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DEPARTMENT OF
MINERALS AND ENERGY

BUREAU OF MINERAL RESOURCES, GEOLOGY AND GEOPHYSICS

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INTERPRETATION OF GAMMA-RAY SPECTRA OF URANIUM AND THORIUM

by

P.W.B. Bullock

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SUMMARY

Methods of interpreting gamma-ray spectra of naturally occurring uranium and thorium were tested using standard samples of uranium-thorium mixtures. The equipment used to obtain spectra was a 256-channel gamma-ray spectrometer with a sodium iodide detector.

Several methods of analysis of uranium and thorium using gamma-ray emission of daughters are described. Attempts to make analyses for uranium using gamma-ray emission of uranium-235 led to inconsistent results. Further work is required to find a satisfactory means of assaying for uranium when it is not in equilibrium.

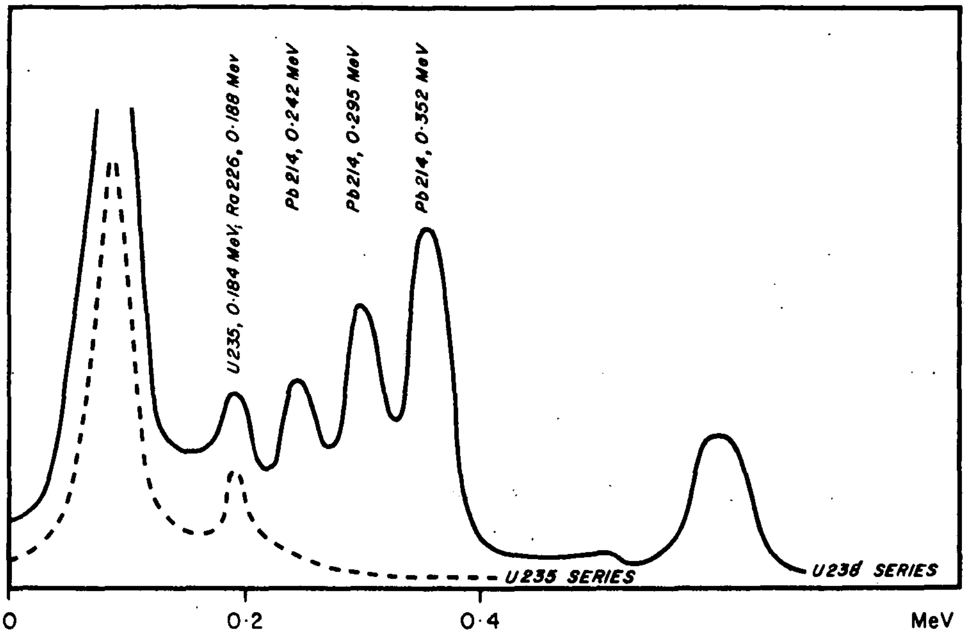
1. INTRODUCTION

The main contributors to the natural gamma-ray activity of rocks and soils are members of the uranium and thorium decay series and potassium-40. Analysis of these radio-elements is fundamental in prospecting for uranium and can also be a useful aid in geological studies; gamma-ray spectrometry is one of the quickest and simplest methods of analysis. This Record discusses problems of interpretation of gamma-ray spectra in the light of experience gained with a multi-channel spectrometer by the Darwin Uranium Group of the Bureau of Mineral Resources (BMR). The instrument is a Nuclear Data Series 1100 Analyzer System with a 256-channel memory and a 3" x 3" (76 mm x 76 mm) cylindrical thallium-activated sodium iodide crystal detector. Measurements may be viewed as a cathode-ray oscilloscope display, typed in digitized form, read out on an X-Y plotter, or punched on tape.

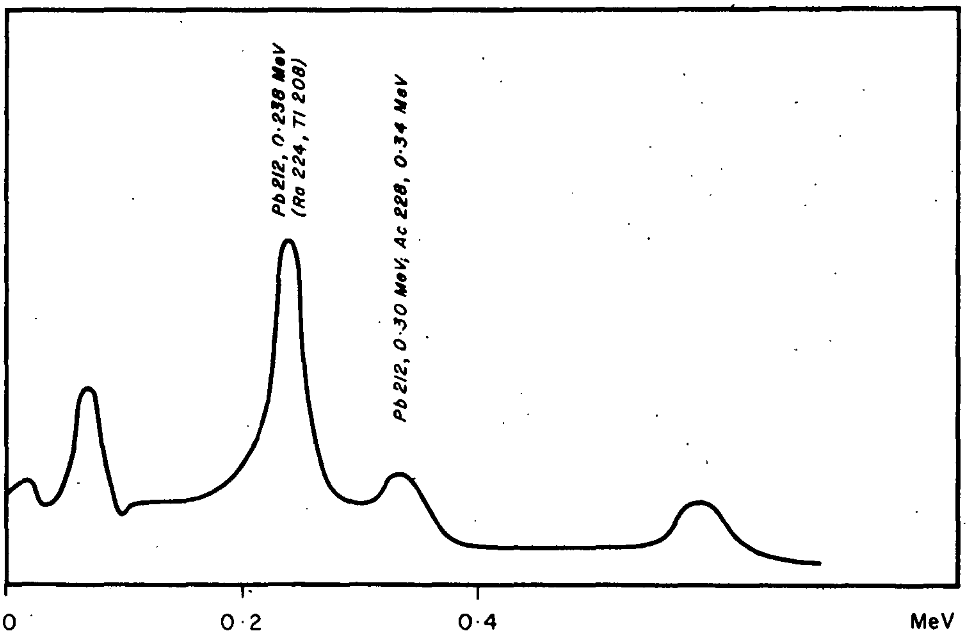
Figure 1 shows gamma-ray spectra of uranium, thorium, and potassium; the energy peaks referred to in the text are shown except for the 2.62 MeV peak of thallium-208. The samples analyzed contained members of the uranium and thorium series with negligible potassium, and potassium analysis is not discussed in this Record; Bunker & Bush (1967) cover the subject. It is apparent from Figure 1 that only superficial examination is required to distinguish between the uranium and thorium series spectra. The gamma-ray emission between 0.15 and 0.40 MeV is usually used in sample analysis. At lower energies difficulties arise from noise, background, scatter, absorption, and a complex superimposition of peaks (see Figure 2). At higher energies the gamma-ray emission is of lower intensity and is more broadly resolved.

The gamma-rays emitted by uranium-238 and thorium-232 are of low energy and intensity, and reliable direct measurements cannot be made. The gamma-rays used in analysis are from daughters. If the uranium or thorium series is in equilibrium, no problem arises because measurement of any peak, and comparison of that peak with the same peak from a standard sample, will give the concentration of the parent. However, the physical and chemical characteristics of the members of the uranium-238 series are such that disequilibrium usually occurs between two groups. The first is the uranium group consisting of the members from uranium-238 to thorium-230; none of these produces peaks measurable with the equipment used. The second group is the radium group, consisting of members from radium-226 on, and contains the strongest gamma-ray emitters of the uranium series. Equilibrium within the uranium group is achieved only on a geological time scale; equilibrium within the radium group is achieved in a few weeks provided that loss of the gaseous member radon-222 is prevented.

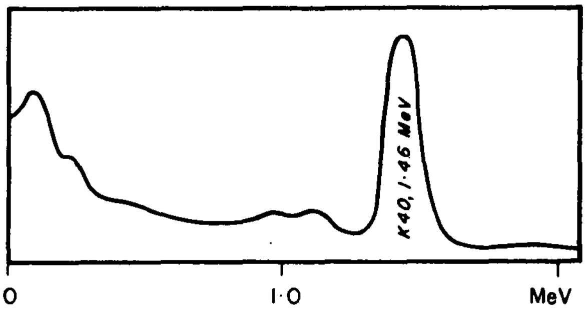
GAMMA-RAY SPECTRA OF URANIUM, THORIUM AND POTASSIUM



THE U238 AND U235 SERIES OF NATURAL URANIUM



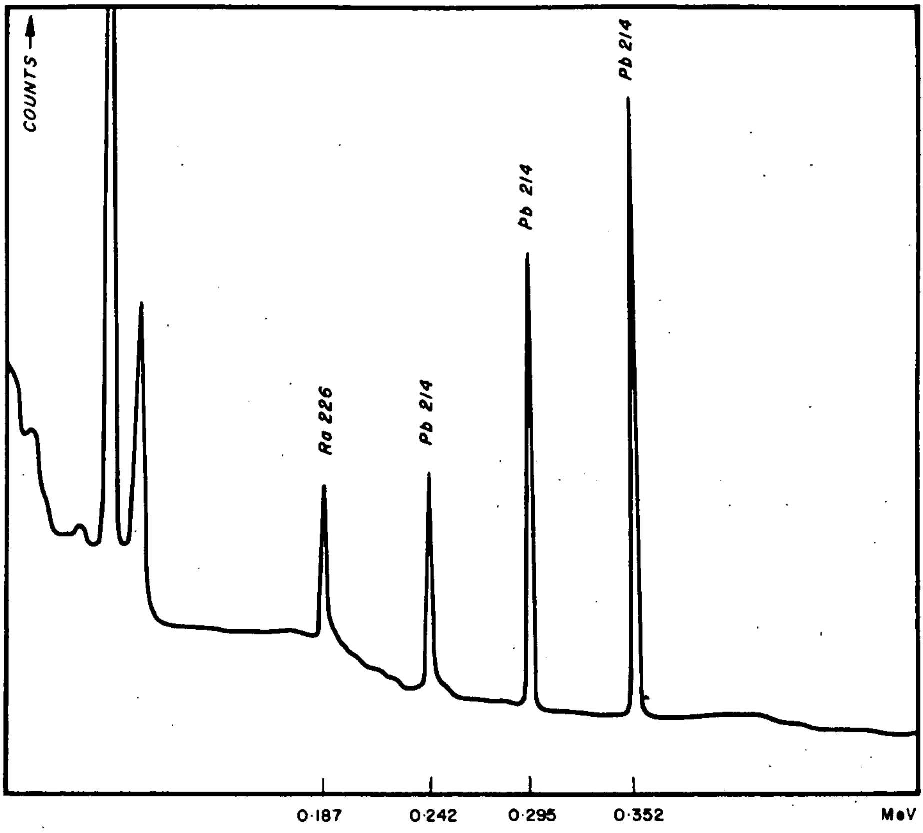
THE THORIUM SERIES



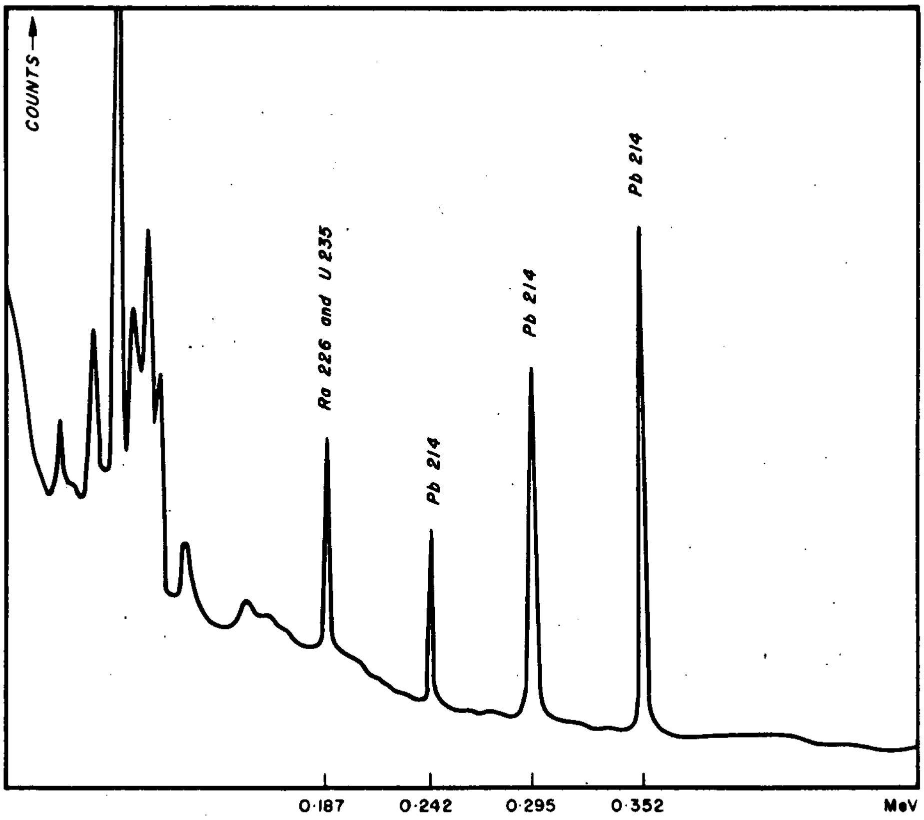
POTASSIUM 40

(Fig. 1)

GAMMA-RAY SPECTRA USING LITHIUM-DRIFTED DETECTOR



Ra 226 AND DAUGHTERS



URANIUM ORE PROBABLY IN EQUILIBRIUM

(Fig. 2)

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These factors impose difficulties in the application of gamma-ray spectrometry to determining the concentration of parent uranium or thorium. In the case of thorium, equilibrium of the series usually exists so that a determination based on the daughters, and termed a determination of 'equivalent thorium', which assumes equilibrium, is satisfactory. In the case of uranium, however, disequilibrium is more likely and determination of 'equivalent uranium' cannot be relied upon unless information on the state of equilibrium is available. Methods of assessing the equilibrium of the uranium series, or of making a more direct assay (see Method 1), are based on the uranium-235 peak which occurs at 0.184 MeV and on the assumption that the ratio of uranium-235 to uranium-238 found in nature is constant.

Mero (1960) describes a method of estimating equilibrium of samples of ore by measuring the ratios of count-rates in channels centred on 0.190 MeV (uranium-235 and radium-226) and 0.242 MeV (lead-214). Ratios of 1.0 to 1.3 indicate equilibrium ores, greater values indicate uranium-rich ores, and lesser values indicate radium-rich ores. It should be pointed out that Mero incorrectly attributes the contribution of uranium-235 at 0.184 MeV to thorium-230, whose gamma-ray emission is of negligible intensity. However, this does not affect his method. Mero's method has given satisfactory estimates of equilibrium. Material known to be in equilibrium gave a ratio of about 1.2 and a radium sample about 0.9 on the spectrometer in Darwin. However, weathered surface samples from the Rum Jungle area, Northern Territory, which were sufficiently radioactive to produce measurable peaks and which contained no detectable thorium, appeared to contain uranium series near equilibrium. This is surprising and suggests that Mero's method of estimating equilibrium has limitations. An alternative method of investigating whether a sample is in equilibrium is mentioned in Method 1 but has not yet been found to be satisfactory.

Methods of analysis of mixed spectra of uranium and thorium series described are a method of direct analysis for uranium-235 plus analysis for equivalent radium, uranium, and thorium (Method 1) and two methods of determining equivalent uranium and thorium (Methods 2 and 3). Equivalent uranium is the amount of primary uranium required to support the amount of daughter product actually present in the sample, on the assumption of radioactive equilibrium. Equivalent thorium and radium are defined in the same way.

2. METHODS OF ANALYSIS OF SPECTRA

Five standard samples were used in the analyses; these were sent to the Australian Atomic Energy Commission (AAEC) in 1971 for assay.

Standard sample	U (%)	Th(%)	Weight (g)
1	0.251	-	83.1
2	-	0.0681	70.0
A	0.0671	0.0355	81.5
B	0.0459	0.0446	79.9
C	0.0277	0.0702	76.0

The equilibrium of the uranium series in the standard samples were described by the AAEC as:

Standards A, B, and 1: out of equilibrium, but not meaningfully so
Standard C : very close to equilbrium
Standard 2 : uranium content too low to reach determination.

The uranium was from pitchblende mixed with dunite, and contained 3.45×10^{-7} gram radium per gram uranium (the theoretical value for the uranium series in equilibrium is 3.42×10^{-7}). The thorium was from monazite (8.44 % thorium) mixed with dunite. These materials were obtained from the United States Atomic Energy Commission and were further diluted with plaster of Paris. The standard samples are kept in airtight polythene containers.

Using these standard samples and a 100-g sample of radium sulphate diluated with plaster of Paris, methods of analysis were tested. Standard samples 1 and 2 were used to evaluate the concentrations of equivalent uranium and thorium in standard samples A, B, and C. The spectra of mixed samples consist of a superimposition of peaks and it is necessary to separate the contributions of the uranium and thorium series before making a comparison of peak heights of sample and standard sample.

Method 1

This method is described by Bunker & Bush (1966) and is a method of direct analysis for uranium-235 and analysis for equivalent radium, uranium, and thorium in mixtures.

Analysis for equivalent thorium is made by utilizing the lead-212 peak at 0.238 MeV. Bunker & Bush observe that in the radium group spectrum the tops of the 0.242, 0.295, and 0.352 MeV peaks are in a straight line. If thorium is present, the 0.238 MeV lead-212 peak is unresolvable from the radium group lead-214 peak at 0.242 MeV. By drawing a straight line through the tops of the 0.295 and 0.352 MeV peaks and extending it to 0.242 MeV, the contribution from the thorium series may be obtained. When this method is used, care must be taken to measure correctly the height of the 0.238 MeV lead-212 peak of the standard sample used for comparison; the standard sample should be of similar composition, weight, and gamma-ray intensity, and preferably should also be a mixture of uranium and thorium series. The straight line peak alighment of the radium group appears to be an approximation. This is illustrated in Figure 2 which shows spectra of the radium group and a uranium ore obtained by AAEC at Lucas Heights with a lithium-drifted germanium detector.

Determination of equivalent radium is made by using the 0.352 MeV lead-214 peak; the height is measured from the level of the valley which occurs between 0.4 and 0.5 MeV, and comparison is made with a standard sample of known radium concentration. Equivalent uranium may be determined in the same way by comparison with a uranium-238 series standard sample.

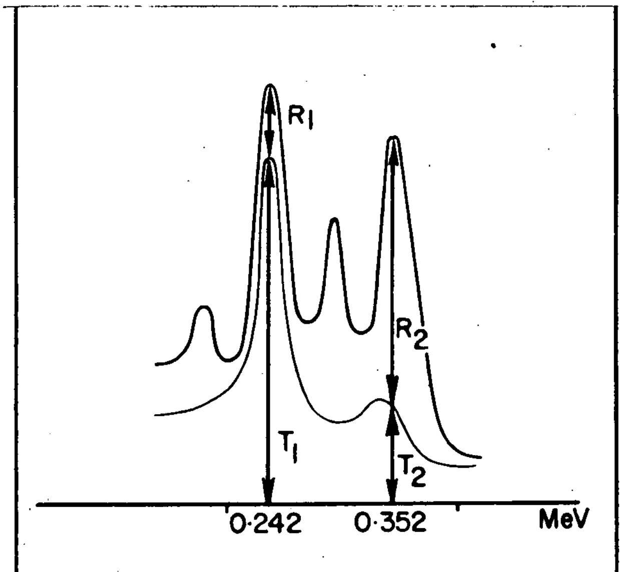
Analysis of uranium-235 is made by comparison with radium and uranium standard samples of similar weight and gamma-ray intensity. The ratios of the 0.188, 0.242, and 0.295 MeV peaks to the 0.352 MeV peak are measured on the spectrum of the radium group standard sample from a baseline at the level of the valley between 0.4 and 0.5 MeV. These ratios are used to produce corrected base points below the 0.295 and 0.242 MeV peaks of the unknown sample; this is after removal of any thorium series contribution. These base points are then joined by a straight line which is extended to give a corrected base point below the 0.188 MeV peak. The theoretical contribution from the radium group to the 0.188 MeV peak can then be subtracted; the difference is the contribution from uranium 235 at 0.184 MeV. Bunker & Bush explain the method in detail. A check on the degree of equilibrium is afforded by a comparison of the uranium assay based on uranium-235 and the equivalent uranium assay based on lead-214.

Results of analysis testing are shown in Table 1. Standard samples A, B, and C were tested against standard samples 1 and 2 and a radium group sample. The determinations based on uranium-235 and lead-214 should agree if the samples are in equilibrium. The fact that the disparity is greatest in the sample containing most thorium suggests that error may be caused by interference from the thorium series. Two possible ways in which the thorium series can affect uranium-235 determinations are: (1) the Compton edge from the lead-212 peak at 0.238 MeV affecting the count-rate at 0.188 MeV; and (2) the lead-212 peak at 0.3 MeV affecting the lead-214 peak. Both could increase the uranium-235 determination. However, Bunker & Bush (1966) state that interpretation problems did not arise until the thorium-uranium ratio exceeded about ten.

Uranium analyses determined from the uranium-235 content are subject to errors from the many adjustments of the spectrum required. Further work is needed on the uranium-235 method for use on material not in equilibrium; standard samples of varying uranium-to-radium ratios would be useful.

Method 2

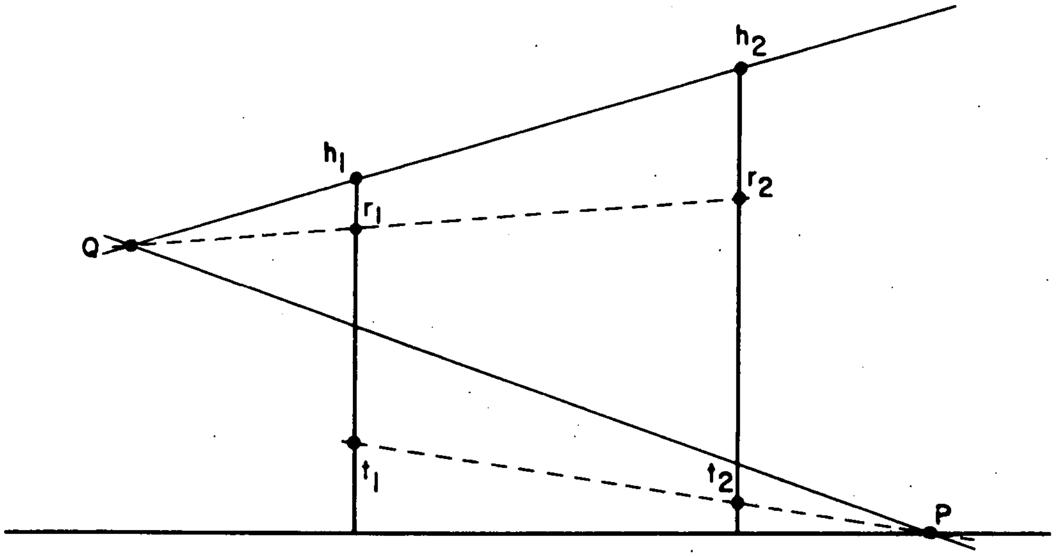
This is an alternative method of separating the contributions of the uranium and thorium decay series when they occur together and of determining equivalent uranium and thorium. Measurements were made of the counts centred on the 0.242 MeV and 0.352 MeV peaks. These counts are designated h_1 and h_2 respectively, and it is assumed that they represent contributions R_1 and R_2 from the radium group and T_1 and T_2 from the thorium series (Figure 3). The ratios R_1 to R_2 and T_1 to T_2 were measured using the uranium and thorium standard samples 1 and 2. If $T_1/T_2 = K$ and $R_1/R_2 = C$, and if $h_1 = T_1 + R_1$ and $h_2 = T_2 + R_2$, it follows that $R_2 = (Kh_2 - h_1)/(K-C)$, $R_1 = CR_2$, $T_1 = h_1 - R_1$, and $T_2 = h_2 - R_2$.



(Fig. 3)

Equivalent uranium and equivalent thorium may be obtained by comparing R_2 and T_1 with the standard samples of uranium and thorium respectively.

A simple graphical technique was discovered which makes the calculation less laborious. First, h_1 and h_2 are plotted using a convenient scale (Figure 4). Points t_1 and t_2 are plotted so that their heights above the



(Fig. 4)

baseline maintain the ratio T_1/T_2; for example, if $T_1/T_2 = 3.1$, then $t_1 = 3.1$ and $t_2 = 1$ in convenient units. Points t_1 and t_2 are joined defining point P. This process is repeated with points r_1 and r_2 ($r_1/r_2 = R_1/R_2$) plotted at distances below h_1 and h_2 so that point Q may be obtained. The line PQ is then drawn to divide h_1 and h_2 into their respective radium and thorium contributions.

Method 3

This is another method for analysis of uranium and thorium occurring together, and assumes both are in equilibrium. The method requires the energy calibration of the spectrometer to be adjusted to include the 2.62 MeV peak of thallium - 208 in the thorium series. The ratio of the 0.35 MeV peak to the 2.62 MeV peak was determined. At 2.62 MeV there is no uranium series contribution, so this peak can be used to determine the amount of equivalent thorium in the sample by comparison with a thorium standard sample. By applying this ratio, the 2.62 MeV peak can be used to strip the 0.35 MeV peak, leaving the contribution due to the radium group. A comparison with the uranium standard sample can then be made, giving the equivalent uranium in the sample.

The main source of error in this method is the large ratio of the 0.35 MeV peak to the 2.62 MeV peak, which is difficult to measure accurately; this produces error in removing the thorium contribution of the 0.35 peak.

3. RESULTS

The results are shown in Table 1. The values obtained assume equilibrium and are percentages of equivalent uranium or equivalent thorium, except for the values based on uranium-235.

TABLE 1

	Standard sample A		Standard sample B		Standard sample C	
	U(%)	Th(%)	U(%)	Th(%)	U(%)	Th(%)
AAEC assay	0.0671	0.0355	0.0459	0.0446	0.0277	0.0702
Method 1 based on uranium	0.12		0.065		0.103	
Method 1 (equivalent uranium & thorium)	0.081	0.033	0.057	0.042	0.042	0.078
Method 2	0.072	0.033	0.044	0.054	0.032	0.072
Method 3	0.072	0.032	0.047	0.055	0.031	0.073

4. CONCLUSIONS

Further work is required on the radium group stripping technique (Method 1) in order to find a satisfactory means of assaying for uranium when it is not in equilibrium, and for determining the state of equilibrium. Standard samples in varying states of equilibrium would be helpful. However, gamma-ray spectrometry is not an ideal method for this kind of work because of the limited number of sufficiently intense gamma-rays emitted by uranium.

An approximate estimate of equilibraium is obtainable with a method described by Mero (1960). However, this method has given apparently incorrect results on weathered surface samples.

Separation of the contribution of the uranium and thorium series to a mixed spectrum can be achieved satisfactorily.

5. REFERENCES

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