solution to volume with distilled water and read the optical density on a Beckman model "B" spectrophotometer at 545 millimicrons. In all the test work described here, a 250 ml final volume was employed, and the concentration of contaminants is expressed as mg in 250 ml volume (except in the case of the tests involving zirconium and mesotartaric acid, where 25 ml volumes were used).

## EXPERIMENTAL

### Use of Ascorbic Acid in the Thorium-Thorin Procedure

Hydroxylamine hydrochloride has been used in this laboratory in the thorium-Thorin colorimetric procedure as a reducing agent for such ions as iron and cerium. A disadvantage of its use is the necessity of boiling the solution to ensure reduction. Ascorbic acid, which

efficiently reduces iron and cerium in the cold, appeared to offer a more convenient way of obtaining reduction. The use of this reagent has been recommended by Nietzel et al[13]. A series of tests was carried out therefore, to test the efficiency of ascorbic acid as a substitute for hydroxylamine hydrochloride. The ions that were chosen as contaminants were either those which would be expected to extract with various amines during solvent extraction, or ions which are commonly found in radioactive ores and the products obtained from them.

a) Pure Thorium Solutions

A comparison was made of the optical densities of solutions containing thorium alone with solutions containing both thorium and ascorbic acid. The thorium was added as the sulphate. From Table 1 it can be seen that the presence of ascorbic acid does not inhibit the thorium-Thorin complex formation.

b) Effect of Iron, Cerium, Vanadium and Uranium

Considerable information is available on the effect of iron, cerium and uranium on the colorimetric procedure in the presence of hydroxylamine hydrochloride (2, 8), but information is scarce on the effect of vanadium. In order to evaluate the effect of ascorbic acid on thorium values in the presence of these ions, sulphate solutions of iron, cerium and uranium were added to aliquots of pure thorium sulphate solution. The vanadium solution was oxidized with nitric-perchloric-sulphuric mixture, and finally taken to sulphuric acid fumes. Results, as shown in Table 1, indicate that these quantities of iron and vanadium have little effect on the colorimetric procedure. Indications are that gross amounts of uranium, and probably cerium,

would tend to give high assays. On solutions containing only these contaminants, ascorbic acid appears to be a satisfactory alternative to hydroxylamine hydrochloride.

TABLE 1

Effect of Iron, Cerium, Uranium and Vanadium on a Thorium-Thorin Procedure Using Ascorbic Acid

| Thorium Present, mg $ThO_2$ | Contaminant Present, mg | Ascorbic Acid Present, ml of 5% Solution | Optical Density in 250 ml Volume |
|---|---|---|---|
| 0.513 | - | - | 0.114 (average of 5 values) |
| 0.513 | - | 5 | 0.114 (average of 5 values) |
| 0.513 | 11 mg Fe | 5 | 0.113 |
| 0.513 | 2.7 mg Ce | 5 | 0.118 |
| 0.513 | 68 mg $U_3O_8$ | 5 | 0.124 |
| 0.510 | - | - | 0.112 |
| 0.510 | 2.6 mg V | 5 | 0.112 |
| 0.510 | 5.1 mg V | 5 | 0.110 |
| 0.510 | 12.8 mg V | 5 | 0.112 |

c) Effect of Zirconium, Titanium and Molybdenum

The effect of zirconium, titanium and molybdenum on the colorimetric procedure using ascorbic acid was next evaluated. All solutions were added as the sulphate. Under these conditions, each ion has a considerable effect on thorium assays (Table 2). Zirconium forms a red complex with Thorin reagent and gives high results.

Titanium and molybdenum both formed coloured complexes with ascorbic acid, but caused low thorium results for reasons not yet understood. It is clear from these results that the use of ascorbic acid is not advisable for thorium determinations on solutions containing titanium, molybdenum or zirconium.

TABLE 2

Effect of Molybdenum, Titanium and Zirconium on a Thorium-Thorin Procedure Using Ascorbic Acid

| Thorium Present, mg $ThO_2$ | Contaminant Present, mg | Ascorbic Acid Present, ml of 5% Solution | Optical Density in 250 ml Volume |
|---|---|---|---|
| 0.510 | - | - | 0.112 |
| 0.510 | - | 5 | 0.112 |
| 0.513 | 2.7 mg Mo | 5 | 0.115 |
| 0.513 | 5.3 mg Mo | 5 | 0.110 |
| 0.510 | 5.3 mg Mo | 5 | 0.097 |
| 0.513 | 10.6 mg Mo | 5 | 0.084 |
| 0.513 | 26.5 mg Mo | 5 | 0.045 |
| 0.513 | 53.0 mg Mo | 5 | 0.013 |
| - | 5.0 mg $TiO_2$ | 5 | 0.000 |
| 0.510 | - | 5 | 0.116 |
| 0.510 | 5.0 mg $TiO_2$ | 5 | 0.088 |
| 0.513 | - | 5 | 0.113 |
| 0.513 | 3.4 mg $ZrO_2$ | 5 | 0.194 |
| - | 3.4 mg $ZrO_2$ | - | 0.066 |

## Use of Hydroxylamine Hydrochloride in the Thorium-Thorin Procedure

### a) Effect of Molybdenum, Titanium and Zirconium

Tests were carried out to evaluate the effect of molybdenum, titanium and zirconium on a thorium-Thorin procedure using hydroxylamine hydrochloride. Accordingly, synthetic samples containing thorium and/or molybdenum, titanium and zirconium, all added as the sulphate, were acidified with hydrochloric acid and boiled for 5 minutes with 5 ml of 10% hydroxylamine hydrochloride solution.

Results showed that molybdenum does not interfere in the thorium-Thorin procedure whether or not hydroxylamine hydrochloride is added (Table 3). Titanium interfered by giving lower thorium optical density readings (Table 3). Here again little difference is noted whether or not hydroxylamine hydrochloride is present. The effect of titanium appears to become constant somewhere between 5 and 10 mg of titanium dioxide. The titanium solution contained some hydrogen peroxide, which resulted in the yellow pertitanate complex being present. This coloured complex was destroyed upon boiling with hydroxylamine hydrochloride.

Zirconium interfered, as expected, by giving high optical density readings (Table 3). The effect of zirconium in the presence of thorium was greater than would be expected from optical density readings given by these ions separately. A precipitate gradually formed at the level of 3.44 and 5.16 mg of zirconium oxide, becoming heavy, particularly at the 5 mg level, after about 20 minutes.

## TABLE 3

### Effect of Molybdenum, Titanium and Zirconium on a Thorium-Thorin Procedure Using Hydroxylamine Hydrochloride

| Thorium Present, mg $ThO_2$ | Contaminant Present, mg | Hydroxylamine Hydrochloride Present, ml of 10% Solution | Optical Density in 250 ml Volume |
|---|---|---|---|
| 0.513 | - | 5 | 0.115 |
| 0.513 | 5.3 mg Mo | 5 | 0.110 |
| 0.513 | 10.6 mg Mo | 5 | 0.115 |
| 0.513 | 15.9 mg Mo | 5 | 0.115 |
| 0.513 | 21.2 mg Mo | 5 | 0.115 |
| 0.513 | 53.0 mg Mo | 5 | 0.110 |
| 0.513 | 2.7 mg Mo | - | 0.115 |
| 0.513 | 5.3 mg Mo | - | 0.108 |
| 0.513 | 10.6 mg Mo | - | 0.104 |
| 0.513 | 13.3 mg Mo | - | 0.110 |
| 0.484 | - | 5 | 0.102 |
| 0.484 | 0.50 mg $TiO_2$ | - | 0.098 |
| 0.484 | 1.0 mg $TiO_2$ | - | 0.094 |
| 0.484 | 1.50 mg $TiO_2$ | - | 0.090 |
| 0.484 | 0.50 mg $TiO_2$ | 5 | 0.095 |
| 0.484 | 1.0 mg $TiO_2$ | 5 | 0.094 |
| 0.484 | 1.50 mg $TiO_2$ | 5 | 0.092 |
| 0.484 | 5.00 mg $TiO_2$ | 5 | 0.076 |
| 0.484 | 10.0 mg $TiO_2$ | 5 | 0.066 |
| 0.484 | 15.0 mg $TiO_2$ | 5 | 0.062 |
| 0.484 | 25.0 mg $TiO_2$ | 5 | 0.065 |
| 0.484 | 75.0 mg $TiO_2$ | 5 | 0.066 |
| - | 1.72 mg $ZrO_2$ | - | 0.034 |
| 0.484 | - | 5 | 0.102 |
| 0.484 | 1.72 mg $ZrO_2$ | 5 | 0.200 |
| 0.484 | 3.44 mg $ZrO_2$ | 5 | 0.282 |
| 0.484 | 5.16 mg $ZrO_2$ | 5 | 0.550 |

b) Effect of Adding Zirconium and Thorium in the Form of Various Salts

It has been shown that zirconium caused high values in the thorium-Thorin colorimetric method in the presence of hydroxylamine hydrochloride. This has been noted earlier by other workers, but there is considerable disagreement as to the extent of this effect (2, 3, 8, 9). The impression here has been that the effect of zirconium varies according to the form in which it is present. To try to verify this point, a number of tests were carried out using zirconium as the chloride, perchlorate and sulphate. Hydrochloric acid and Thorin reagent were then added as in the standard thorium-Thorin procedure. Results as shown in Table 4 indicated that the effect of zirconium added as the sulphate was roughly one-half that shown if zirconium was added as the perchlorate or chloride.

The effect of salt form on thorium assays was shown by fuming aliquots of a thorium nitrate solution with perchloric acid or sulphuric acid. The thorium sulphate solution gave a lower optical density reading than the thorium perchlorate solution (Table 4). Sulphate has been generally found to have a depressing effect on the thorium-Thorin colour in work carried out in this laboratory, but it has not been found that perchloric acid enhances absorbance readings. These findings are in at least partial agreement with those of Clinch[8], who reported that the presence of sulphate lowered, and of perchloric acid raised, optical density readings. The discrepancy in the case of perchloric acid may be accounted for by the larger volume used here for final colorimetric readings.

TABLE 4

Effect of Adding Zirconium and Thorium as Various Salts on the Thorium-Thorin Procedure

| Thorium Added, mg $ThO_2$ | Zirconium Added, mg $ZrO_2$ | Optical Density in 250 ml Volume | Remarks |
|---|---|---|---|
| - | 1.72 | 0.034 | as zirconyl sulphate |
| - | 3.44 | 0.066 | " |
| - | 1.13 | 0.030 | " |
| - | 1.13 | 0.055 | as zirconyl chloride |
| - | 2.26 | 0.110 | " |
| - | 3.39 | 0.145 | " |
| - | 1.13 | 0.059 | as zirconyl perchlorate |
| - | 2.26 | 0.110 | " |
| - | 3.39 | 0.148 | " |
| 1.04 | - | 0.206 | as thorium sulphate |
| 1.04 | - | 0.221 | as thorium perchlorate |

c) Use of Mesotartaric Acid as a Masking Agent for Zirconium

Grimaldi and Fletcher[10] and Fletcher, Grimaldi and Jenkins[11] have used mesotartaric acid as a masking agent for zirconium to prevent its effect on thorium assays using the thorium-Thorin procedure. This technique was also used successfully by Everest and Martin[12] for the same purpose. These investigators found that up to 5 mg of zirconium could be tolerated without interfering with thorium assays. Several tests were carried out here using meso-tartaric as a masking agent for zirconium. Results, as shown in Table 5, confirm the findings of these workers. One ml of 10% hydroxylamine hydrochloride solution and four ml of 10% mesotartaric acid solution were added in each case and the final volume adjusted to 25 ml.

TABLE 5

Use of Mesotartaric Acid as a Masking Agent for Zirconium in the Thorium-Thorin Procedure

(4 ml 10 % mesotartaric acid solution added in all cases)

| Thorium Added, mg $ThO_2$ | Zirconium Added, mg $ZrO_2$ | Optical Density per 25 ml Volume | Remarks |
|---|---|---|---|
| 0.049 | - | 0.068 | - |
| 0.049 | 2.25 | 0.068 | - |
| 0.098 | - | 0.184 | - |
| 0.098 | 4.50 | 0.186 | Turbid after 20 min |
| 0.147 | - | 0.264 | - |
| 0.147 | 6.75 | 0.274 | Turbid after 20 min |

## CONCLUSIONS

Hydroxylamine hydrochloride appears to be more satisfactory than ascorbic acid for use as a reducing agent in the thorium-Thorin colorimetric procedure. Both compounds were satisfactory reducing agents in the presence of iron, cerium, uranium and vanadium. Although ascorbic acid is more convenient to use than hydroxylamine hydrochloride, the effect of molybdenum on thorium assays when ascorbic acid is present eliminates this reducing agent from consideration for use in a general procedure, unless a preliminary removal of molybdenum is carried out.

Zirconium was found to have a serious effect on thorium assays under normal conditions. This effect varied with respect to the form in which it was present. The effect of zirconium could be overcome by adding mesotartaric acid as a masking agent. In this manner up to approximately 5 mg of zirconium may be tolerated in the final 25 ml volume for colorimetric assay. As the practical lower limit for thorium is about 50 micrograms per 25 ml volume, this represents a 100 to 1

ratio of zirconium to thorium which may be tolerated in the presence of mesotartaric acid.

Titanium (as sulphate) interfered in the colorimetric finish under all conditions tried. The tolerance limit for this ion must be set at close to nil. When working at the level of 0.5 mg thorium for the final colorimetric reading, a negative error of about 10% was found with a 2 to 1 ratio of titanium (in sulphate form) to thorium. This error increased to about 40% at a point somewhere between 10 to 1 and 20 to 1, titanium to thorium, whereupon no further increase in error was noted at levels of over 100 to 1.

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THE QUEEN'S PRINTER AND CONTROLLER OF STATIONERY
OTTAWA, 1959