

THE ESTIMATION OF URANIUM AND THORIUM FROM THE β -RADIOACTIVITY OF MINERALS.

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ABSTRACT.

A method of estimating the quantity of uranium and thorium in minerals and rocks by measuring the β -ray activity of the samples has been developed. A β -ray ionisation chamber was constructed in our workshop and was used together with a F.P. 54 electrometer amplifier circuit similar to that of Dubridge and Brown, with a sensitive galvanometer for measuring ionisation currents. Sources were used in the form of thin films of radioactive samples on aluminium discs protected by very thin cellophane paper. The ionisation currents due to the emitted β -particles were detected by the deflection of the light spot of the galvanometer on a scale. The minerals Thorianite (Ceylon), Samarskite and Pitchblende (Geological Survey of India) were investigated and their uranium and thorium contents were found in all cases within the accuracy mentioned against them. The method has proved very quick and reliable for radioactive measurements of minerals and rocks where the total radioactive content is above 1% of the mineral or rock. Concentrations of 10^{-3} gm. of U or Th per gm. of rock or mineral could be estimated. The thorium and uranium contents of minerals which have been investigated have been given.

INTRODUCTION.

The well-established fact that uranium and thorium disintegrate naturally to form ultimately isotopes of lead makes possible the measurement of geological age of minerals containing uranium and thorium. Because the intermediate members of the radioactive families have short lives in comparison to the ages of the minerals with which we are concerned, we can write the following equations (Nier *et al.*, 1941) relating to the numbers of atoms of radiogenic lead, thorium and uranium isotopes :—

$$N(\text{Pb}^{206}) = N(\text{RaG}) = N(\text{UI})(\text{exp. } [\lambda(\text{UI})t] - 1) \quad \dots \quad (1)$$

$$N(\text{Pb}^{207}) = N(\text{AcD}) = N(\text{Ac-U})(\text{exp. } [\lambda(\text{Ac-U})t] - 1) \quad \dots \quad (2)$$

$$N(\text{Pb}^{208}) = N(\text{ThD}) = N(\text{Th})(\text{exp. } [\lambda(\text{Th})t] - 1) \quad \dots \quad (3)$$

A chemical analysis of the mineral gives the relative amounts of U, Th and Pb. An isotopic analysis of the lead after being corrected for common lead contamination yields the relative amounts of RaG, AcD and ThD. Thus as the decay constants are known, three independent determinations of the minerals' age are possible.

Equations (1) and (3) can be applied directly for age determination, whereas to apply equation (2) we have to use an indirect way.

$$\frac{\text{AcD}}{\text{RaG}} = \frac{N(\text{Ac-U})}{N(\text{UI})} = \frac{\text{exp. } [\lambda(\text{Ac-U})t] - 1}{\text{exp. } [\lambda(\text{UI})t] - 1} \quad \dots \quad (4)$$

As $\lambda(\text{Ac-U})$ is not known directly it may be evaluated by means of the expression

$$R = \frac{\lambda(\text{Ac-U})N(\text{Ac-U})}{\lambda(\text{UI})N(\text{UI})}$$

where R is the present-day ratio of the activities of the actinium and uranium series. Since $N(\text{UI})/N(\text{Ac-U})$ has been shown to be 139.4 equation (4) may be written as

$$\frac{\text{AcD}}{\text{RaG}} = \frac{1}{139} \cdot \frac{\exp. [139R\lambda(\text{UI})t] - 1}{\exp. [\lambda(\text{UI})t] - 1}$$

Thus all methods of the determination of the geological age based on radioactivity depends on the requirements of the accurate estimation of the U and Th contents of the rocks and minerals.

This was first attempted by Joly (1909 and 1912) in a rather crude way by the removal of radon and thoron (in equilibrium with their parent elements). The quantitative estimations of these gases were made through the ionisation produced by the emitted α -rays. Evans (1935) developed the direct fusion method in which the separation of radon and thoron was very quickly effected, the intensity of the α -rays emitted from these gases being measured with the help of a double ionisation chamber coupled to a high sensitivity string electrometer. This method though quite satisfactory for the measurement of U-content was not at all adoptable to the determination of the amount of thorium present in the sample, owing to the very short life of thoron (15.4 sec.). So in the year 1935 Evans developed the method of counting α -particles emitted from the smooth surfaces of radioactive samples by means of vacuum tube electrometer. By using two different absorbers and noting the counts in each case, both the uranium and thorium contents of the sample and their ratio can be quite independently determined. This method has been tried in this laboratory by Nag *et al.* (1944). The method suffers from the defect that it is not very suitable for determining the U and Th-contents of strongly radioactive substances, as in this case the sample is required to be very much diluted to bring the counts within the resolving power of the instrument. This is a source of error in the determination of the amount, the quantity being very small great accuracy is needed. Also tedious and lengthy observations are required as no arrangements for automatic counts could be made here. To overcome these disadvantages recourse was taken to a method of estimating the U and Th-contents of the rocks and minerals by observation of β -ray intensities of the experimental material. The apparatus was standardised using known amounts of standard samples of U and Th and absorption curves of these standard samples in the aluminium were drawn. The absorption curves of the unknown samples were drawn in the same way and the activities due to U and Th were estimated from analysis of the curves. Also by placing absorbers over the source plate which will cut off all the activities due to β -ray from Th, the activity due to uranium alone could be determined from the ionisation current measurements. Subtraction of this from the total activity will give us the activity due to thorium alone.

The present β -ray method is semi-empirical. Certain approximations, lying well within the experimental error from other sources, have been made. The self-absorption of the source is not taken into consideration in contrast to the case of the α -ray method. The effect due to γ -ray is not taken into account. The neglect of the ionisation current due to γ -ray is minimised by using air chamber where only a small fraction of the γ -ray energy is absorbed. For further minimising this effect, certain modification is made in the construction of the β -ray chamber. A mesh of wire rolled into a cylinder surrounding the central electrode forms the real chamber while the outer brass wall is used to reduce the effect due to photo-electrons and pair production electrons by the γ -rays. It is estimated that the error introduced due to neglect of this effect is not more than one per cent which is within our present experimental error. Self-absorption introduces errors of even less magnitude.

'Uranium Ochre' and chemically pure ThO_2 are taken as the standard samples (Chatterjee and Sarkar, 1944) of uranium and thorium for the purpose of standardising our apparatus. The absorption curves of these standard samples are drawn by using Al-foils of different thickness as absorbers. In the absorption curves ionisa-

tion current is plotted as ordinate and the weight of the Al-foils in gm./cm.² as abscissa. The nature of the two absorption curves is found to be quite different.

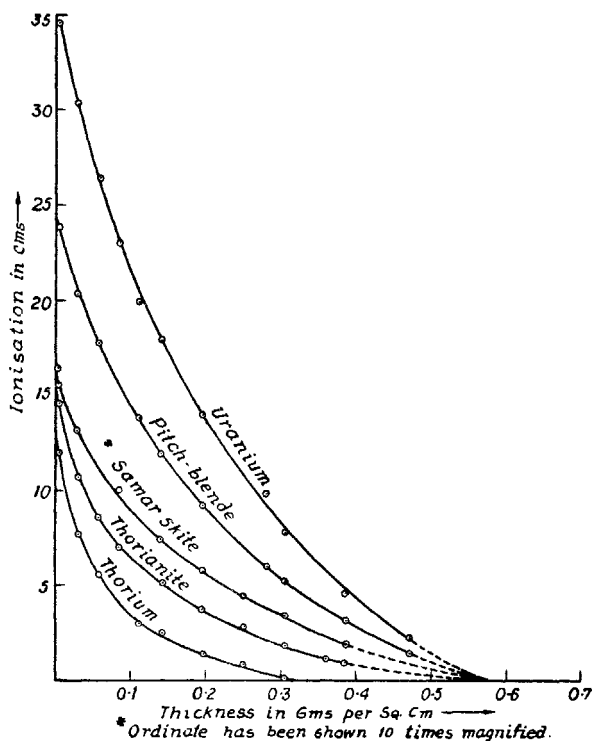


FIG. 1.

Corresponding to the same amount of thorium, the ionisation current due to uranium is found to be about three times greater with no absorber, as would be expected from the ratio of their half-lives. When the absorbers are used, it is noted that the decrease in ionisation in the case of thorium is much sharper than in uranium as is evident from the two absorption curves of uranium and thorium shown in Fig. 1. Ultimately the rate of decrease in the ionisation current becomes more and more similar. Also the thickness of the Al-absorber which is sufficient to cut off the whole of the activity due to thorium is not sufficient to cut off the whole of the activity due to uranium.

These differences between the maximum energy of β -rays and the total number of β -rays emitted per gm. of uranium and thorium at a particular energy provide us with two independent methods of separating these effects in ionisation experiment and determining from the absorption measurement both the uranium and thorium contents of rocks and minerals.

Measurement of total β -ray emission from radioactive rocks and minerals are complicated by the presence of the members of more than one radioactive series. Regarding the specimen as sufficiently old to reach radioactive equilibrium, the number of β -rays emitted per gm. per sec. is essentially the same for each member of a radioactive decay series and is evidently given by

$$N = \frac{6.06 \cdot 10^{23} \cdot q \cdot \lambda}{M}$$

where M is the molecular weight of a radioactive element, q the fractional concentration of a radioactive material in gm. per gm. of the solid and λ the decay constant. Thus for uranium substituting the value of λ (correcting for Ac-U) as given by Kovarik and Adams (1932), we have

$$N_U = \frac{6.06 \cdot 10^{23} \cdot 4.77 \cdot 10^{-18}}{238.14} = 1.22 \cdot 10^4 \text{ gm.}^{-1} \text{ sec.}^{-1}$$

while for thorium taking the value of $\lambda = 1.7 \cdot 10^{-18}$ as given by H. Fesefeldt (1933) or Rutherford (1910)

$$N_{Th} = 0.44 \cdot 10^4 \text{ gm.}^{-1} \text{ sec.}^{-1}.$$

THEORY.

A β -ray ionisation curve follows to a first approximation, the exponential form. Assuming it does so, the ionisation current due to β -rays can be used to measure both the energy and the amount of radioactive material. Let the ionisation current due to p gm. of uranium passing through an absorber thickness ' t ' be I_U , then

$$I_U = pI_{0U} e^{-\mu t}$$

to a first approximation, where I_{0U} is the ionisation current due to one gramme of uranium without using any absorber.

Similarly the ionisation current due to q gm. of thorium passing through an absorber thickness ' t ' may be expressed as

$$I_{Th} = q \cdot I_{0Th} e^{-\mu' t}.$$

Let us suppose that the unknown source contains p gm. of uranium and q gm. of thorium per gm. of the sample so that the total ionisation current for one gramme of the sample will be

$$I = I_U + I_{Th} = pI_{0U} e^{-\mu t} + q \cdot I_{0Th} e^{-\mu' t}$$

and

$$I' = I'_U + I'_{Th} = pI_{0U} e^{-\mu t'} + q \cdot I_{0Th} e^{-\mu' t'}$$

where I and I' are the total ionisation currents for absorber thickness t and t' .

From this p and q of the source can be determined.

If the ionisation current does not depend exactly exponentially with the absorber thickness our result remains unaltered, since the function I_U is proportional to the quantity of radioactive matter and decreases monotonously with increasing thickness ' t ' of the absorber. More rigorously the exact absorption curve of β -rays may be represented by adding a correction term to the exponential. The argument remains unaltered if this correction term is proportional to the amount of radioactive matter, which is a reasonable assumption.

EXPERIMENTAL ARRANGEMENTS.

For determining the U and Th-contents of rocks and mineral samples by measurement of their β -activity β -counters or linear amplifier and F.P. 54 circuit may be used. The total number of β -particles emitted per second from a given weight of the sample is estimated. There are certain disadvantages in carrying out such experiments with counter circuits, e.g. (1) Large number of counts over a long period of time are required to eliminate the statistical fluctuation; (2) Solid angle calculation comes into consideration in a complicated way; (3) Low energy β -particles may not be registered in the counters. The ionisation chamber in the F.P. 54 current amplifier circuit gives an estimate of the total ionisation current due to the β -rays. This

is a quicker method and is equal or better in sensitivity to the best type of electrometers.

The circuit set up in this laboratory for the present investigation is a modification of the circuit used by Dubridge and Brown (1933). The diagram of the present circuit with the circuit constants are the same as shown by Nag, Das and Das Gupta (1944). A Leeds and Northrup *R*-type reflecting galvanometer of sensitivity $4 \cdot 10^{-9}$ amp./mm. is used to detect the amplified current. The voltage sensitivity of the circuit is equal to 4,450 mm. per volt. With the resistance $R = 5 \cdot 10^{11} \Omega$ a current sensitivity of $2 \cdot 10^{-15}$ amp./mm. is obtained.

The circuit is normally adjusted and the filament is heated for several hours for steady emission. The chamber containing the F.P. 54 electrometer valve and the high grid leak resistance was evacuated to a desired pressure by means of a pump to prevent any moisture or humid air from reducing the grid leak resistance.

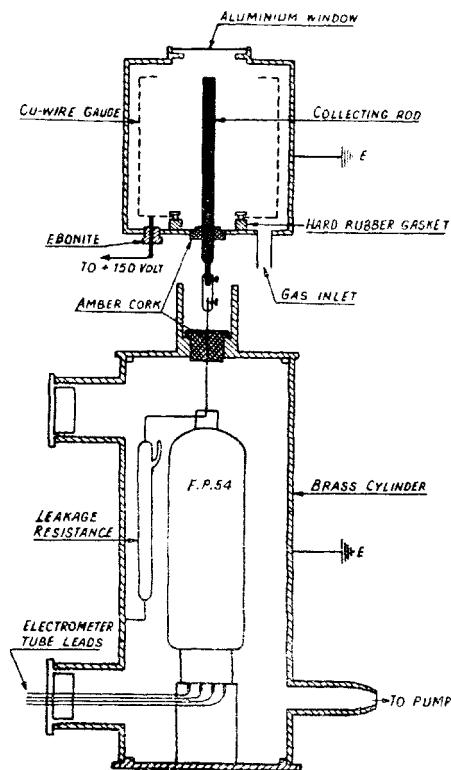


FIG. 2.

The ionisation chamber is shown in Fig. 2 and was constructed in this laboratory from a $3/16$ " brass cylinder, the diameter of which was about 10 cms. The height of the chamber was also about 10 cms. The chamber was provided with a window on the top for the passage of β -particles. The collecting electrode was a brass rod of about 2 mm. in diameter passing through an amber cork for insulating it from the main body of the chamber. The collecting electrode was again surrounded by a co-axial cylinder made from a sheet of copper net of mesh about 16 per sq. cm. The height as also its diameter was about 8 cms. This copper mesh cylinder was insulated from the brass chamber by means of a hard rubber gasket. A saturation voltage

of 150 volts was applied between this wall of the *cu*-mesh cylinder and the collecting electrode which forms the cathode and connected with the control grid of F.P. 54 electrometer tube. The ionising space is the gap between these two electrodes so that really the inner cylinder of *cu*-mesh together with the brass collecting rod formed the β -ray chamber of our experiment. The outer brass cylinder is earthed and is used to shield the ionisation chamber and the *cu*-mesh cylinder helps to minimise effects due to γ -ray by Compton recoil, etc. within the active volume of the ionisation chamber. The electrometer valve container shown in the same Figure consisted of an evacuated brass cylinder with various leads for electrical connection, and the grid leak high resistance and an amber seal at the top of the chamber for the connection to the collector rod of the ionisation chamber. The high leakage resistance was prepared by filling a clean pyrex glass tube 15 cms. in length and 1.5 mm. in diameter with pure xylol and sealing two tungsten electrodes at the two ends.

The source plate was prepared with the desired mineral sample as follows. The mineral was grinded to a very fine powder in agate mortar to obtain uniform mixing and was then sieved. It was then mixed with ethyl alcohol in a crucible and a diluted paste of the same was prepared. The paste was then poured over an aluminium plate whose weight was previously determined. It was then spread uniformly over a marked circle on the plate. The plate was then allowed to dry up and its weight was again taken. The difference between this and the previous weight gave the weight of the quantity of the mineral taken. The source was always protected by a thin film of cellophane paper. In each of the source plate the area of the marked circle was kept constant in order to make the geometry of the apparatus the same in each case. The collecting electrode was kept at a negative potential, since re-combination is less with the positive ions. The ion-currents leaking through the high resistance induced voltage on the control grid of the F.P. 54 and the galvanometer recorded the amplified plate current due to the change in grid voltage. The galvanometer gave a steady deflection which was a measure of the total activity due to the emitted β -particles. Total radioactivity and the uranium and thorium contents of the mineral samples, different readings of the galvanometer were taken using Al-absorbers of various thickness. The absorption curves of all the mineral samples examined as well as those of uranium and thorium have been shown in Fig. 1.

EXPERIMENTAL RESULTS.

TABLE I.

Name of the sample.	Absorber thickness in gm./cm. ²	Deflection in cm. from the graph for 0.1 gm. of uranium.	Deflection in cm. from the graph for 0.1 gm. of thorium.	Deflection in cm. from the graph for 0.1 gm. of the sample.	Radioactive concentration in the sample.
Samarските	0.325	7.3	..	0.30	U = (4.03 ± 0.1) × 10 ⁻² gm./gm.
	0.350	6.2	..	0.25	
	0.375	5.3	..	0.21	
	0.025	31.3	8.5	1.34	Th = (1.00 ± 0.1) × 10 ⁻² gm./gm.
	0.120	19.7	2.9	0.82	
	0.050	27.4	6.0	1.17	
	0.100	21.2	3.5	0.89	
	0.150	17.2	2.0	0.71	

TABLE I—continued.

Name of the sample.	Absorber thickness in gm./cm. ²	Deflection in cm. from the graph for 0.1 gm. of uranium.	Deflection in cm. from the graph for 0.1 gm. of thorium.	Deflection in cm. from the graph for 0.1 gm. of the sample.	Radioactive concentration in the sample.
Thorianite	0.320	7.4	..	1.6	U = (21.16 ± 1.1) × 10 ⁻² gm./gm.
	0.335	6.8	..	1.5	
	0.350	6.2	..	1.3	
	0.025	31.3	8.5	11.4	Th = (60.24 ± 2.0) × 10 ⁻² gm./gm.
	0.120	19.7	2.9	5.7	
	0.050	27.4	6.0	9.3	
	0.100	21.2	3.5	6.6	
	0.150	17.2	2.0	4.9	
Pitchblende	0.350	6.2	..	4.0	U = (65.3 ± 1.2) × 10 ⁻² gm./gm.
	0.400	4.5	..	3.0	
	0.450	2.8	..	1.8	
	0.025	31.3	8.5	21.1	Th = (7.23 ± 0.4) × 10 ⁻² gm./gm.
	0.120	19.7	2.9	13.1	
	0.025	31.3	8.5	21.1	
	0.075	24.0	4.5	16.0	
	0.100	21.2	3.5	14.1	

The results of analysis of the Indian minerals carried out in this laboratory show as in Table I that Pitchblende and Samarskite (from the Geological Survey of India) and Thorianite (Ceylon) have the thorium contents of $7.23 \cdot 10^{-2}$ gm./gm., $1.0 \cdot 10^{-2}$ gm./gm. and $60.24 \cdot 10^{-2}$ gm./gm. respectively, i.e. the respective percentage concentration is 7.2%, 1.0% and 60.2% of the thorium in the mineral. The uranium contents of the above minerals have also been determined. The percentage concentration of uranium in Pitchblende, Samarskite and Thorianite are 65.3%, 4.0% and 21.2% respectively. Due to the large proportion of uranium present in each of the above minerals examined, the determination of uranium concentration is much more reliable and accurate than that of thorium. Also since the activity due to uranium is about three times greater than that of thorium for the same weight, the accuracy of determination of uranium concentration is increased three times compared to thorium. This is another reason which facilitates the accurate determination of uranium. For the same reason the determination of thorium is more uncertain when the latter is present in comparatively low proportion in uranium-bearing minerals.

One of the samples of Das Gupta was tested as a check to our measurements. Our determination of uranium and thorium concentration in Thorianite from Ceylon gave the following percentage concentration in the mineral: U = 21.2% and Th = 60.2% while the determination of uranium and thorium concentration of the same mineral made by Das Gupta gave the following results: U = 20.1% and Th = 61.9%. Hence the agreement is fairly well and within the experimental errors and subject to uncertainties of the choice of the samples for measurements.

The present method suffers from the following defects: (1) It is useable only for fairly strong samples and not basalts and other weakly active rocks. (2) The approximation involved in neglecting the effects due to γ -ray and self-absorption. (3) The use of radioactive samples as standards.

The advantages of the method are (1) that it provides a ready method and quicker results, and (2) the approximations involved are within the errors of experiment from other sources and hence it gives as good results as before; so (3) this method gives good results where α -ray method fails, (4) this method can be suitably adopted for field experiment.

The β -rays of uranium or thorium are complex. The β -spectrum of uranium, for example, contains the β -rays from UX₁, UX₂, UZ, UY, RaB, RaC, RaC', RaD and RaE, besides electrons obtained from the conversion of the various γ -rays in the internal electron shells of the radioactive atom. It is a very difficult process to try to find out the β -spectrum of each of the emitting bodies, nevertheless it can be generally stated that in equilibrium 6 electrons are emitted for every uranium atom that disintegrates. If there are N uranium atoms, λN uranium atoms and $6\lambda N$ electrons are emitted per second. The electrons, however, have a complicated distribution of velocities which distribution remains unaltered after equilibrium is achieved. If the number of electrons of all velocities could be counted per second, a direct determination of uranium could be obtained but a large percentage of the slower electrons are cut off by the measuring device. Hence recourse has to be taken to a method of comparison using as a standard sample containing a known amount of uranium (in equilibrium) and calculating the amount of activity as proportional to the amount of uranium. An additional check is maintained by taking the absorption curves of the uranium and the minerals and making comparisons at various parts of the absorption curves. This also eliminates errors arising from photo-electrons and subsidiary electrons that usually accompany β -disintegration. A comparison with the maximum absorption equivalent of the RaC electron and that of uranium sample shows a large discrepancy due to the fact that near the maximum energy only a small number of electrons are emitted and are not detected in the ionisation chamber.

By the β -ray method discussed above we have been able to estimate the amounts of thorium and uranium present in the samples examined. There are not, however, sufficient data for determining the age of these minerals. To do so, it is required to estimate the amounts of different isotopes of lead present as end products of disintegration in the sample, by using a mass spectrograph. Efforts are being made for setting up one in our laboratory. Chemical analysis may yield the total lead content of the samples but that does not help to solve the problem unless the amounts of different isotopes of lead can also be estimated. It is hoped that in a future paper the further problem of isotope ratios of lead in these minerals may be dealt with.

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