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SCINTILLATION SPECTROMETER II: SIMULTANEOUS MEASUREMENT OF URANIUM, THORIUM AND POTASSIUM IN COMMON ROCKS*

By

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By Patrick M. Hurley

ABSTRACT

A method is described for the simultaneous radioassay of the uranium and thorium series and potassium in common rocks, or materials of comparable activity, in which the series are in secular equilibrium. The method is based on the measurement of the counting rate in three bands of the photon energy spectrum derived from the gamma-ray excitation of a scintillation crystal. Two of these bands correspond to the 238 kev gamma of Pb^{212} and the 1.46 Mev gamma of K^{40}, and the third band is centered in a region in which the count is derived largely from scattered gammas from all the radioactive constituents. Under normal conditions the time required for the analyst to make the three determinations is about 15 minutes, and by use of multiple sources the same length of time is sufficient for the count.

INTRODUCTION

In a previous report (Hurley, 1955) a method was given for the analysis of the uranium and thorium series in equilibrium in materials containing more than 0.01 percent equivalent uranium, by use of the gamma-ray scintillation spectrometer. The method consisted of determining a ratio of gamma-ray counts on a sample of known weight inside the well of a well-type scintillation crystal. Counts were taken in a two-channel scintillation spectrometer from two bands in the gamma-ray spectrum, one of which selected the 238 kev gamma ray of Pb^{212}, and the other recorded dominantly Compton-scattered photons from both series.

This present report covers an investigation of possible methods of direct radiometric assay of uranium and thorium in common rocks. As the radiation from K^{40} is important at this level of activity, it must be assayed separately and taken into account. This requires either a three-channel instrument or else a two-channel instrument with a separate measurement needed for the potassium.

The method requires that the scintillation crystal be surrounded by the powdered sample in order to obtain sufficient counts for analysis, but, at the same time, the thickness of the layer of the sample must not be so great that the photopeaks are swamped by Compton-scattered radiation from within the source. A sample weight of approximately 200 grams with a layer surrounding the scintillation crystal of about half an inch was found to be satisfactory. The method is capable of analyzing, to a few parts per million, rocks or other solid materials in powdered form, or liquids containing the radioactive series in equilibrium. Similarly potassium can be analyzed to a fraction of a percent.

It is necessary for the uranium and thorium series to be in equilibrium in order that these parent elements can be determined. Actually the method measures the quantities of the elements in the series below radium 226 and radium 224. A consideration of this question is important in any interpretations derived from the method. The elements in the uranium series above radium do not have gamma rays of sufficient energy to give counts in the range that is measured, except for a possible slight contribution from protactinium 234. The radium 226 gamma at 188 kev lies in the band accepted by the lowest energy channel.

The question of whether the radioactive series are in equilibrium in a sample, and therefore whether the sample should be analyzed by this method, is a difficult one; but it may be possible in most cases to judge fairly well if geological information on the sample is available. The area of usefulness of the method may be largely restricted to fresh samples of common rocks or minerals in which the uranium and thorium are fairly uniformly distributed and preferably syngenetic. Epigenetic enrichments of uranium by hypogene or supergene processes may be sufficiently rapidly leached to be seriously out of equilibrium at times, although it is probable that these are generally less out of equilibrium than suspected.

The reason for this tendency to overestimate the lack of equilibrium may be due to the fact that equilibrium is continuously re-establishing itself at a rate that is usually fairly rapid compared to the lowering of the whole surface zone by chemical weathering and erosion. For example, if a surface zone consists of a leached zone above a zone of enrichment, both of these zones will have been in existence a long time compared to the half lives of Ra^{226} (1622 years), Ra^{228} (6.7 years), or Th^{230} (80,000 years) which control the rate at which equilibrium is maintained. Spotty concentrations of uranium in material containing limonite may give spurious counts due to excess thorium 230; and similarly, recent efflorescences or depositions of uranium may give low results due to lack of the equilibrium amount of thorium 230. Control assays for uranium by standard methods should be made to establish the validity of the assumption of equilibrium in any area being sampled.

The escape of radon from the sample after it is pulverized must also be considered. The principal contributions to the counts below radium are from Pb^{214} and Bi^{214}. A reduction in the amount of these will be controlled by the

27-minute half-life of Pb^{214} if radon is removed. The highest ratio of emanating radon to total radon that is expectable in a pulverized sample of common rock is about 25 percent, if the radium in the rock is 50 percent in surface films and half of its radon recoils inward rather than outward. Usually granitic rocks show only a small percent emanation, and volcanic, sedimentary, and metamorphic rocks none. In the worst case the radon loss may be a few percent and this can be taken care of by the use of a plastic sample holder with cover in which the rock sample is stored for a week or two before measurement and then run in the spectrometer without removing the cover.

METHOD OF ANALYSIS

Except for the correction for potassium the method of analysis for uranium and thorium is similar to that described in the above-mentioned report (Hurley, 1955). A 200-gram sample of rock or mineral powder is placed in the low-activity source holder and counts are made with the base level of the first two channels set at 168 and 226 kev, respectively. A channel width of 25 kev is commonly used in each of these. Figure 1 shows the uranium and thorium spectra up to 0.6 Mev from samples in a well-type crystal and is reproduced from the previous report. It can be seen that the first channel admits gammas from the region of the valley centered at 180 kev, and the second channel admits gammas from the region of the 238 kev peak of Pb^{212}.

A spectrum was plotted for a sample in the low activity sample holder surrounding the crystal to see if the peaks are reduced in height somewhat compared to those illustrated in figure 1. Figure 2 illustrates this spectrum from a synthetic mixture containing 200 grams of quartz and olivine, and 0.612 gram of thorium and 0.0245 gram of uranium. The ratio of channel 2 over channel

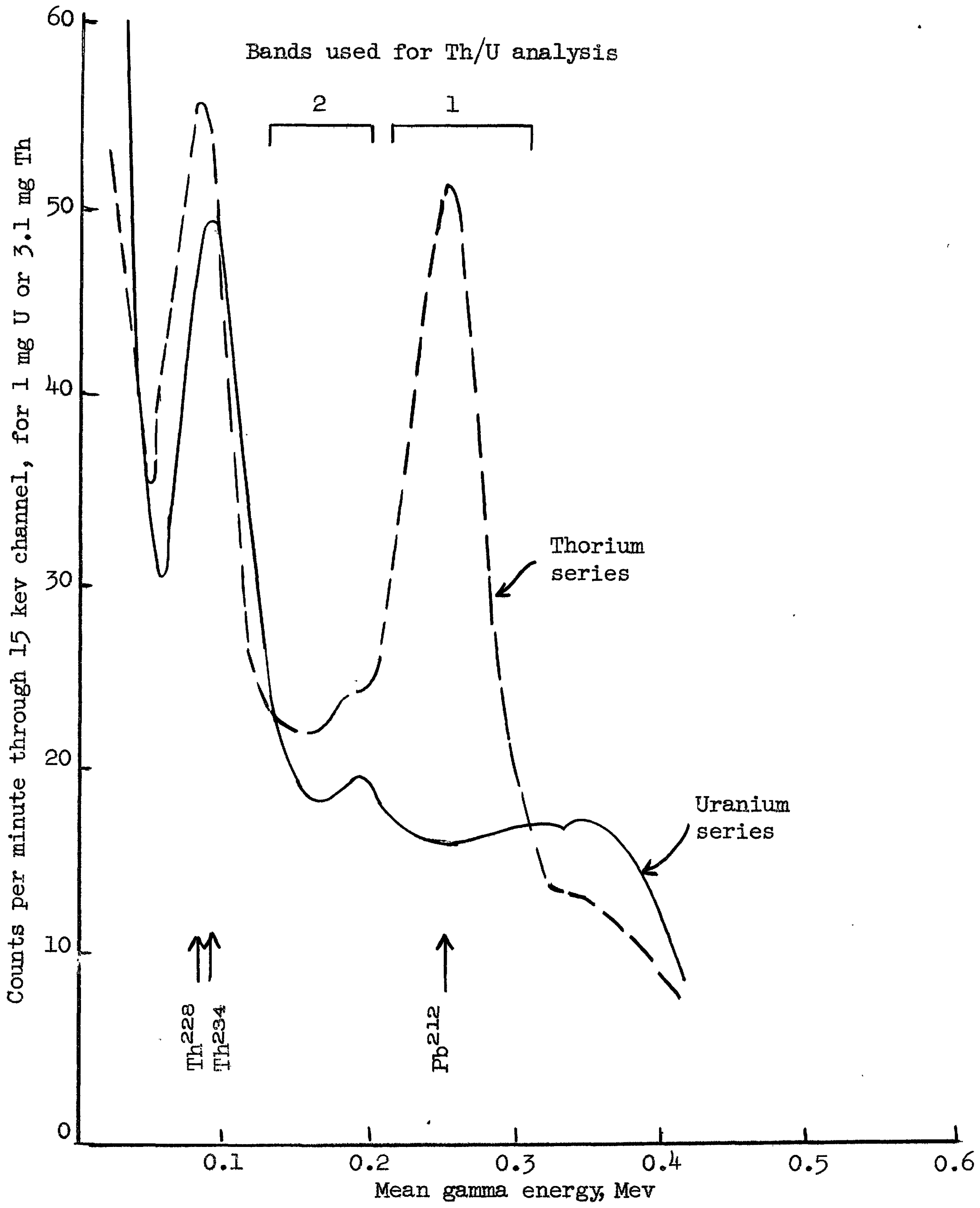

Figure 1.--Comparison of U and Th series spectra below 0.4 Mev showing bands used for Th/U analysis. (Plotted on basis of equal parent disintegrations in each source.)

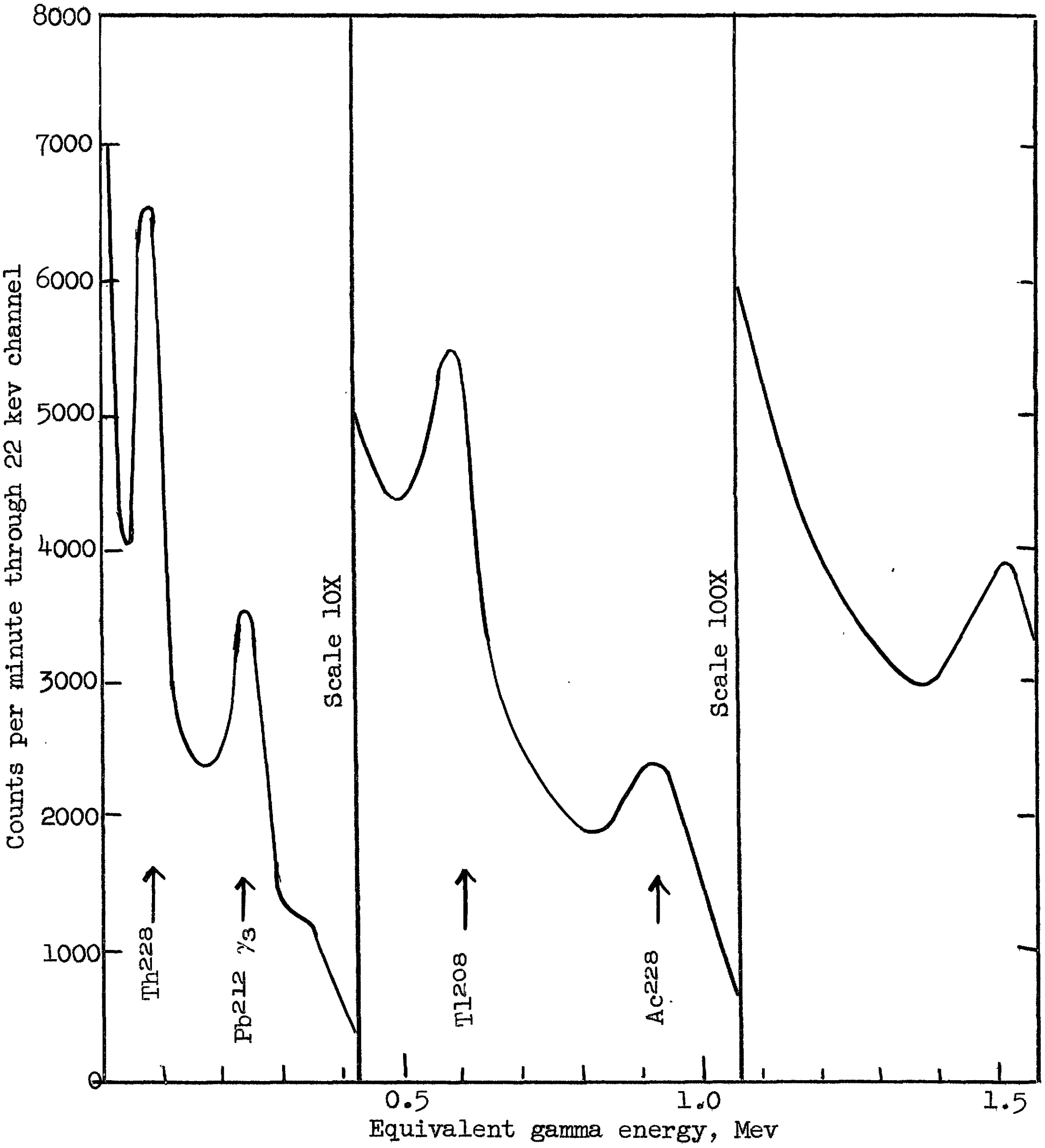

Figure 2.--Scintillation spectrum for 200-g sample containing 0.6124 g Th and 0.0245 g U.

1 is 1.370 in the case of a pure thorium standard and 0.718 for a pure uranium standard. The ratio of these two figures is 1.91, which is actually no less than in the case of a sample located in the center well for equal channel widths. The effect of the source absorption, therefore, does not decrease the sensitivity of the method at the thickness of sample used.

Tests were made on the effect of source absorption using different types of rock that were enriched by known amounts of uraninite and monazite. No difference was observed between the most felsic and most mafic rocks tested, which permits the indiscriminate analysis of quartz- and silicate-bearing rocks without the necessity of a source absorption correction, so long as the weight is kept constant and the sample occupies approximately the same volume. It has been found that leaving the heavier rocks in open packing and shaking the sample holder so that light rocks are closer packed permits the maintenance of a fairly constant volume despite the slight differences in densities of the materials.

The third channel is centered on the photopeak of K^{40} and pulses are admitted through a channel width equivalent to 134 kev. These three channels provide three equations for the three unknowns which can be solved simply for the three constituents.

The discrimination of thorium from uranium is provided by the ratio of counts from channel 2 over channel 1. As mentioned above this ratio for pure thorium series is 1.91 times greater than for pure uranium series. The discrimination of potassium from uranium and thorium is given by the ratio of channel 3 over channel 1. For a sample containing only potassium this ratio is 13.4 times greater than for a sample containing only uranium series, and 16.5 times greater than a sample containing only thorium series. This is due to the fact that the potassium scintillation spectrum is very different in shape from that of the uranium or thorium series. The spectrum is sharply terminated above 1.46 Mev which is the energy of the K^{40} gamma and, as shown in figure 3, the scattered gammas of lower energy increase in abundance very little in the range down to 0.5 Mev.

About the same conditions, as mentioned in the previous report, hold for the drift of the instrument. An improvement in the method of correcting for drift is suggested at this time and will apply also to the analytical techniques of the previous report. The largest drift effect is that of base level voltage setting in channel 2, which is centered on the top of a fairly narrow peak. In practice two of the channels are used briefly to count this peak on the standard and are set so that one channel is 10 kev below the peak and the other channel is 10 kev above the peak. Any drift will cause one of the channels to rise in count and the other to fall. This gives the direction of drift, and the ratio of the counts is diagnostic in giving the extent of the drift. By using a carefully plotted standard curve of the peak shape, it is simple to make the necessary correction for the drift in the unknown. For precise work this procedure is used on the unknown also. A short run with two channels on the peak is sufficient to make the correction. For routine work in which a lower precision is acceptable, it is sufficient to make a short run on a standard with the normal channel settings between analyses.

Standards were made by adding a known amount of uraninite or monazite to 200 grams of an intermediate igneous rock. In using the thorium standard a correction is made for the amount of uranium in the monazite. Both the uraninite and the monazite must be carefully analyzed for both uranium and

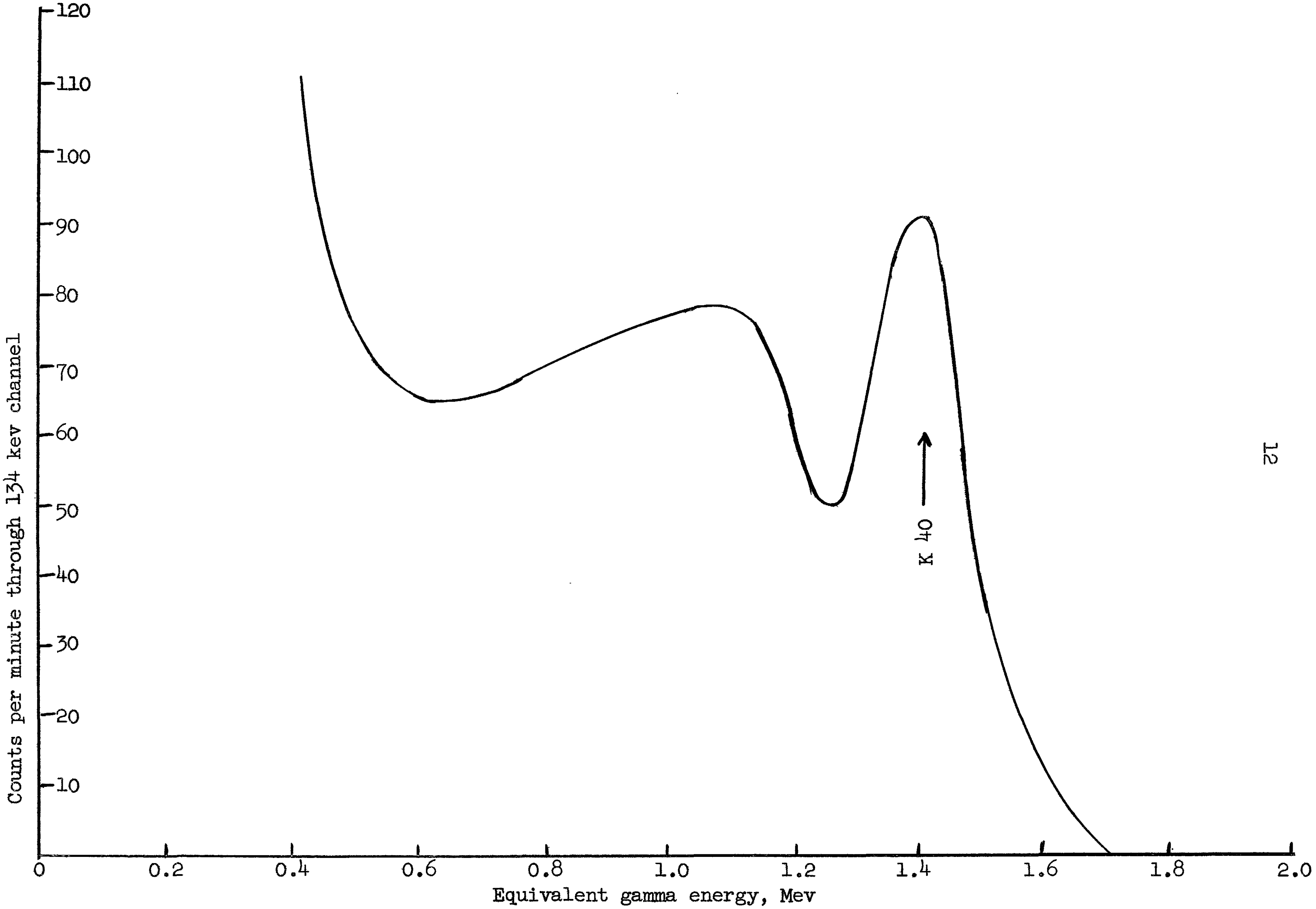

Figure 3.--Gamma scintillation spectrum for 150-g sample of K_2CO_3.

thorium. Potassium carbonate is usually used for an additive to make up potassium standards. The uraninite and monazite used for all standards were supplied by the New Brunswick Laboratory of the Atomic Energy Commission through the kindness of C. J. Rodden, Director. All analyses are therefore based on these A.E.C. chemical analyses for uranium and thorium.

CALCULATION OF RESULTS

Channels 1, 2 and 3 are those with base-level settings at 0.168, 0.226 and 1.39 Mev, respectively. All references to counting rate mean net counting rate, after background has been removed and corrected for drift. Unless otherwise specified, the counting rate also refers to that obtained from a 200-gram sample in the standard sample holder.

U = uranium content of uranium standard, ppm.

U_1, U_2, U_3 = counting rate from uranium standard in channels 1, 2 and 3, counts per minute.

T = thorium content of thorium standard, ppm.

T_1, T_2, T_3 = counting rate from thorium standard in channels 1, 2 and 3, due to thorium only (uranium contribution subtracted).

K = potassium content of potassium standard, percent.

K_1, K_2, K_3 = counting rate from potassium standard in channels 1, 2 and 3.

R_1, R_2, R_3 = counting rate from unknown sample in channels 1, 2, and 3.

In the value found for R_1 if X, Y, Z are the counts per minute due to U, Th, and K, respectively, the solution of the following equations will give the required results.

$$\begin{aligned} X + Y + Z &= R_1 \\ (U_2/U_1)X + (T_2/T_1)Y + (K_2/K_1)Z &= R_2 \\ (U_3/U_1)X + (T_3/T_1)Y + (K_3/K_1)Z &= R_3 \end{aligned}$$

$$\text{Or } X = \begin{vmatrix} \dfrac{\begin{matrix} R_1 & 1 & 1 \\ R_2 & T_2/T_1 & K_2/K_1 \\ R_3 & T_3/T_1 & K_3/K_1 \end{matrix}}{\begin{matrix} 1 & 1 & 1 \\ U_2/U_1 & T_2/T_1 & K_2/K_1 \\ U_3/U_1 & T_3/T_1 & K_3/K_1 \end{matrix}} \end{vmatrix} = \frac{A_1R_1 + A_2R_2 + A_3R_3}{A_4}$$

$$\text{where } A_1 = \frac{T_2}{T_1} \cdot \frac{K_3}{K_1} - \frac{K_2}{K_1} \cdot \frac{T_3}{T_1}$$

$$A_2 = \frac{T_3}{T_1} - \frac{K_3}{K_1}$$

$$A_3 = \frac{K_2}{K_1} - \frac{T_2}{T_1}$$

$$A_4 = \frac{U_3}{U_1} A_3 + \frac{U_2}{U_1} A_2 + A_1$$

Similarly:

$$Y = \frac{B_1R_1 + B_2R_2 + B_3R_3}{A_4}$$

$$\text{where } B_1 = \frac{K_2}{K_1} \cdot \frac{U_3}{U_1} - \frac{U_2}{U_1} \cdot \frac{K_3}{K_1}$$

$$B_2 = \frac{K_3}{K_1} - \frac{U_3}{U_1}$$

$$B_3 = \frac{U_2}{U_1} - \frac{K_2}{K_1}$$

$$\text{Uranium} = X \cdot U/U_1 \text{ parts per million}$$

$$\text{Thorium} = Y \cdot T/T_1 \text{ parts per million}$$

$$\text{Potassium} = \frac{K}{K_3}\left\{R_3 - X \cdot \frac{U_3}{U_1} - Y \cdot \frac{T_3}{T_1}\right\} \text{ percent}$$

Because the calibration constants are determined on the basis of standard sample weight (e.g., 200 grams), the unknown must also be this weight.

In the spectrometer used in this investigation, the following values were found for the various constants:

$U_2/U_1 = 0.718$

$U_3/U_1 = 0.133$

$T_2/T_1 = 1.370$

$T_3/T_1 = 0.107$

$K_2/K_1 = 0.800$

$K_3/K_1 = 1.770$

$U/U_1 = 0.470$ ppm U per c/m

$T/T_1 = 1.265$ ppm Th per c/m

$K/K_3 = 0.451$ percent K per c/m

Average backgrounds are 14.1, 12.5, and 8.0 c/m for channels 1, 2, and 3, respectively.

From these values:

$A_1 = 2.34$ $A_2 = -1.66$ $A_3 = -0.57$ $A_4 = 1.069$

$B_1 = -1.164$ $B_2 = 1.637$ $B_3 = -0.082$

TEST RESULTS

In tables 1 and 2 are shown lists of test analyses on synthetic samples and on samples of rock that have been analyzed by different methods. The synthetic materials were made up from mixtures of quartz and dunite, or

Table 1.--Test measurements for uranium and thorium.

Sample	Uranium (ppm) By scintillation count	Uranium (ppm) By other methods	Thorium (ppm) By scintillation count	Thorium (ppm) By other methods
Synthetic mixture Quartz and dunite	134	122	3010	3062
Synthetic mixture Palisade diabase	203	204	0	< 1
Palisade diabase	0.7	0.6	1.6	2.1
NBS Milford granite	0.8	0.7	9.0	Unknown
NBS Deccan trap	0.7	0.6	2.8	Do.
Conway granite (54-S-137)	10.3	7.6	32	Do.
Conway granite (54-S-121)	9.1	10.7	46.4	Do.
Conway granite (54-S-128)	12.7	12.1	67	Do.
Conway granite (54-S-109)	13.8	17.8	61	Do.

Note. Values given by other methods may be in considerable error.

Table 2.--Potassium test analyses.

Sample	K_2O by other methods (percent)	K_2O measured (percent)
NBS Gabbro-diorite	1.56	1.56
NBS Deccan trap	0.78	0.75
NBS Chelmsford granite	5.5	5.0
NBS Columbia basalt	0.98	0.80
NBS Kimberlite	1.2	1.1
Conway granite		
54-S-137	4.6	4.5
54-S-121	4.7	4.6
54-S-128	4.3	4.7
54-S-109	4.2	4.5

diabase, to which were added known amounts of standard uraninite or monazite, provided by the Atomic Energy Commission's New Brunswick laboratory, similar to the standards used for calibration.

The National Bureau of Standards (NBS) samples are standard rock samples that were analyzed for radium by the Bureau and by other laboratories. Analyses for potassium were also provided but not for thorium. The Palisade diabase was analyzed for radium and thorium by the author, using radon and thoron alpha counting (Hurley and Goodman, 1941). The samples of Conway granite were supplied and analyzed for uranium and potassium by members of the U. S. Geological Survey. No thorium analyses were available on these. The results show agreement within the expectable error.

Thorium analyses of common rocks by other methods are sufficiently difficult to make so that reliably analyzed samples were not available for this test. However, there is no reason to expect that the accuracy of a thorium analysis by this method will be any less than the accuracy of a uranium analysis if the calibration standards are correct and if the thorium activity in the rock is similar to the uranium activity. Fortunately this last condition is generally true in common geological materials.

OPERATING PROCEDURE AND ERROR

Operating procedure is similar in principle to that described in the previous report. The gain controls and voltage on the photomultiplier tube are adjusted experimentally to give optimum response and to cover the range of the spectrum that is of interest within the maximum spread of the base-level discriminators. This is done to spread out the low-energy part of the spectrum as much as possible. Pulses are shaped with minimum rise time available. Zero points for each high-level discriminator are determined by a plot of count versus channel width in a flat part of a spectrum. The correlation of base level discriminator voltage with gamma energy is established by use of gamma sources of known energy, although this is not necessary if the uranium and thorium series spectra are plotted in terms of base-level voltage because the settings for the different channels are adjusted to lie on the tops of the peaks of K^{40} and Pb^{212} and the bottom of the valley immediately below Pb^{212}. For this work an adjustment of over-all gain so that 1 percent of the base-discriminator range is equivalent to about 25 kev gamma energy is found to be about right. A lower ratio could be used if potassium were not being measured.

Instrument drift is critical in attempts to stay close to the top of a peak, so it is necessary to run standards at frequent intervals. Rather than change all of the calibration constants slightly for each run, it is more convenient to find an average value for each constant and to use these as arbitrary constants for each channel. From there on all readings on samples are corrected according to the amount the standard source is above or below this arbitrary value at that time. This process removes the effect of long period drifting above or below the arbitrary value which may last for days. Short period drifting can only be offset by voltage regulation and repeated analyses.

Errors depend on the relative abundance of the uranium and thorium in the sample. The smaller the amount of thorium relative to uranium, the greater is the precision of the uranium analysis and the less the precision of the thorium analysis, and vice versa. Since precision is gained both by larger numbers of counts and by more frequent calibrations, it will depend principally on the length of the run. Normally the assay time will be set by the precision specifications.

The equivalent uranium, or uranium plus thorium equivalent in activity, can be obtained much more precisely than the separate values for uranium and thorium. A small error in the channel-1 or -2 counts will cause a relatively larger error in the ratio of thorium to uranium. As other methods of thorium analysis are so tedious, it would be worth while to combine this method of analysis with a separate uranium analysis on the sample in order to gain the great improvement in precision, if the thorium analysis is the principal objective.

In the previous report an estimate was made of the expectable error of analysis as a function of the proportion of uranium or thorium in the sample. These calculations and the results illustrated in figure 8 of that report will apply to uranium and thorium determinations in common rocks, except that an error in potassium determination will contribute an error in the channel-1 and channel-2 readings that is of the same sign so that the effect on the ratio will be slight. Also the signal-to-background ratio is much lower in these low-activity samples which increases the standard deviations of the net counts substantially. As the last factor can be partly compensated for by longer runs, a single measurement on a sample containing a few parts per million of uranium and thorium should have errors that are less than twice those given in figure 8 of the previous report but should have the same function of the Th/U ratio.

A normal granite will run 20 to 60 counts per minute above a background of 14 counts per minute in channels 1 and 2 and about 10 counts per minute above a background of 8 in channel 3. The standards are made to have high counting rates and a 10-minute run is sufficient. Thus the total time for the measurement of uranium, thorium and potassium in a granite sample would be about 2 hours with counting error less than drift error, for a single-crystal counter, and total time actually required of the analyst would be about 15 minutes. This time could be reduced proportionately to the number of crystals and sources used to feed the spectrometer.

SMALL SAMPLES OF INTERMEDIATE GRADE

Samples containing more than 100 ppm of uranium or thorium and their series in equilibrium may be assayed for these constituents in quantities of only 1 to 10 grams. The sample is carried in a glass bottle (1 1/2 cm outside diameter) that fits into a well-type scintillation crystal. The potassium contribution is negligible at this level of activity. In the previous report a method of analyzing ore-grade samples of uranium- and thorium-bearing materials was described, in which source absorption was eliminated by use of a small bore sample holder and a sample of about 200 mg. When 1 or more grams are assayed in the glass bottle, it is necessary to correct for source absorption.

The curves in figure 4 indicate for samples of different materials the variation in counting rate per gram as the sample size is increased. It can be seen that a set of such curves covering the range of materials to be analyzed will provide corrections for source absorption. For any weight of unknown used the increase in counting rate with no source absorption is obtained from the appropriate curve.

OTHER GEOLOGICAL APPLICATIONS

Instrument drift that causes a single channel to shift off a peak can be taken care of largely by covering a width greater than the peak by more than one channel. Instruments are now being made that have as many as 50 channels. The entire spectrum can be plotted in detail with such an instrument and

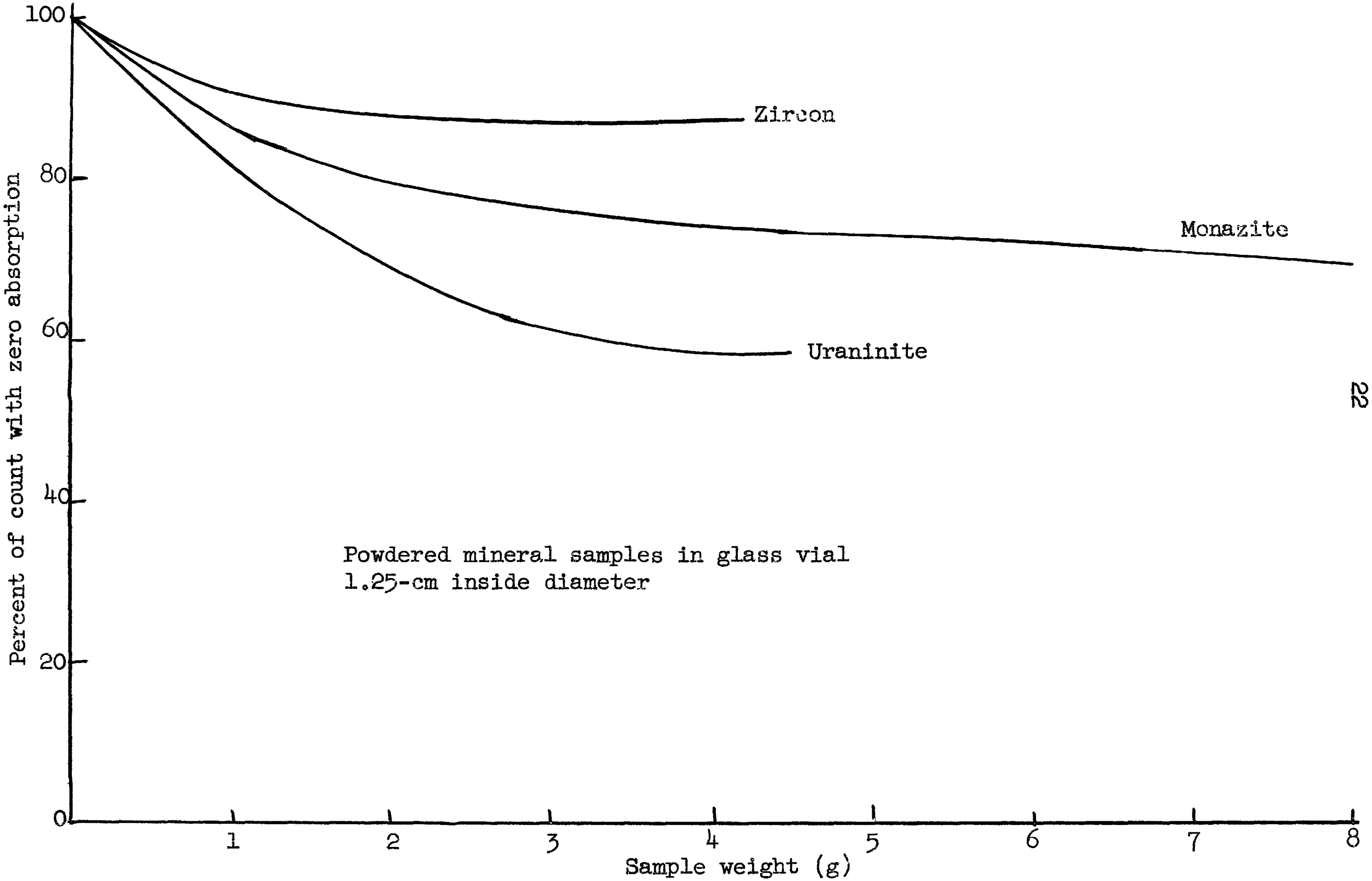

Figure 4.--Effect of source absorption in thick sources of heavy minerals in well-type crystal.

compared with a similarly plotted spectrum for the standard. Recording counting-rate meters will give a continuous plot of the activity in any channel, and the ratios of channels can also be recorded. Counting rates can be increased by larger crystals or several crystal sources feeding into the single spectrometer. Larger crystals will also increase the amplitude of the photopeaks relative to scattered background.

With these possibilities it is feasible to make devices that will contincusly record the grade of ore in a mill or serve as quality-control or monitoring devices for a variety of materials handled in continuous streams that contain any or all of these constituents. For example, the silica content of bauxite ores is frequently related to the potassium content through the presence of clay minerals. Uranium ores, monazite sands, potassium salts in brine are other more obvious examples. As a general geological tool the spectrometer can find uses in stratigraphic correlation or any mapping in which chemical variations involving these constituents form the basis of the lithologic units. An investigation is being planned on the measurement of Th^{230} in ocean core material utilizing its 68-kev peak that appears in the spectrum and eliminating the contribution from interfering photons of nearly the same energy by a separate determination of Th^{232}.

There is also a good possibility that the well cuttings from oil wells can be passed in a continuous stream over a number of crystal detectors and recorded as a "mud-log" based on the relative abundances of uranium, thorium and potassium. This would have obvious advantages over simple gamma-ray logs. Shales can be identified by potassium content, and the U/Th ratios are known to be distinctively related to distance off-shore under many sedimentational conditions. In all cases it is essential that the thickness of the stream of material or the individual sample is small enough so that photopeaks are not obliterated by Compton-scattered radiation. This can be done by using an annular source volume, surrounding the crystal, through which the material passes.

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