

**GAMMA-RAY SPECTROMETRIC SET UP AT NGRI
FOR ANALYSIS OF U, Th and K IN ROCKS**

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Abstract

A gamma-ray spectrometer with a NaI (TI) detector and a single channel analyser has been set up for analysis of rocks for radio elements uranium, thorium (at ppm level) and potassium. Constructional details, operational procedures and method of analysis of the output from the spectrometer are given. Errors, limits of detectability, sample counting time, reproducibility and an inter-laboratory comparison of results are discussed. Further plans of work in this direction are outlined.

Introduction

A knowledge of the distribution of the natural radioactive elements, U, Th and K, in crustal materials is fundamental to the solution of many geologic problems. Analysis of rocks for determining the concentrations of these elements has several economic as well as academic aspects. Well known among these are the investigations of the contribution of these elements to environmental radioactivity, estimation of radiogenic heat production of the crust and upper mantle in geothermal problems, geochemical studies on differentiated magma series, delineation of U and Th rich provinces, differentiation of mantle, etc.

Over the last two decades, several groups have collected and analysed data on U, Th and K in rocks. Some of the significant contributions are those of ADAMS *et al.* (1962), WHITFIELD *et al.* (1959),

LARSEN and GOTTFRIED (1960) and PHAIR and GOTTFRIED (1964) in USA, SHAW (1968) and EADE and FAHRIG (1971) in Canada, HEIER and ADAMS (1965), and HEIER and THORESEN (1971) in Norway, LAMBERT and HEIER (1967) in Australia and RONO and MIGDISOV (1970) in USSR. A compilation of all the data was last given by CLARK *et al.* (1966).

Rocks show an enormous range of radioelemental contents. Granites have typically about 10 times as much uranium as basalts, several hundred times as much as chondrites and at least a thousand times as much as peridotites. Techniques for analysis are therefore varied, depending on the concentration level involved. Over the last decade, sophistication has also increased in the analysis, with the increasing developments in the field of nuclear detectors and instrumentation. For the very low levels encountered in ultramafics and meteorites (ppb and less), neutron activation analysis is resorted to. In most other rocks, with concentrations of uranium from about a tenth of a ppm and above, gamma-ray spectrometry is the most widely used technique. It is very versatile since no wet chemistry is involved and is rapid and efficient compared to any other analytical method such as colorimetry or fluorimetry. Another very useful advantage over other methods is the fact that few hundred grams

of rock are generally used in this analysis, which gives a true bulk concentration of these elements in a rock body.

In India, data has been reported by Gamma-ray spectrometric analysis by Prof. Venkata Subramanian and his group (PAL *et al.* 1967, NARAYANASWAMY and VENKATA SUBRAMANIAN 1969, NARAYANASWAMY 1972). Analysis by other methods has been reported on few rocks by SAHA *et al.* (1970), DIVAKARA RAO *et al.* (1972) and GANGADHARAM and ASWATHANARAYANA (1969).

This paper describes the experimental set up, analysis of the out put and other relevant details of the Gamma-ray spectrometer established by the author in NGRI. About 150 rock samples have so far been analysed and many more are in progress. Further developments planned in this direction are outlined.

Procedure in brief

A functional block diagram of the spectrometer is shown in Fig. 1. Gamma rays from a sample placed on the detector,

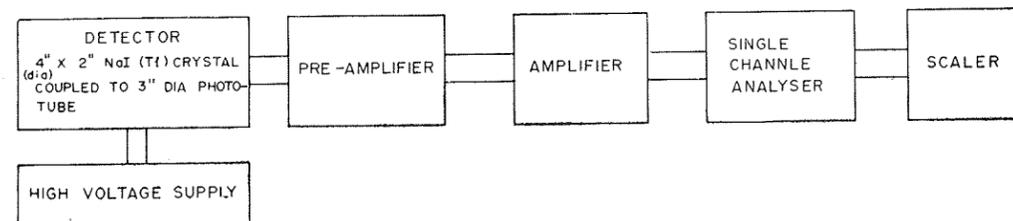


Fig. 1. Functional block diagram of gamma-ray spectrometer.

passing through the NaI (TI) crystal produce scintillations which are converted into electrical pulses by the application of high voltage to the phototube. After amplification, they are fed to a single-channel analyser and are counted by the scaler. The amplitude spectrum of pulses (pulse height *vs* count rate) with a rock sample, consists of photopeaks of daughters of U series and Th series and that of K ⁴⁰ superimposed over the Compton continuum of higher energy peaks. Because of the limited resolution of the detector, the peaks revealed by the amplitude spectrum combine several closely spaced peaks characteristic

of the individual daughters in the U and Th series.

Count rates obtained under three distinct segments of the amplitude spectrum, with the rock sample as well as with standard samples containing known amounts of uranium, thorium and potassium, under identical sample-detector conditions and fixed sample-detector geometry, yield estimates of U, Th and K in the rock sample. Inherent in this analysis is the assumption of secular equilibrium of U ²³⁸ and Th ²³² with their respective daughter isotopes down the series.

Details of Detector Assembly

The detector is an integral assembly consisting of a 4" (dia) x 2" NaI (TI) crystal coupled to a 3" RCA-8054 photo multiplier tube obtained from Messrs Nuclear Supplies, USA. Resolution of the detector is 8.2% for Cs ¹³⁷. After several trials, an optimal voltage of 1200v was chosen for the photo-tube. The gain of the amplifier was set at about 70. Spectra obtained with one volt window setting of

the single channel analyser with three sources, are shown in Figures 2, 3 and 4, respectively. A one volt window corresponds to about 40 Kev.

Background Reduction :

A basic requirement in low level counting is reduction of background radiation and enhancement of Total/Background ratio. Utilising the mild steel shield fabricated for the Tritium laboratory, a few experiments were performed. Count rates were first obtained by placing the detector in a 3"-thick lead shield. Later, they were repeated by placing the detector

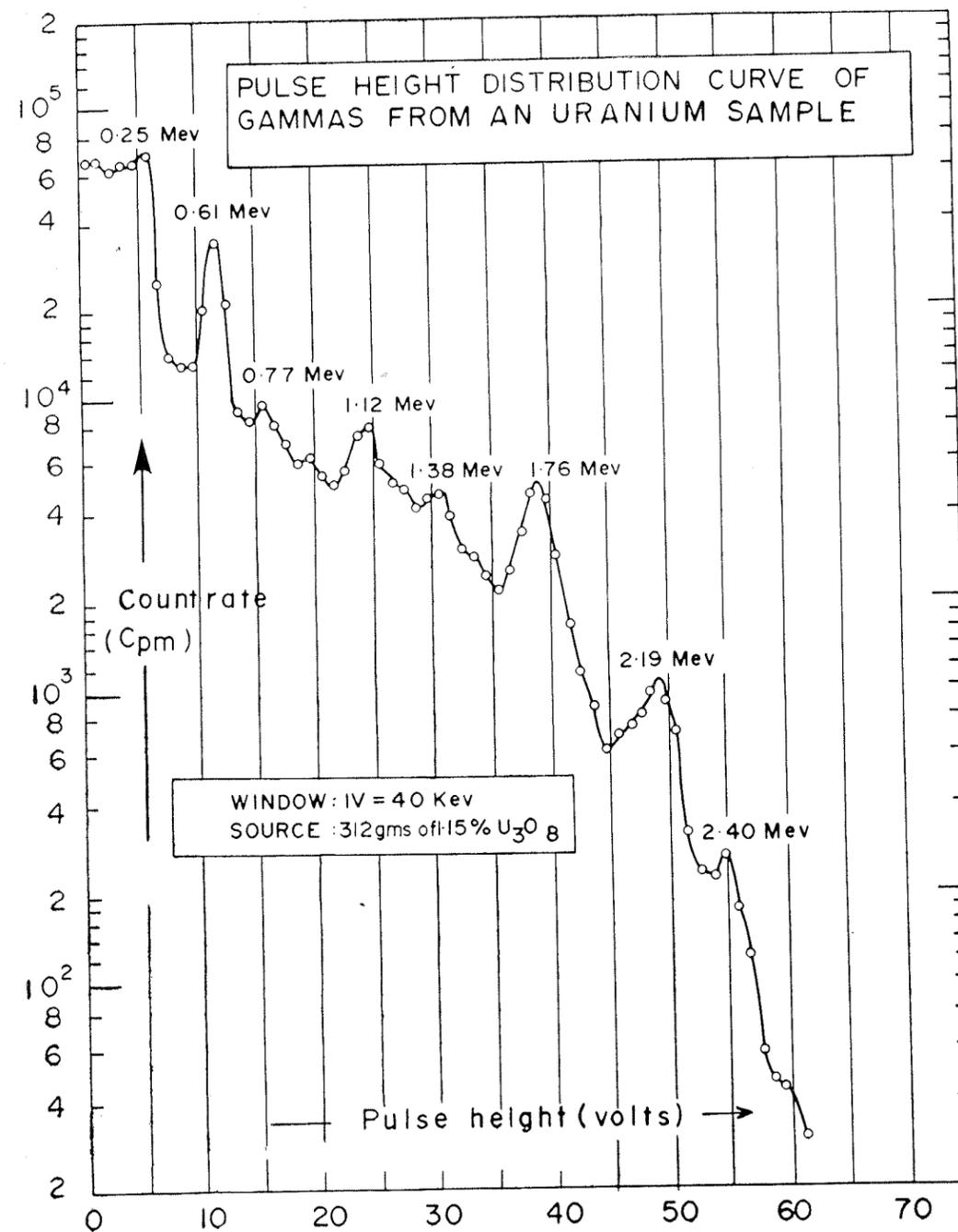


Fig. 2. Pulse height distribution curve of gammas from an uranium sample.

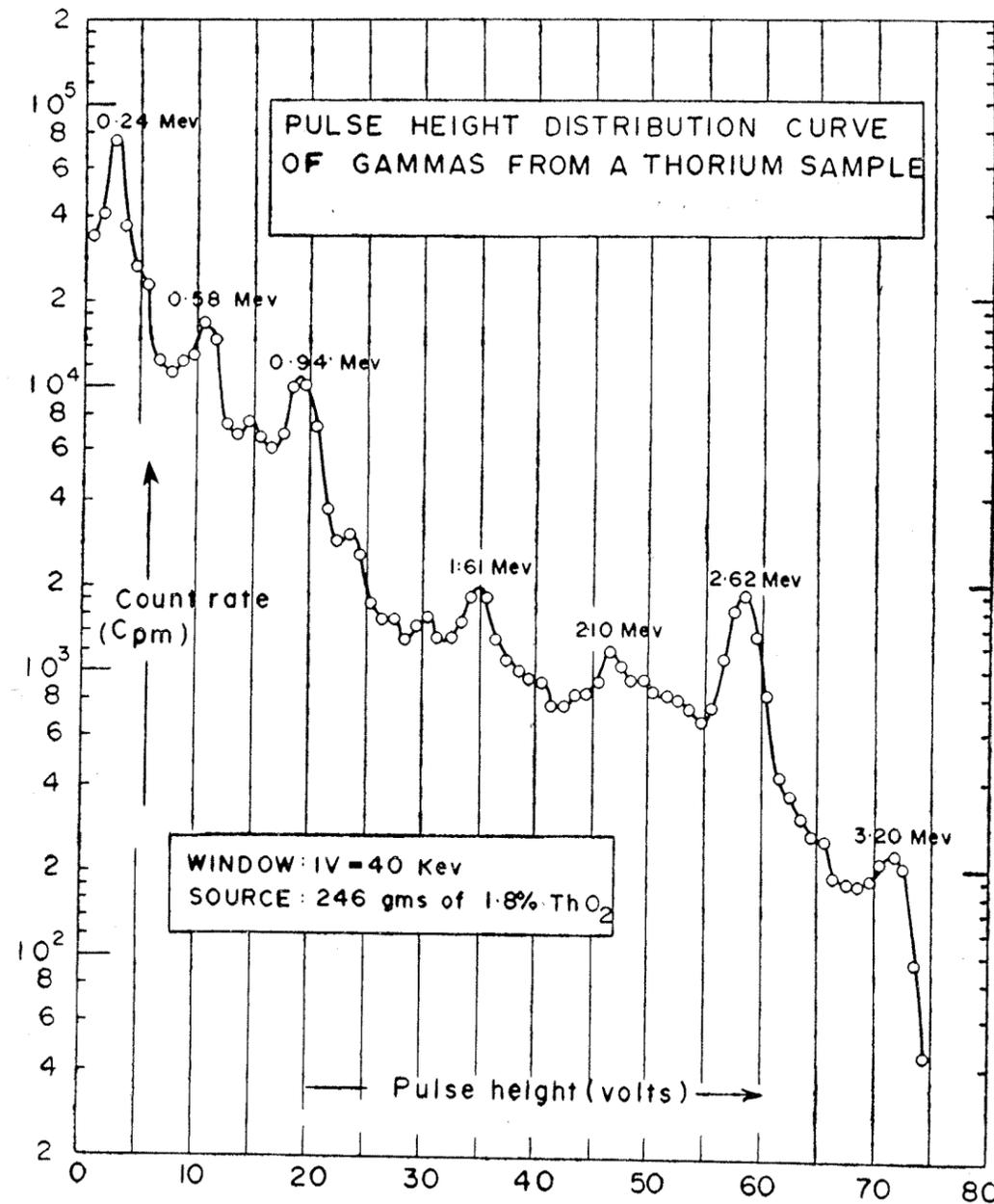


Fig. 3. Pulse height distribution curve of gammas from a thorium sample.

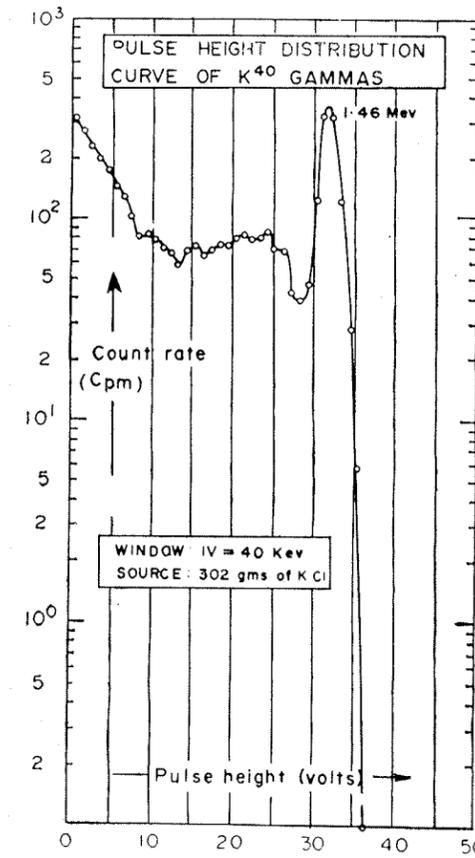


Fig. 4. Pulse height distribution curve of gammas from a potassium sample.

in background when 3" thickness of lead was added to 6" thickness of steel, and keeping in view other practical considerations, a shield was constructed with lead bricks of sizes 6" x 4" x 1" and 8" x 4" x 1". The shield has internal dimensions of 10" x 10" x 16" (high), presents at least 8" thickness of lead to all external sources and yields background count rates as those shown for the 6" steel plus 3"-lead shield. It has been lined with an Al sheet. The background count rates with a similar size crystal under similar energy ranges reported by WOLLENBERG and SMITH (1964) in their shield in the Lawrence Radiation Laboratory of University of California, are also shown for comparison. Their shield comprises 4" thickness of lead, which in turn is surrounded by 8" low activity concrete blocks.

Selection of Channels for Counting:

The most generally used energy ranges of the gamma spectrum with a single channel analyser set up are those centred around 1.46, 1.76 and 2.62 Mev peaks of K^{40} , Bi^{214} and Tl^{208} respectively. Channels centred around lower energy peaks, which give higher count rates and also higher Total/Background ratio were tried but in view of the drift problems, it was found more practical to use the higher energy peaks. The present set up consists of two separate single channel analysers. Pulses from the output of the amplifier are fed to the two analysers, the baseline and window width of which are set to cover two different energy ranges, and pulses from their output are counted

TABLE 1
Results of background count rate measurements in different shields.

| Energy Range Centred around peak | width | Results of background count rate measurements in different shields. | | | Lawrence Ra- diation Lab. 4" lead + 8" low activity concrete blocks |
|---|--------|---|---------------------------|--|--|
| | | 3" thick lead. | 6" thick mild steel | 6" thick mild steel + 3" thick lead | |
| 0.94Mev | 200Kev | — | — | 13.1 cpm | 14.7 cpm |
| 1.12Mev | 200Kev | — | — | 9.2 cpm | 10.3 cpm |
| 1.46Mev | 240Kev | — | 23.1 cpm | 8.4 cpm | 10.5 cpm |
| 1.76Mev | 240Kev | — | 11.8 cpm | 5.7 cpm | — |
| 2.62Mev | 240Kev | 11.7 cpm | 6.9 cpm | 3.0 cpm | — |

simultaneously. Because of the low count rate under the 2.62 Mev peak, one analyser was always used to cover the 280 Kev energy range centred around this peak. The other analyser was used to cover two energy ranges, each 280 Kev, but centred around 1.46 and 1.76 Mev peaks. The window of this analyser was set to cover the two peaks, one after another, each time till sufficient number of counts were obtained under the set window.

Standard Samples

Uranium and thorium standards were prepared from samples obtained from the U.S. Atomic Energy Commission's New Brunswick Laboratory. These samples, 100 gms each, are U and Th ores diluted in and thoroughly mixed with fine ground dunite, and with accurately known U and Th concentrations. 25 gms of 1.01% U sample was taken and thoroughly mixed with about 400 gms of fine ground dunite, to constitute the U standard (U=590 ppm), and 40 gms of 1.0% Th sample with 400 gms of dunite to constitute the Th standard (Th=900 ppm). The K standard consists of 330 gms of KCl. While the uranium standard contains negligible thorium, the thorium standard contains 0.04% uranium, and its effect is taken care of in the analysis of data.

Sample Preparation

Cylindrical plastic sample containers, 4" (dia) x 1½" (high) have been used in this work. Samples to be analysed are ground to -120 mesh. About 400 gms of powder are required for filling the container in the case of a typical granite sample and about 440 gms in the case of a dunite sample. With practice, it has been found possible to fill all the samples with the same degree of compaction. One sample was counted twice, first with powder of -120 mesh and later, the same powder reground to -60 mesh. The counts per minute per gm of the sample did not change and hence grinding of all samples to -120 mesh was fixed. Containers filled with powders were sealed off with a tape and counted after at least three days' storage, for radon loss to be repaired. Fig 5

shows sample container in place on the detector.

Counting Procedure

After allowing for the initial warming up period of about 2 hours for the electronic units, the position of the peaks (under which counting has to be done) in terms of the base line setting of the two analysers, are found by using strong sources of U and Th (300 gms of 1.15% U_3O_8 and 250 gms of 1.8% ThO_2). With the windows of the two analysers set to cover the two peaks, counting is started with the rock samples. At the end of 2 or 3 hours of counting, the peak positions are again checked to ensure that there has been no drift. Most of the time, there is a very slow but steady drift of about 0.2 to 0.4 volts in terms of the base line setting of each window over many hours and therefore baseline is constantly reset according to the new peak position every 2 or 3 hours. When the positions of the peaks drift by more than one volt, the gain of the amplifier is adjusted to bring them back to their original standard setting. Thus short term as well as long term drifts are off-set. The spectrometer room is air conditioned and maintained at about 20°C. All the power for the electronics is derived through voltage stabilizers. Counting is continued with a sample till sufficient number of counts are obtained under three energy ranges, to the required percent counting error, corresponding to the Total/Background ratio of the sample, according to the curves given by LOEVINGER and BERMAN (1951). In the case of high activity samples a standard background count rate which has been established by counting background at regular intervals over several months, has been used for arriving at the net count rate of the samples. In the case of low activity samples, background and sample are counted alternately at one hour intervals and the background count rate thus established nearer the sample counting time is used. A dummy sample consisting of pure NaCl is used for background counting.

Computation

The results are computed as follows to yield U, Th and K concentrations. Let the net count rates be as follows:

| | Energy Ranges | | |
|--|-----------------|-----------------|-----------------|
| | (1) 1.46 Mev | (2) 1.76 Mev | (3) 2.62 Mev |
| Uranium standard (Containing U grams of uranium) | U_1 | U_2 | U_3 |
| Thorium standard (Containing T grams of thorium and T_u grams of uranium) | T_1 | T_2 | T_3 |
| Potassium standard (Containing K grams of Potassium) | K_1 | — | — |
| Rock Sample | R_1 | R_2 | R_3 |

With the concentration of the standards and the corresponding net count rates as shown above, the amount of thorium, uranium and potassium in the sample (R_r , R_u & R_k) are computed as:

$$R_r = \frac{R_3 U_2 - R_2 U_3}{U_2 T_3 - U_3 T_2} \cdot T$$

$$R_u = \frac{R_2 T_1 - R_3 T_2}{U_2 T_1 - T_2 U_3} \cdot U$$

$$R_k = \left[R_1 - \left(\frac{U_1}{U} \cdot R_u + \frac{T_1}{T} \cdot R_r \right) \right] \cdot \frac{K}{K_1}$$

where $T'_1 = T_1 - \frac{U_1}{U} \cdot T_u$

$$T'_2 = T_2 - \frac{U_2}{U} \cdot T_u$$

and $T'_3 = T_3 - \frac{U_3}{U} \cdot T_u$

are the count rates of the thorium standard under the respective energy ranges, stripped off the effect of its small uranium content. The above quantities are divided by the weight of the sample to yield U, Th & K concentrations. After counting has been completed on several samples, all the results are computed at one time, using IBM 1620 computer. The computer program incorporates computation of Th/U, U/K ratios and heat generation values also, corresponding to each sample.

Sample counting time, errors and lower limits of detection:

Sample counting time depends upon the amount of activity and precision required for the data. Lower radioactive content requires longer count time for any specified accuracy; conversely, greater accuracy demands longer count time for any given radioactive content. The number of counts that need to be obtained with a sample and the background, for a required percent counting error in the net count rate, can be read off from the curves given by LOEVINGER and BERMAN (1951). The period for which counting has to be done with the set up reported here, for 5% and 3% counting error in the net count rates under the three energy ranges, in the case of two samples (one with typical granitic concentration and the other with basaltic concentration) is shown in Table 2. All the high activity samples have been counted for a 3% counting error. In the case of low activity samples where counting time for 3% error exceeds a day, counting has been restricted to 5% error.

TABLE 2
Counting time for 5% and 3% error in net count rates under three energy ranges, for two sample types.

| | 1.46 Mev | | 1.76 Mev | | 2.62 Mev | |
|---|----------|-------|----------|---------|------------|---------|
| | 5% | 3% | 5% | 3% | 5% | 3% |
| Sample No. 1 Th : 21.8 ppm U : 5.3 ppm K : 3.45% | 15min | 20min | 1 hr. | 2 hrs. | 1 1/2 hrs. | 3 hrs. |
| Sample No. 2 Th : 1.7 ppm U : 0.6 ppm K : 0.85% | 1 hr. | 3 hrs | 14 hrs. | 40 hrs. | 27 hrs. | 75 hrs. |

Standard samples were counted for very long times so that their count rates can be considered to have negligible error. The errors in the final analyses of U, Th & K (due to counting error), depend not only on the percent counting error in the net count rates under the three energy ranges but also on the relative concentrations of the three elements in the sample. The relative error, defined here as the ratio of error in the analysis of the element to the percent counting error in the three net count rates (assuming that counting has been made to the same percent error under the three energy ranges), has been computed for the

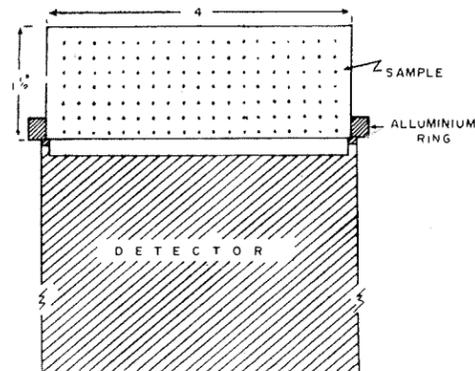


Fig. 5. Sample in place on detector.

three elements ($R.E._T$, $R.E._U$ & $R.E._K$) and shown in Figures 6 and 7. The actual error in the analysis would thus be product of this relative error and % error in the three net count rates. For example, for a sample with a Th/U ratio of 0.1, the relative error in thorium would be 2.3 according to Fig 6a; if counting is made for 3% error in the net count rates, error in final Th analysis would be 2.3×3 i.e., 6.9%, and for 5% counting error in the net count rates, the corresponding figure would be 11.5%. The relative errors for thorium and uranium are dependent only on Th/U ratio and not on actual concentrations of these elements while for potassium, the relative error depends on the actual concentration of all the three elements. This is due to the three particular energy ranges chosen for counting. While the count rate under the energy range centred around 2.62 Mev peak is almost dependent on Th content,

the count rate under 1.76 Mev peak is dependent on Th and U contents, while that under 1.46 Mev peak is dependent on Th, U and K.

Level of detectability, i.e., the lowest concentration of an element that can be detected, depends in a complicated way on several factors such as length of time that could be devoted to counting, concentration of the other two elements present, the desired accuracy etc. If a 24 hr limit is placed on the counting time under each energy range, then the levels of detectability would be as follows. Uranium can be detected down to 0.25 ppm even with Th/U ratio of 10, with an error of about 12%. Thorium can be detected upto 0.5 ppm even with a Th/U ratio of 0.1, to the same error. Potassium can be detected down to 0.1%, with an error of 20% in the presence of 10 ppm U and 1 ppm Th, and with 10% error in the presence of 2 ppm U and 20 ppm Th.

It is to be emphasized that the above errors are only statistical errors due to background and sample fluctuations inherent in radioactivity assays. The actual errors including other effects such as spurious counts, coincidence losses, self absorption in the source etc., are more than those indicated above and cannot be easily evaluated.

Reproducibility and inter-laboratory comparison

To obtain an idea of reproducibility, a granite sample has been measured at five different times and results are given in Table 3. An inter-laboratory comparison

TABLE 3
Results of repeated analysis on a single sample

| | Th (ppm) | U (ppm) | K (%) |
|----|-------------|------------|----------|
| 1. | 23.07 | 7.89 | 0.95 |
| 2. | 23.55 | 7.90 | 0.98 |
| 3. | 23.19 | 8.42 | 0.99 |
| 4. | 22.42 | 7.68 | 0.99 |
| 5. | 23.30 | 7.80 | 0.98 |

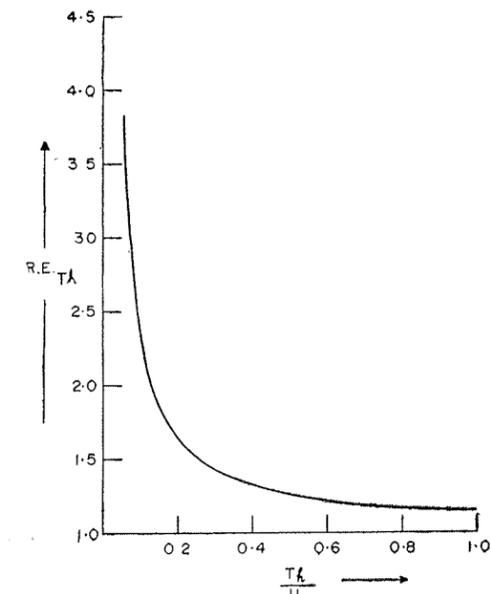


Fig. 6a. Relative error of thorium as a function of Th/U ratio.

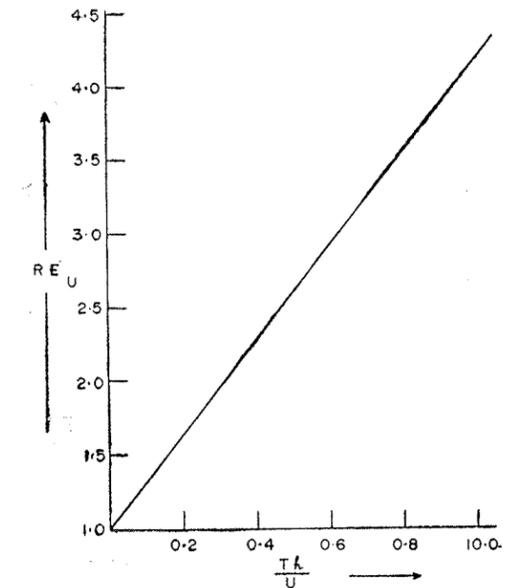


Fig. 6b. Relative error of uranium as a function of Th/U ratio.

has been made by analysing six samples with the present set up. These samples were already analysed by Trevor Lewis with a Gamma-ray set up using solid state detector and a multichannel pulse height analyser (LEWIS, 1974) at the Earth Physics Branch of the Department of Ener-

gy, Mines & Resources, Ottawa. Results of both the analysis are given in Table 4. The agreement between the two is excellent particularly in view of the two different types of detectors as well as methods of analysis of data, used.

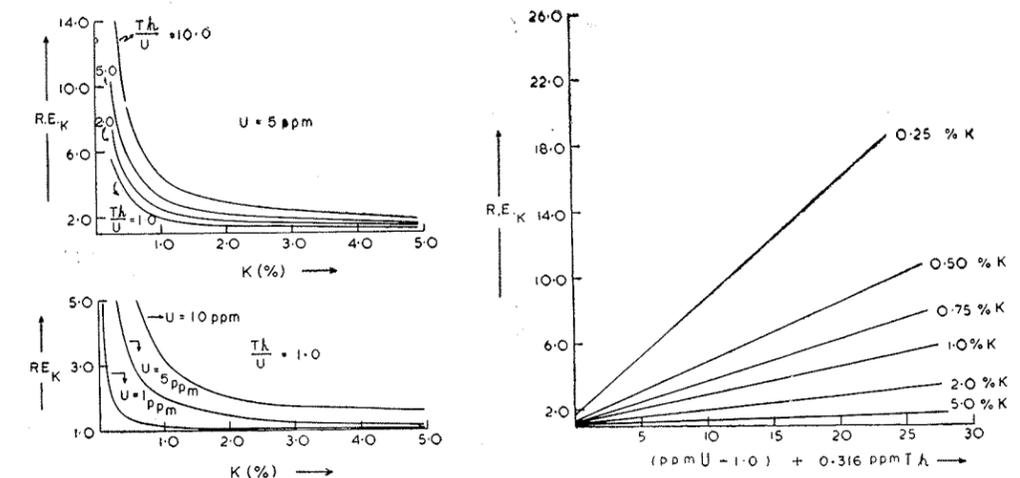


Fig. 7. Relative error of potassium as a function uranium, thorium and potassium.

TABLE 4
Inter laboratory comparison of analysis on six samples.

| Sample | Th (ppm) | | U (ppm) | | K (%) | |
|--------|----------|-------|---------|-------|-------|------|
| | (1) | (2) | (1) | (2) | (1) | (2) |
| 1. | 14.50 | 13.54 | 5.69 | 5.66 | 2.63 | 2.61 |
| 2. | 3.23 | 2.70 | 11.20 | 11.66 | 5.79 | 5.15 |
| 3. | 0.30 | 0.14 | 3.05 | 3.32 | 0.04 | 0.00 |
| 4. | 13.20 | 12.75 | 0.78 | 0.74 | 2.91 | 2.74 |
| 5. | 4.27 | 3.33 | 1.14 | 1.36 | 1.89 | 1.96 |
| 6. | 0.95 | 0.75 | 5.27 | 5.31 | 0.44 | 0.36 |

(1) — Analysis at the Earth Physics Branch, Ottawa, using a solid state detector, Ge (Li), a multi-channel analyser and least square analysis. (Lewis, 1974).

(2) — Analysis with the set up reported here.

Further plans of work :

Analysis of about 150 samples from various heat flow sites in India, has been completed with this set up. Many more are in progress and analysis of samples from all heat flow sites upto date, is expected to be completed shortly.

A multi-channel analyser with conversion gain upto 1024 and a 256 channel memory is now being put into operation. It is proposed to analyse data from all the channels covering energy spectrum upto 2.80 Mev, using the method of least squares (SALMON 1961). Total/Background ratio is to be increased using an annular canister and thus presenting a larger sample to the detector. This would not only speeden-up analysis but also enable to go to much lower levels of detection. Work on a portable Gamma-ray unit for in-situ analysis is being taken up. A systematic study on regional variations of radioelemental contents of the Peninsular shield is envisaged.

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