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by Gamma Spectrometry
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Abstract

A brief investigation has been made of the feasibility of measuring thorium in rock samples by use of scintillation spectrometry facilities available in the ORNL Analytical Chemistry Division. Results of measurement of eleven samples have indicated that the method is usable and that agreement with chemical analysis is reasonable.

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DETERMINATION OF THORIUM IN ROCK SAMPLES BY GAMMA SPECTROMETRY

I. PURPOSE

It was desired to collect data on analysis for low concentrations of thorium in rocks, particularly granite, by chemical and "radiometric" techniques.

II. EXPERIMENTAL

Thorium was measured by counting the 2.6-Mev gamma radiation of its daughter, Tl-208.^(1,2,3) In radioactive equilibrium, as in rocks, a 2.6-Mev photon is emitted following about 35% of the disintegrations of Th-232.⁽⁴⁾ No significant interference was anticipated because of the absence of gamma radiation of such high energy in other natural materials, e.g., uranium^(5,6) and potassium.⁽⁴⁾

The instruments employed consisted of two conventional 20-channel analyzers receiving pulses from (a) a 3 x 3-in. NaI(Tl) crystal, and (b) a 4 x 4-in. crystal, each surrounded by a massive lead shield. Most of the work was done on (a). Samples of finely ground rock were placed in 250-ml Erlenmeyer flasks, which have flat bottom surfaces about three inches in diameter. The flasks were placed directly on the detector.

No rock samples of known thorium content were available for use as standards at the beginning of the program. Weighed portions of thorium oxide, which was over 40 years old (i.e., essentially in radioactive equilibrium) had been dissolved ~ 1.5 yr. before. These were diluted in Erlenmeyer flasks to the volume of the granite samples. Portions of thorium standard No. 83, 102 ± 2 ppm,⁽⁷⁾ were later received from New Brunswick Laboratory. Weighed portions of this standard material were placed in

Erlenmeyer flasks and the 2.6-Mev activities were compared in equal weights of standard and sample.

It proved impossible to make measurements during the day because of the use of the spectrometers for other purposes and because of high and variable backgrounds. Overnight counts (~ 15 hours) were taken.

III. DATA

A. Standards

When used for calibration, the solutions mentioned above gave 8.94 ± 0.14^a counts per hour in the 2.6 Mev gamma peak per part per million thorium, over a period of almost two months. However, the New Brunswick Laboratory standard gave 11.0 ± 0.1 cph/ppm; the discrepancy was ~ 20%. In attempting to account for this discrepancy, various analyses were done. Spectrographic and chemical analysis by C. A. Pritchard and P. F. Thomason showed no significant impurities in the original ThO_2 . Alpha spectrometry of a small amount of the oxide, reported by J. H. Cooper and C. L. Burros, indicated that the activities of Th-232 and Th-228 were essentially equal, proving that the material was indeed practically in radioactive equilibrium. The possibility that the scattering and absorption properties of water and rock might be different enough to account for some of the discrepancy was investigated by suspending a small source of thorium above samples of dunite (rock) and water and comparing the transmission of the 2.6 Mev gamma against air. Only small and predictable differences were detected. One plausible explanation of the discrepancy is that Ra-228 (and Ra-224) may have been lost in part from the solutions, permitting decay of Th-228 and its daughters, including Tl-208.

^a95% C.L. throughout.

Calibrations involving the solutions were disregarded; all analyses (Section C) were based on the NBL standard.

B. Background

Several overnight measurements were made of background in the 2.6 Mev region; see Table I. Flasks containing 100 g of dunite or an equal volume of water were placed on the detector. Dunite is the rock used by New Brunswick Laboratory to dilute monazite to prepare Th standards. Its Th content was not known by NBL.⁽⁸⁾ Therefore, the upper limit was determined by comparing its 2.6-Mev "background" with that of water. Values were 0.2 ± 1.0 and 0.0 ± 1.6 ppm (two spectrometers). Therefore, it is reasonable to assume that its Th content is < 1.2 ppm. In Table I, note that background was significantly high on two occasions compared to five others. The reason, whether electrical noise or actual radiation, is not known. The average value was assumed in all calculations. The background of the spectrometer in the ORNL Low Level Radiochemical Laboratory (C. L. Burros, Supervisor) is about one-third as high as that above, and should be less erratic.

Table I
Backgrounds

<u>Date</u>	<u>cph</u>
Feb. 4-5	273
Feb. 7-8	257
Feb. 19-21	292 ^a
Mar. 15-16	260
Mar. 22-23	323 ^a
Mar. 24-25	253
Mar. 30-31	263
Average	261

^aRejected.

C. Analyses of Samples

Eleven samples were furnished by J. C. White and were analyzed as described above. Results are shown in Table II. The average difference between chemical and "radiometric" analysis was 5.4%, and, if the results on Sample GD-6 are eliminated, the difference becomes 3.3%.

Table II
Thorium Analyses

Sample	Thorium, ppm		
	Gamma	Chemical ^a	Other ^b
G-1 ^c	51	51	51-52
GA-1	115	112	95
GA-2	77	76	70
GA-3	80	76	77
GB-1	9	9-10	
GB-2	20	20	
GB-3	30	30	
GB-4	12	10	
GC-1	93	91	
GD-6	24,25	18	21
GD-7	12(20 ^d)	12	12

^aData from J. C. White, May 6, 1960 (not necessarily final results).

^bUSGS, Rice Institute, or other.

^c"Standard rock."

^d"Flier" (high background?), discarded.

IV. CONCLUSIONS

The feasibility of determining thorium in rock samples by direct gamma spectrometry has been confirmed. Employing the NBL standard, results are in good agreement with chemical analyses. Background of the spectrometers employed in this preliminary study are sufficiently erratic to indicate

that future analyses should be done elsewhere, preferably in the Low Level Radiochemical Laboratory. A recommended procedure, Section V, was supplied to C. L. Burros on March 31, 1960. In the absence of unpredictable difficulties, e.g., malfunction of spectrometer, or background change, the accuracy of the method (95% C. L.) appears to be about $\pm 3\%$ or ± 1 ppm, whichever is greater. This is deduced from the 2% uncertainty in the Th content of the standard,⁽⁷⁾ assumed to be the "limit of error," combined with the random error in counting, which is equivalent to ~ 1 ppm at low concentrations, and $\sim 2\%$ at high levels. The limit of detection is ~ 1 ppm, and the limit of analysis ~ 2 ppm.

V. PROCEDURE^a

1. Place in a suitable container^b a weighed sample (preferably at least 100 g) of the powdered rock.
2. Place in an identical container the same weight of NBL standard #83 (102 ppm Th).
3. Place in another identical container the same weight of dunite (serves for background).
4. Count each of the three overnight,^c using a multichannel analyzer with amplifier gain set for 0-4 Mev.
5. For sample, standard, and background, sum the counting rates^d in seven or nine channels centered on the 2.6-Mev peak.

Calculation: Let A = gross counting rate of sample in 7 or 9 channels,

B = background rate (dunite),

C = gross counting rate of standard.

Then Th conc., ppm = $102(A-B)/(C-B)$

^aAdapted for Low Level Radiochemical Laboratory.

^bCylindrical container, preferably plastic, 3-4 in. dia.

^cA set of background and standard counts can probably be used for at least a week.

^dExpression in counts per hour, cph, recommended. For 100 g samples 1 ppm Th = ~ 11 cph.

VI. FUTURE WORK

No further study of the method is planned. Future samples, if any, will be analyzed in the Low Level Radiochemical Laboratory.

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