

(200)
T672
No. 692

DETERMINATION OF THORIUM IN THE
PARTS PER MILLION RANGE IN ROCKS

By Harry Levine and Frank S. Grimaldi

Trace Elements Investigations Report 692

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

(200)
T672
no. 692

Chemistry

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

DETERMINATION OF THORIUM IN THE PARTS PER MILLION RANGE IN ROCKS*

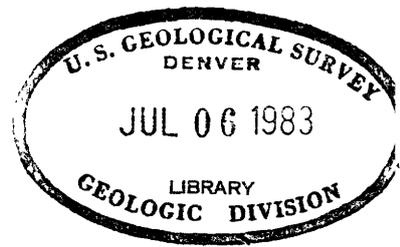
By

Harry Levine and Frank S. Grimaldi

July 1957

Trace Elements Investigations Report 692

This preliminary report is distributed without editorial and technical review for conformity with official standards and nomenclature. It is not for public inspection or quotation.



*This report concerns work done on behalf of the Division of Research of the U. S. Atomic Energy Commission.

USGS - TEI-692

CHEMISTRY

<u>Distribution</u>	<u>No. of copies</u>
Argonne National Laboratory	1
Atomic Energy Commission, Washington	2
Division of Raw Materials, Albuquerque	1
Division of Raw Materials, Austin	1
Division of Raw Materials, Casper	1
Division of Raw Materials, Denver	1
Division of Raw Materials, Ishpeming	1
Division of Raw Materials, Phoenix	1
Division of Raw Materials, Rapid City	1
Division of Raw Materials, Salt Lake City	1
Division of Raw Materials, Spokane	1
Division of Raw Materials, Washington	3
Division of Research, Washington	1
Exploration Division, Grand Junction Operations Office	1
Grand Junction Operations Office	1
Technical Information Service Extension, Oak Ridge	6
Tennessee Valley Authority, Wilson Dam	1
U. S. Geological Survey:	
Foreign Geology Branch, Washington	1
Fuels Branch, Washington	1
Geochemistry and Petrology Branch, Washington	15
Geophysics Branch, Washington	1
Mineral Deposits Branch, Washington	2
P. C. Bateman, Menlo Park	1
A. L. Brokaw, Grand Junction	2
N. M. Denson, Denver	1
R. L. Griggs, Albuquerque	1
W. R. Keefer, Laramie	1
H. W. Lakin, Denver	1
L. R. Page, Washington	1
P. K. Sims, Denver	1
Q. D. Singewald, Beltsville	1
F. N. Ward, Denver	1
A. E. Weissenborn, Spokane	1
TEPCO, Denver	2
TEPCO, RPS, Washington, (including master)	2
	<hr/>
	61

CONTENTS

	Page
Abstract	4
Introduction	4
Procedure and discussion	4
Experimental results	7
References	11

TABLES

Table 1. Effectiveness of lanthanum or yttrium fluorides as carriers for thorium fluoride (15 mg of each carrier used, calculated as oxide)	8
2. Recoveries of thorium added to gabbro	8
3. Reproducibility of results on standard diabase W-1 and granite G-1	9
4. Comparison of spectrophotometric and mass spectrometric results on two basalts	9
5. Thorium determinations on Laramide intrusive rocks from the Front Range, Colorado	10

DETERMINATION OF THORIUM IN THE PARTS PER MILLION RANGE IN ROCKS

By Harry Levine and Frank S. Grimaldi

ABSTRACT

A procedure is presented for the determination of thorium in the concentration range of 0.2 to 10 parts per million ThO_2 in felsic or mafic rocks. Thorium is extracted by mesityl oxide and purified by iodate precipitation from nitric acid medium containing tartaric acid and hydrogen peroxide. The thorium is determined spectrophotometrically with thoron from meso-tartaric acid medium.

INTRODUCTION

Studies on the geochemistry of thorium require data on the thorium content of various rocks. This paper presents a procedure that is useful for determination of thorium in the range of 0.2 to 10 ppm thorium dioxide in felsic and mafic rocks. Above 10 ppm thorium dioxide, advantage may be taken of the simpler procedure of Grimaldi, Jenkins, and Fletcher (1957).

PROCEDURE AND DISCUSSION

The main steps in the procedure involve decomposition of a 5-g sample of rock, extraction of thorium nitrate with mesityl oxide, purification of thorium by iodate precipitation from nitric acid medium containing tartaric acid and hydrogen peroxide, and spectrophotometric determination of thorium with thoron in meso-tartaric acid medium.

The mesityl oxide extraction of thorium nitrate was originally introduced by Levine and Grimaldi (1950, 1954) for macro amounts of thorium and has also been used by others (Banks and Byrd, 1953; Banks, Klingman, and Byrd, 1953). Maréchal-Cornil and Picciotto (1953) have shown that thorium is quantitatively extracted in concentrations as low as 10^{-12} g of thorium per ml of solution. The iodate separation of thorium as described by Grimaldi and others (1957) is quantitative down to 1 microgram of ThO_2 in 50-ml volume. The spectrophotometric determination of thorium with thoron in meso-tartaric acid medium allows the determination of as little as 1 microgram of ThO_2 in a volume of 25 ml; details of this procedure are given by Fletcher and others (1957). Only a few notes on the procedure are given here.

Samples are decomposed with a mixture of HF-HNO_3 , followed by several evaporations with HNO_3 to decompose fluorides. Rocks containing appreciable amounts of magnesium give large precipitates of MgF_2 , and it may be difficult to convert the insoluble fluorides to nitrates by nitric acid alone. In such cases addition of no more than 1.5 g of boric acid in increments of about 0.5 g along with the nitric acid materially hastens the removal of fluoride. Ordinarily, complete decomposition of rocks is obtained by this treatment, and it has not been necessary to collect any undecomposed sample for solution by some other method such as a carbonate fusion and subsequent solution in nitric acid.

Some mafic rocks contain appreciable amounts of titanium which may hydrolyze from solution on evaporation, especially with prolonged baking. Such a hydrolytic precipitate can be filtered, ignited, and dissolved in HF . Any thorium in the hydrolytic precipitate is recovered from the HF solution

as the insoluble ThF_4 by using a carrier such as yttrium or lanthanum, total carrier 15 mg, calculated as the oxide. If necessary the carrier stock solution can be freed of thorium by the addition of ammonium hydroxide (a small amount of H_2O_2 is helpful) until a small amount of precipitate of rare-earth hydroxide plus thorium is formed. The residue is filtered and rejected.

Thorium and rare-earth fluorides are filtered, ignited, and dissolved in HNO_3 and the solution added to the reserved main solution. Finally, a solution containing 3.75 ml HNO_3 in a total volume of 25 ml is obtained.

After the addition and solution of 47.5-g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ crystals as a salting agent, the solution is extracted twice with mesityl oxide, once with a 50-ml and then with a 25-ml portion. The aluminum nitrate is also effective in dissolving any small amounts of insoluble fluorides not decomposed by previous treatments.

After washing the organic layer with three separate 40-ml portions of aluminum nitrate wash solution (aluminum nitrate dissolved in 15+85 HNO_3 in the proportion of 9.5 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to 5 ml of the diluted HNO_3) the thorium nitrate is stripped from the organic solvent with two 45-ml portions of water.

The aqueous solution is evaporated and the organic matter destroyed with the aid of 10 ml HNO_3 and 2 ml HClO_4 . The perchloric acid is then removed by heating on a sand bath at a temperature of 170° to 180° C. After adding 6 ml of 1 + 1 HNO_3 to dissolve the residue, the iodate separation and colorimetric estimation is made according to procedures described by Fletcher and others (1957), and Grimaldi and others (1957). Blanks should be carried through the analysis. The blank with ordinary reagent grade chemicals is about 0.5-microgram ThO_2 .

EXPERIMENTAL RESULTS

Table 1 illustrates the effectiveness of the fluoride separation of microgram amounts of thorium when 15 mg of either La_2O_3 or Y_2O_3 is used as a carrier. The iodate separation was used to free thorium from the carrier, and the determination of thorium was made spectrophotometrically with thoron. Thus the recoveries include any errors introduced by the iodate separation and colorimetric estimation.

Experiments on a 5-g sample of San Marcos gabbro from the southern California batholith spiked with known amounts of thorium and carried through the complete procedure gave excellent recoveries of the thorium added, as shown in table 2.

The reproducibility of the results on a standard diabase W-1 and granite G-1 (Fairbairn and others, 1951; Schlecht, 1951) are shown in table 3. The first four represent separate determinations on each sample but run at the same time. The excellent reproducibility for these is clearly fortuitous. The next two determinations on each sample were made a month later. Also shown are the results obtained by P. M. Hurley, Massachusetts Institute of Technology (personal communication), by gamma-ray spectrometry. Hurley states that the thorium content of W-1 was too low for a good gamma-ray determination. In the range below 1 ppm, a greater scatter in results was obtained. For example, the results of three determinations made on different dates on the San Marcos gabbro were 0.3, 0.4, and 0.2 ppm ThO_2 . Here variations in blank values exert a significant effect.

Table 1.--Effectiveness of lanthanum or yttrium fluorides as carriers for thorium fluoride (15 mg of each carrier used, calculated as oxide).

Carrier	Thorium added (micrograms ThO ₂)	Thorium found (micrograms ThO ₂)	Percent recovered
Yttrium	3.02	2.9	97
Yttrium	3.02	3.2	107
Yttrium	15.09	14.7	97
Yttrium	15.09	15.7	104
Yttrium	30.18	29.8	99
Yttrium	503	500	99
Lanthanum	30.18	30.5	101
Lanthanum	503	490	97

Table 2.--Recoveries of thorium added to gabbro.

ThO ₂ added		ThO ₂ found <u>1/</u>
(micrograms)	(ppm)	(ppm)
2	0.4	0.4
3	0.6	0.6
5	1.0	1.0
10	2.0	2.0
25	5.0	4.5
30	6.0	5.8
50	10.0	9.8

1/ Thorium content of the gabbro, 0.3 ppm ThO₂, was subtracted.

Table 3.--Reproducibility of results on standard diabase W-1 and granite G-1.

Diabase W-1	ThO ₂ (ppm)	Granite G-1
2.1 <u>1</u> /		52 <u>1</u> /
2.1 <u>1</u> /		52 <u>1</u> /
2.1 <u>1</u> /		52 <u>1</u> /
2.1 <u>1</u> /		52 <u>1</u> /
2.2 <u>2</u> /		51 <u>2</u> /
2.3 <u>2</u> /		51 <u>2</u> /
3.6 <u>3</u> /		61 <u>3</u> /

1/ Run simultaneously.

2/ Rerun one month later.

3/ By gamma-ray spectrometry. P. M. Hurley, Massachusetts Institute of Technology (personal communication).

Table 4.--Comparison of spectrophotometric and mass spectrometric results on two basalts.

Sample	Spectrophotometric		Mass spectrometric <u>1</u> / ThO ₂ (ppm)
	Weight of sample (g)	ThO ₂ (ppm)	
Basalt of the Hualalai volcanic series, Hawaii Island, T. H. (western branch of 1800 flow)	3.00	3.9	1.8
	0.80	4.2	
Snake River basalt (1.8 mi north of Shoshone, Idaho on U. S. Highway 93)	5.00	2.9	2.3
	1.00	3.2	

1/ Analyst, George Tilton, Geophysical Laboratory, Carnegie Institution of Washington (personal communication).

The results on two basalts obtained from George Tilton, Geophysical Laboratory, Carnegie Institution of Washington, and previously analyzed by Tilton by an isotope dilution mass spectrometric procedure are compared in table 4. The reason for the discrepancies between the two methods is not definitely known. Tilton states that only single determinations were made and that the basalt of the Hualalai volcanic series was not completely decomposed in his procedure, much of the spinel being unattacked and discarded.

Table 5 gives a comparison of thorium determinations by two methods on Laramide intrusive rocks from the Front Range, Colorado. In the first method, a 0.3-g sample is used and the mesityl oxide separation is omitted. The second set was analyzed by the procedure of this report on 5-g samples.

Table 5.--Thorium determinations on Laramide intrusive rocks from the Front Range, Colorado.

Sample no.	Description	ThO ₂ (ppm)	
		Without mesityl oxide extraction <u>1/</u>	With mesityl oxide extraction <u>2/</u>
P 118L	Alkalic rhyolite	100, 107	105
P 370L	Rhyolite	33, 36	33
P 581L	Alkalic rhyolite	213, 218	240
P 633L	Alkalic rhyolite	75, 84	74
P 914L	Syenodiorite	39, 37	27
P 640L	Granodiorite	17, 17	17

1/ Analyst, Marjorie Malloy, U. S. Geological Survey; method of Fletcher and others, 1957, and Grimaldi and others, 1957.

2/ Method described in this report.

This work is part of a program being conducted by the U. S. Geological Survey on behalf of the Division of Research of the U. S. Atomic Energy Commission.

REFERENCES

- Banks, C. V., and Byrd, C. H., 1953, Spectrophotometric determination of thorium in monazite sands: *Anal. Chemistry*, v. 25, p. 416-419.
- Banks, C. V., Klingman, D. W., and Byrd, C.H., 1953, Spectrophotometric determination of thorium in black sands: *Anal. Chemistry*, v. 25, p. 992-993.
- Fairbairn, H. W., and others, 1951, A cooperative investigation of precision and accuracy in chemical, spectrochemical and modal analysis of silicate rocks: *U. S. Geol. Survey Bull.* 980, 71 p.; see p. 54.
- Fletcher, Mary H., Grimaldi, F. S., and Jenkins, Lillie B., 1957, Thoron-meso-tartaric acid system for determination of thorium: *Anal. Chemistry*, v. 29, p. 963-967.
- Grimaldi, F. S., Jenkins, Lillie B., and Fletcher, Mary H., 1957, Selective precipitation of thorium iodate from a tartaric acid-hydrogen peroxide medium: *Anal. Chemistry*, v. 29, p. 848-851.
- Levine, Harry, and Grimaldi, F. S., 1950, Application of mesityl oxide to the determination of thorium: *AECD-3186*, 16 p., issued by the U. S. Atomic Energy Comm. Tech. Inf. Service Extension, Oak Ridge, Tenn.
- _____, 1954, Part 21. Mesityl oxide extraction method for thorium analysis, in Grimaldi, F. S., *Collected papers on methods of analysis for uranium and thorium*: *U. S. Geol. Survey Bull.* 1006, 184 p.; see p. 177-184.
- Maréchal-Cornil, J., and Picciotto, E., 1953, Séparation des radioéléments naturels par l'oxyde de mésityle: *Soc. Chim. Belge Bull.*, tome 62, p. 372-382.
- Schlecht, William G., 1951, Cooperative investigation of precision and accuracy in chemical analysis of silicate rocks: *Anal. Chemistry* v. 23, p. 1568-1571.