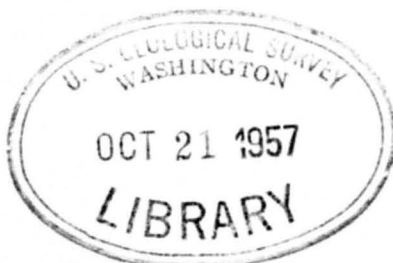A GAMMA-RAY ABSORPTION METHOD FOR THE

DETERMINATION OF URANIUM IN ORES*

Alfred F. Hoyte

UNITED STATES GEOLOGICAL SURVEY

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This report is preliminary and has not
been edited or reviewed for conformity
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A GAMMA-RAY ABSORPTION METHOD FOR THE

DETERMINATION OF URANIUM IN ORES

Alfred F. Hoyte

U. S. Geological Survey

ABSTRACT

Current radioactivity methods used for the determination of uranium in ores are based on the assumption that secular equilibrium exists between the daughter products. Eichholz has developed a method which is claimed to be independent of the degree of equilibrium, but it has been found to be inadequate when used with some types of disequilibriated ores.

An absorption method has been developed for the determination of uranium which is independent of the secular equilibrium of the series. With some refinement this method may be used to determine the state of equilibrium of an ore.

ACKNOWLEDGMENT

INTRODUCTION

The conventional method of determining the uranium content of rocks by radioactivity measurements yields a value of equivalent uranium, that is, the amount of uranium corresponding to the radio-activity if perfect equilibrium conditions existed. Because many ores and minerals are out of equilibrium, this method is not satis-factory if one wishes to determine the actual amount of uranium present. An attempt has therefore been made to devise a new non-destructive radioactivity method for uranium analysis that would be virtually independent of the state of equilibrium of the sample.

Eichholz and coworkers (1953) have described a method that they claim is capable of making uranium analyses irrespective of the equilibrium condition of the uranium and its daughter products in the sample. They have shown that this method works satisfactorily for most Canadian ores. However, recently it has been shown to give erroneous results when applied to certain disequilibriated ores from other localities. In the above method several assumptions are made, namely, (1) most of the measurable gamma radiation comes from the daughter products from radium to lead and a negligible amount originates with the emitters from uranium to radium, (2) disequilibrium is caused primarily by loss of radon, and (3) the $U^{238}/Pa^{234} + Th^{234}$ ratio has not been disturbed.

The first assumption is only partly true. Above 0.1 Mev only a small fraction of the total gamma radiation of the uranium series is emitted by the daughter products from uranium to radium. As Eichholz points out this radiation can be partly attenuated by an absorber and the total counting rate from this source reduced to only a few percent. However, as is readily seen in figure 1, there are a number of peaks below 0.1 Mev which are emitted by the daughter products from uranium to radium. If the detector is sufficiently sensitive to measure any of these, the first assumption of the Eichholz method would not be valid. Eichholz used an absorber that combined 1/16-inch brass and 1/8-inch aluminum. Using a brass and aluminum absorber, each 1/8-inch thick, we find that about 15 percent of the radiation of 0.1 Mev is detected. This is a significant fraction of the total gamma emission, and this source of radiation may well be a source of error in the method if a very sensitive detector is used.

Assumption two seems reasonable and was shown to be correct for most of the samples from Canada analyzed by Eichholz and others. However, it is conceivable that thorium, uranium, or both have been added or removed from some ores during their past geologic history. If thorium and uranium in the uranium series were in equilibrium in all samples, one would expect to get the same specific activity for the short-lived Th^{234} (24.1d) and the long-lived Th^{230} (8×10^4 y) from sample to sample. To check this point several samples both in and out of equilibrium were analyzed on the gamma-ray spectrometer.
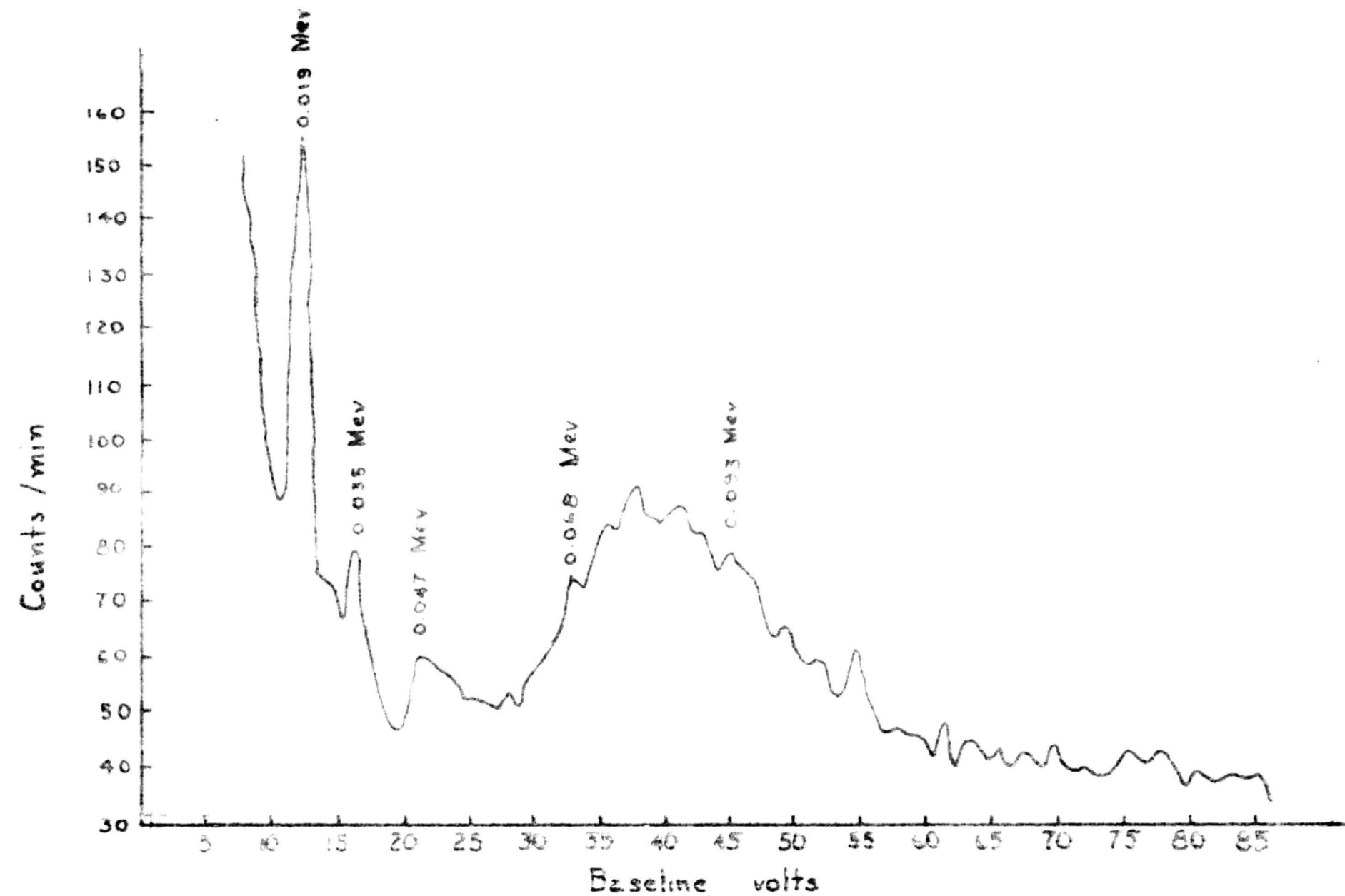
Fig. 1 -- Low - energy gamma spectrum of uranium.

The specific activity of the unresolved peak of 0.068 Mev of Th^{230} and 0.093 Mev of Th^{234} was measured for each sample (see Fig. 1). Where radon loss was the cause of disequilibrium the specific activity of this combination peak was essentially the same for the sample out of equilibrium as that obtained on samples known to be in equilibrium. The specific activities of a number of samples from the western United States (Wyoming) had specific activities which were several times higher than those of the equilibrium samples. Radiochemical analyses of these samples showed that the Th^{230} content was much higher than the equilibrium amount for the uranium present. Because thorium is a relatively difficult element to put into solution compared to uranium, it is possible that uranium has been leached out of the samples leaving it enriched in Th^{230}. As there are a number of examples of this and similar types of disequilibrium, assumption two is not universally correct.

Assumption three can be considered essentially correct. The half-lives of Pa^{234} (1.2 m) and Th^{234} (24.1 d) are so short that secular equilibrium is ensured.

When the above assumptions are considered, it appears that the method developed by Eichholz and coworkers cannot be applied in all cases of radioactive disequilibrium. To circumvent the inadequacies in this method an attempt was made to develop other techniques that could be applied to all ore samples irrespective of the type of disequilibrium.

APPROACH TO THE PROBLEM

In considering a problem of this type where there are a large number of possible solutions, one must limit the possibilities to those that are practical. For a routine counting method an alpha-counting procedure has been considered an inadequate solution to the problem. For this reason only beta and gamma methods were tried, and the gamma method was most successful.

As U^{238} is an alpha emitter it cannot conveniently be measured directly. Thus, the method must be capable of measuring a daughter product that is known to be in equilibrium with uranium. The first two daughters of U^{238} are Th^{234} ($T_{1/2} = 24.1$ d) and Pa^{234} ($T_{1/2} = 1.2$ m). Because both have relatively short half-lives, secular equilibrium is essentially assured. The third daughter U^{234} has a half-life ($T_{1/2} = 2.5 \times 10^5$ y) that is too long to assure equilibrium amounts at all times. Hence any radioactivity method of measuring uranium must involve the measurement of one or both Th^{234} and Pa^{234}.

Th^{234}, which is always in equilibrium with U^{238}, emits a γ-ray of energy 93 kev. If then, it is possible to compare the 93 kev counting rate of a fixed mass of an unknown sample of ore with the 93 kev counting rate of the same mass of a standard sample (preferably one in equilibrium) the uranium content, in percent uranium of the unknown sample, can thus be determined.

The difficulty here encountered is that it is impossible with the NaI(Tl) crystals currently available to resolve the 93 kev (Th^{234}) and the 68 kev (Th^{239}) peaks. In addition there is the Compton peak produced in the crystal by the Ra^{226} γ of energy 188 kev. This Compton peak is a γ of energy about 80 kev and thus makes the possibility of resolution even more remote.

It would seem, then, that the solution lies in setting the pulse height selector so as to detect only three peaks. Absorption of these γ-rays in various metals could then be used to formulate a method for determining the uranium content.

DESCRIPTION OF APPARATUS

The scintillation detector consists of a NaI(Tl) crystal optically coupled to a ten dynode RCA 5819 photomultiplier tube operated at 1200 volts.

The negative pulses emitted by the photomultiplier (the amplitude of these pulses being proportional to the energy of the incident gamma-ray) are fed into a linear nonoverload amplifier, and these pulses are amplified so that they fall within the range of the pulse-height analyzer (see Fig. 2).

The pulse-height analyzer is an instrument that measures the number of pulses of magnitude V per unit time, as a function of V, that is, the instrument plots N(V) versus V (Birks, 1953). Figure 3 is a plot of the unresolved peak which was used. The pulse-height analyzer used was
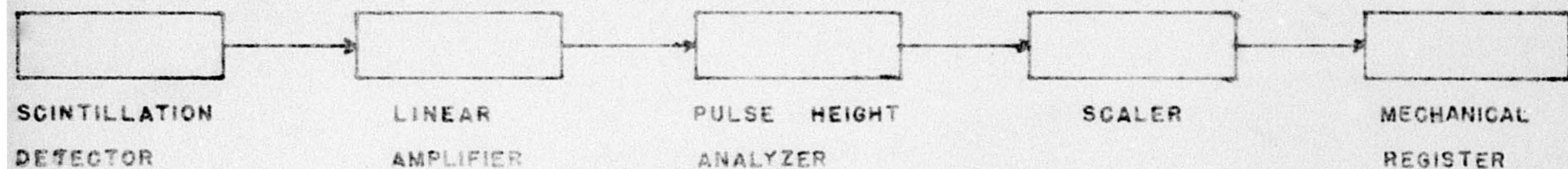
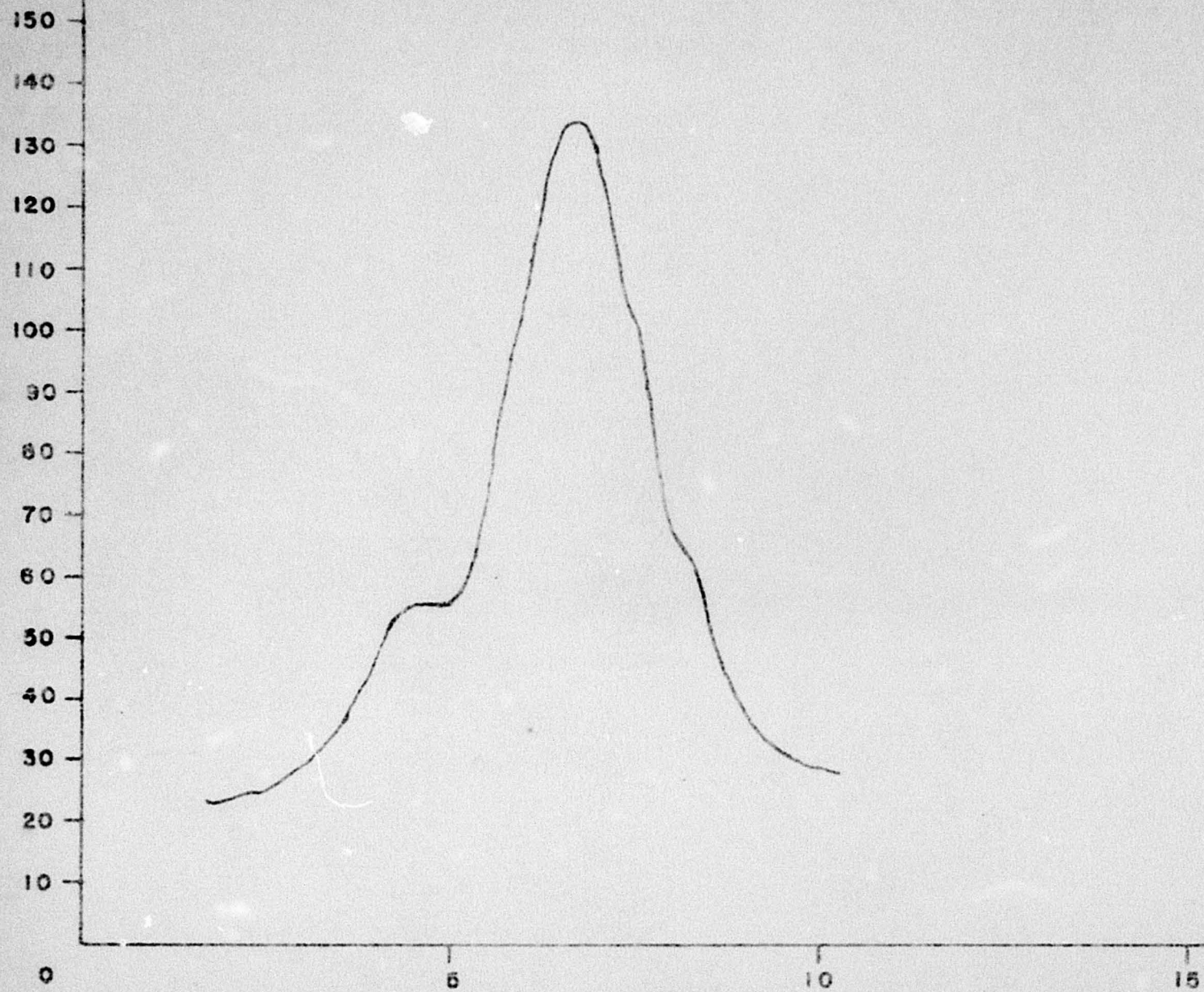| SCINTILLATION DETECTOR | → | LINEAR AMPLIFIER | → | PULSE HEIGHT ANALYZER | → | SCALER | → | MECHANICAL REGISTER |

FIGURE 2. BLOCK DIAGRAM OF APPARATUS

FIGURE 3. THE UNRESOLVED PEAK

a single channel one. To calibrate this instrument the 1.17 Mev and 1.33 Mev peaks from Co^{60}, the 0.67 Mev peak from Ce^{137}, and the 0.08 Mev peak from Th^{228} were used. Once a day the apparatus was checked for drift by plotting the distribution of some known peak.

The sample of ore to be assayed is crushed into powdered form, thoroughly mixed, then put into a cardboard pillbox two inches in diameter which has been previously weighed. The weight of the sample is obtained correct to 0.1 milligram.

THE METHOD

It is assumed that the counting rate (counts per minute per gram) of a sample at a given setting of the pulse-height analyser is directly proportional to:

the percent uranium,

the percent equivalent thorium,

the percent equivalent radium,

in a sample of ore, where the equivalent of any daughter product is the amount of uranium that would be required in the sample to support it (Rosholt, 1957).

To check this assumption, a sample which is in radioactive equilibrium and two other samples which are out of equilibrium to a given and known extent were used to determine

(a) the uranium counting rate

(b) the thorium counting rate

(c) the radium counting rate

in each of these samples. Using the information on any one of these three standards the theoretical counting rates of several other samples were computed from the known radiochemical data. If the above theory is correct, these results should be in good agreement with the measured counting rates.

To determine the theoretical counting rates let N_U, N_{Th}, N_{Ra} represent the uranium, thorium, and radium counting rates, respectively, of the standard (in equilibrium) sample with no absorber. Then,

$$N_U + N_{Th} + N_{Ra} = N_t, \tag{1}$$

where N_t is the total counting rate of the standard (counts/minute/gram).

The uranium counting rate of a given sample which is out of equilibrium would thus be given by the relation

$$\frac{\% \text{ uranium of sample}}{\% \text{ uranium of standard}} \quad N_U = aN_U.$$

Similarly its thorium counting rate would be

$$\frac{\% \text{ equivalent thorium of sample}}{\% \text{ equivalent thorium of standard}} \quad N_{Th} = bN_{Th}$$

and the radium counting rate

$$\frac{\% \text{ equivalent radium of sample}}{\% \text{ equivalent radium of standard}} \quad N_{Ra} = cN_{Ra}.$$

The total counting rate of a sample which is out of equilibrium would then be

$$aN_U + bN_{Th} + cN_{Ra} = N_t', \tag{2}$$

where N_t' is in counts/minute/gram of the sample.

Similarly the counting rate of a second sample which is out of equilibrium may be written

$$xN_U + yN_{Th} + zN_{Ra} = N_t''. \tag{3}$$

The standard sample (in equilibrium) is known to contain 6.84% U; 6.84% equivalent thorium; 6.84% equivalent radium. By the procedure described above the counting rate was computed as follows:

Uranium   15.7 counts/min/gram

Thorium   8.1 counts/min/gram

Radium   16.4 counts/min/gram

Total   40.2 counts/min/gram

Using these values the counting rates for the samples which are out of equilibrium were also computed. Table 1 is a comparison of the experimental and theoretical counting rates. From equations (1), (2), and (3) one can then obtain the values of N_U, N_{Th}, and N_{Ra}.

One can now use this information along with the radiochemical analyses on other known disequilibrium samples to calculate their theoretical counting rates, and check them by experiment.

Table 1 gives the results of a test on 8 samples.

By use of the radiochemical information already known on other samples one can calculate the total counting rates.

Table 1.--Specific counting rates.

Sample no.	Sample description	Total no. of counts/min/gram Calculated	Experimental
229176	U_D(3.02% U; 15% Th; 14.7% Ra)	58.9	59.1
229184	U_{D_1} (.75% U; 8.76% Th; 6.07% Ra)	26.1	26.8
253133	U_{D_2} (.3% U; 9.12% Th; 6.62% Ra)	27.6	27.4
211894	U_{D_3} (.01% U; 5.85% Th; 5.17% Ra)	19.9	21.4
18734	U_{D_4} (2.01% U; 2.02% Th; 1.99% Ra)	11.7	11.5
229176	U_{D_5} (.61% U; .59% eq. Th; .24% eq. Ra)	2.3	2.13
248147	U_{D_6} (.13% U; .091% Th; 1.90% eq. Ra)	10.61	10.43
30063	U_{D_7} (17% U; 13.9% eq. Th; 13.2% eq. Ra)	87.13	85.92

ABSORPTION IN LEAD

Since the counting rates for uranium, thorium, and radium have been computed and checked in a large number of samples, it is possible to get a relationship to determine quantitatively the absorption of each of the three radiations in lead.

Here it should be noted that a number of other absorbers have been tried, and lead was chosen as most desirable because of its k-absorption edge at 88 kev which greatly attenuates the 93 kev peak of Th^{234}.

For a given thickness of absorber, let the ratio between transmitted (I) and incident (I_o) radiation be as follows:

For 93 kev $\frac{I}{I_o} = p$.

Here it is clear that

$$p = \frac{I}{I_o} = \frac{U \text{ counts/min/gram with absorber}}{U \text{ counts/min/gram without absorber}}.$$

Similarly for the 68 kev peak Th^{230}

put $\frac{I}{I_o} = q$

and for the 188 kev peak put

$$\frac{I}{I_o} = r.$$

Thus for the standard sample it may be shown that

$$pN_U + qN_{Th} + rN_{Ra} = N_D \tag{4}$$

where N_D is the number of counts/minute/gram with absorber.

Similarly for the first sample which is out of equilibrium the equation is

$$paN_U + qbN_{Th} + ncN_{Ra} = N_D' \text{ (counts/min/gram)} \qquad (5)$$

and for the second

$$pxN_U + qyN_{Th} + rzN_{Ra} = N_D''. \qquad (6)$$

From equations (4), (5), and (6) it is possible to determine the values of the coefficients p, q, and r.

From the nature of the equations it is obvious that p, q, and r are really the transmission coefficients for the radiations from the three nuclides-uranium, thorium, and radium, respectively.

In order to derive three equations in three unknowns (U, Th, and Ra), one needs but to measure the transmission coefficients for two thicknesses of absorber. It is useful to note that, with some refinement, this method may be used to determine the amount of U, Th, and Ra in the sample.

The system of equations thus obtained should be as follows:

$$N_U + N_{Th} + N_{Ra} = C'$$
$$\alpha N_U + \beta N_{Th} + \gamma N_{Ra} = C''$$
$$\xi N_U + \eta N_{Th} + \lambda N_{Ra} = C'''.$$

Units are in counts/min/gram; α, β, γ, ξ, η, λ are the measured transmission coefficients.

It is then possible to determine the number of counts/min/gram due to each component of the radiation. A calculation of the ratios

of the counts in the sample to those of the standard will give a determination of the percent U, percent equivalent Th, and percent equivalent Ra in the sample; the equations being as follows:

$$\text{percent U sample} = \frac{\text{Uranium counts/min/gram of sample}}{\text{Uranium counts/min/gram of standard}} \times \text{percent U of standard}$$

CONCLUSION

As shown in table 2, the method gives good results with samples of reasonable uranium content.

However, for samples of low uranium content, that is, for percent U less than 0.30, the method gives unreliable results. The reason for this, in our opinion, is the lack of stability in the equipment. In trying to recheck some of the counts the magnitude of the error in the total number of counts/min/gram was much greater than the number of counts that would be produced by the uranium in the sample. It is obvious then that the uranium counts could easily be lost.

One improvement would seem to suggest itself here. Since there is a large error in the channel width of the pulse-height selector, the method should be improved by omitting this part of the equipment using only a lower discriminator. A thin crystal should be used in order to eliminate the higher energy gamma-rays.

Table 2.--Some typical determinations.

Sample no.	eU	eTh^{230}	eRa	Chem U (%)	% U (This Method)
30063	0.220	-	-	0.280	0.283
253133	3.500	9.12	6.62	0.300	0.296
18734	.200	-	-	0.32	0.369
30016	.53	-	-	0.55	0.590
20031	.43	-	-	0.68	0.614
229184	3.9	8.76	6.07	0.75	0.713
229176	9.2	15.0	14.7	3.02	2.96
248147	13.1	13.9	13.2	17.00	17.40

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