

INVESTIGATIONS ON THE RADIOACTIVE CONTENTS OF CERTAIN INDIAN MINERALS.

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ABSTRACT.

The method of direct counting of α -rays emitted from rocks, developed by Finney and Evans, has been adopted for the determination of radioactive contents of Indian rocks and minerals. The countings were effected by setting up an electrometer tube along with an amplification circuit similar to that of Dubridge and Brown with a sensitive galvanometer of short time period. Sources were used in the form of thin films of the radioactive samples on aluminium disks, and the ionisation currents due to the emitted α -particles were detected by the movements of the light spot of the galvanometer on a scale. A properly adjusted circuit could detect a current of the order of 10^{-15} amp., thus making it possible to detect individual α -particle kicks and distinguish successive α 's up to 0.5 per second by naked eye estimations. The amount of Uranium or Thorium occurring separately or jointly in the samples can be determined by noting down the counts with different absorbers. A complete mathematical theory has been worked out by Finney and Evans. The Indian minerals Allanite (Ranchi), Thorianite (Ceylon), Columbite (Gaya) were examined and their Uranium and Thorium contents completely determined. Concentrations of 10^{-6} gms. of U or Th per gm. of rock or mineral could be estimated. Results of the earlier works have been collected as far as practicable and have been arranged systematically. Names of the radioactive minerals occurring in India have also been listed. The Thorium and Uranium contents of minerals which have been investigated have been given. The Pb contents and the lead ratio have also been mentioned in the case of thorianites, thorites and uranites.

INTRODUCTION.

Geochemical investigations have already been made on a few Indian minerals and the quantity of Thorium and Uranium have been estimated in them. Such investigations are only possible of a sample in a fairly pure and unmetamorphosed condition. The available results of these analyses are given in Table I. Actually however, these minerals occur as small intrusions in the mother rock and a more representative sample is the mother rock itself for the estimation of age or of radioactive contents. In basaltic rocks and other igneous rocks the whole rock may contain Uranium and Thorium distributed throughout its volume. Chemical methods fail completely when these small quantities have to be measured. The present method is very sensitive in this respect and is capable of detecting small quantities of Uranium and Thorium of the order of 10^{-7} gm. in 1 gm. of the mother rock. It is also capable of giving very quick and accurate results with minerals and strongly radioactive samples. In Table II is listed the Indian minerals which are known to be radioactive but U, Th determinations are incomplete.

The principle involved in the present method of detection of small quantities of radioactive matter is to count the α -particles given out from the radioactive source by the help of a shallow nitrogen ionisation chamber which is connected to the grid of a low input grid capacity valve like that of FP 54 electrometer tetrode. A galvanometer in the plate circuit of the valve registers a small ionisation current in the chamber by a throw proportional to the ionisation current due to an α -particle traversing the ionisation chamber.

TABLE I.

	U	Th	Pb	$\frac{\text{Pb}}{\text{U} + 0.36\text{Th}}$
<i>Thorianites from Ceylon.</i>				
Blake (1905) (a)	9.87	63.50	2.09	0.062
" (b)	12.87	69.32	2.40	0.064
" (c)	10.87	67.00	2.66	0.067
Jones (1906) (a)	11.36	69.42	2.36	0.065
" (b)	27.76	51.72	2.38	0.051
" (c)	24.81	54.64	2.13	0.048
" (d)	23.74	55.69	2.69	0.061
" (e)	22.91	55.66	2.77	0.065
Imp. Inst. London (1910) (a)	21.16	45.00	2.77	0.074
Ramsay (1904)	13.14	67.16	1.86	0.050
Büchner (1907)	11.13	62.37	2.25	0.067
Dennison (1907)	12.64	67.16	1.86	0.050
Gimingham (1907)	11.22	68.14	3.17	0.089
Rosignol (1907)	10.98	67.74	2.24	0.063
Kobayashi (1912) (a)	28.21	51.31	3.53	0.076
" (b)	28.19	52.28	3.49	0.074
" (c)	12.33	68.56	2.47	0.067
Jacob and Toloczko (1911)	19.90	57.46	2.66	0.066
Hönigschmid (1919) (a)	11.80	68.90	2.34	0.064
" (b)	20.20	62.70	3.11	0.073
" (c)	26.80	57.00	3.50	0.074
<i>Thorites and Uranite from Ceylon.</i>				
Soddy and Hyman (1914)	0.72	54.45	0.36	0.180
Imp. Inst. (1914) (b)	3.41	59.11	0.81	0.032
" (c)	4.56	61.64	1.30	0.049
" (d)	1.87	65.31	1.71	0.067
Blake (1906)	71.22	7.88	4.80	0.065
<i>Uranites from Gaya district, Bihar, India.</i>				
Tipper (1919) (a)	56.17	11.60	11.59	0.192
" (b)	29.46	20.36	17.72	0.48
Croper (1902)	67.46	8.66	0.12
Holmes (1919)	64.30	8.92	0.13

THEORY.

The theory of emission of α -particles from a solid of finite thickness has been already worked out by Finney and Evans (1935), and they obtained the number of counts per cm.³ per sec. with an absorber of thickness a to be

$$n_a = \frac{N\mu\tau}{4} [2(R-\rho-a)-\tau]/(R-\rho)$$

where N = number of α -rays emitted per sec. per sq. cm. of the source with a mean range of R air cm.

μ = absorption coefficient of the source.

τ = thickness of the source in air cm.

ρ = minimum residual range above the absorber which can be detected by the recording instrument.

If now the source thickness be such that $\tau = R - \rho - a$ then

$$n_a = \frac{N\mu}{4} (R-\rho-a)^2/(R-\rho) \quad \dots \quad \dots \quad \dots \quad (1)$$

N may be expressed in terms of the fractional concentration of radioactive material Q gm. per gm., its decay constant λ sec.⁻¹, its atomic weight W and the density d of the source; thus:

$$N = 6.06 \times 10^{23} Q\lambda d/W \quad \dots \dots \dots (2)$$

Complications arise in this formula when there are more than one element, i.e. U+Th occurring together and several ranges of α 's have to be taken into account.

With an absorber a we then have $n_a = v_a U + w_a Th$
 and with b $n_b = v_b U + w_b Th$

where $v_a, v_b; w_a, w_b$ are the number of counts from one gm. of the sample with an absorber a or b when U gm. of Uranium and Th gm. of Thorium are present.

Combining these two equations

$$Th = \left(\frac{n_a}{w_a}\right)\left(\frac{n_b - v_b}{n_a - v_a}\right) / \left(\frac{w_b - v_b}{w_a - v_a}\right) \quad \dots \dots \dots (3)$$

$$U = \left(\frac{n_a}{v_a}\right)\left(\frac{w_b - n_b}{w_a - n_a}\right) / \left(\frac{w_b - v_b}{w_a - v_a}\right) \quad \dots \dots \dots (4)$$

Here n_a, n_b are values which can be observed experimentally, while v_a, v_b, w_a, w_b are computed theoretically with the help of a table given by Finney and Evans (*loc. cit.*).

TABLE II.

Name of the mineral.	U & Th in % wt. of the mineral.	Locality.	Name of the mineral.	U & Th in % wt. of the mineral.	Locality.
1. Allanite or orthite.	Sankara allanite contains $U_3O_8 = 5.39\%$	Gaya, Nellore (Sankara).	8. Samarskite	??	Nellore micr belt.
2. Columbite ..	$U_3O_8 = 0.80\%$	Gaya.	9. Sipykite ..	??	Sipykite is reported to occur in a mica pegmatite about 3 miles to the north-west of Sankara mine in association with Samarskite.
3. Cyrtolite	Nellore.			
4. Gadolinite ..	??	Bombay, Palanpur.			
5. Hatchetolite	??	Travancore.			
6. Monazite ..	Travancore monazite contains ThO_2 , 9 to 10%. Ceylon variety contains ThO_2 10%.	Travancore, Ceylon.	10. Torbernite.	??	Occurs in mica bearing pegmatites, Gaya.
			11. Tscheffkinitite.	??	Salem, Madras.
			12. Xenotime	??	A yttrium phosphate with cerium has been reported from Aru-Buru, Bihar.
7. Pitchblende	$U_3O_8 = 66.24\%$	Singer zemin-dary, Gaya. Abraki pahar south-west of Pichhli.	13. Zircon ..	??	Kanagayam, Coimbatore district, Seitur graphite mine, Ramnad, Madras, Nellore, Gaya.

Moll type, the sensitivity being 7×10^{-8} amp. per mm. so that ionisation currents of 2×10^{-15} amperes gave 1 mm. throw.

The circuit was normally adjusted and the filament was heated for several hours for steady emission. A pump was run to evacuate the chamber containing the F.P. 54 electrometer valve and the high grid leak resistance, to prevent any moisture or humid air from reducing the grid leak resistance. The source plate was prepared with the desired mineral and was placed in the ionisation chamber. It was kept at a positive potential of 60 volts supplied from a dry battery, the negative of which was grounded.

The α -particles from source plate ionised the nitrogen gas inside the chamber. The collecting electrode was negative with respect to the source electrode and therefore collected the positive ions. The ion-currents leaking through a high resistance induced a voltage on the control grid of the F.P. 54 and the amplified plate currents due to the grid voltage were recorded by the galvanometer. The ionising agents being the intermittent α -particles, the movements of the light spot of the galvanometer were in the form of kicks. The number of kicks per second determined the number of α -particles emitted from the source per second corrected by the factor of solid angle and the formula given earlier. From the number of counts the radioactive contents of the minerals were calculated. Each mineral was examined with two different absorbers and its Th and U contents were found out from (3) and (4). For each of the samples a neutral observation was taken for background counting due to spurious counts and contaminations without the source on the plate. These background counts were subtracted from the counts with source. Corrections for statistical fluctuations were also taken into account by counting over a very long period of time. The circuit could resolve counts of about 30 per minute.

The F.P. 54 Container, the Ionisation Chamber.

The electrometer valve housing chamber which is shown in fig. 3 was constructed in the laboratory from $\frac{1}{16}$ " rolled brass sheet, brass being chosen for having very little radioactive contamination. The sheet was rolled into a cylinder about 20 cm. in height and 10 cm. in diameter. One end of the cylindrical chamber was firmly soldered while the other end was made tight by an outside fillet of soft solder. The two side tubes were for the leads of F.P. 54. The cylinder was provided with a proper base for the F.P. 54.

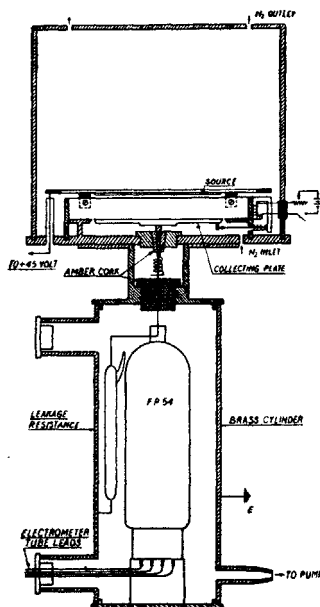


FIG. 3.

TABLE III.

Absorber.	Amount of the mineral per gm. of the mixture.	Back-ground counts per hour.	Time in hours.	Count N	Count/hour $\frac{N}{T} \pm 68 \frac{\sqrt{N}}{T}$	Count/hour due to source alone.	v_a	w_a	Radioactive concentrations in the mineral.
Allanite (Ranchi).									
2-19 air cm.	10 ⁻² gm./gm. of the mixture.	12.75 ± .54 hr. ⁻¹	5 hrs.	1358	271.6 ± 5.01 hr. ⁻¹	258.85 ± 5.038 hr. ⁻¹	3899.6	2384.46	Th = (3.004 ± .17) × 10 ⁻³ gm./gm. U = ? ~ (16.6 ± .9) × 10 ⁻⁶ gm./gm.
3-8 "	"	"	10 hrs.	812	81.2 ± 1.94 hr. ⁻¹	68.45 ± 2.014 hr. ⁻¹	346.7	632.06	
Columbite (Gaya).									
0.78 air cm.	10 ⁻³ gm./gm. of the mixture.	12.75 ± .54 hr. ⁻¹	5 hrs.	9767	553.4 ± 7.1 hr. ⁻¹	540.65 ± 7.17 hr. ⁻¹	17636	9088.6	Th = (5.2 ± .13) × 10 ⁻⁴ gm./gm. U = (7.987 ± 1.12) × 10 ⁻³ gm./gm.
2-19 "	"	"	10 hrs.	1337	133.7 ± 2.48 hr. ⁻¹	120.95 ± 2.54 hr. ⁻¹	3899.6	2384.46	
4-9 "	1 gm./gm. of the mixture.	"	5 hrs.	1668	333.6 ± 8.17 hr. ⁻¹	320.85 ± 8.18 hr. ⁻¹	171.217	
Thorianite (Ceylon).									
2-19 air cm.	10 ⁻⁴ gm./gm. of the mixture.	12.75 ± .54 hr. ⁻¹	5 hrs.	4132	826.4 ± 8.74 hr. ⁻¹	813.65 ± 8.75 hr. ⁻¹	3899.6	2384.46	Th = (61.94 ± 2.2) × 10 ⁻² gm./gm. U = (20.08 ± 1.42) × 10 ⁻³ gm./gm.
4-9 "	"	"	15 hrs.	76.4	50.33 ± 1.25 hr. ⁻¹	38.18 ± 1.361 hr. ⁻¹	171.217	

The collecting electrode of the ionisation chamber (fig. 2) is an aluminium disk of 10 cm. in diameter surrounded by an annular brass guard ring, 2.5 cm. wide, with an annular gap of 1 mm. all round the aluminium electrode. The function of the guard ring is to protect the electrode system from leakage currents and to provide electrostatic shielding. The upper electrode is also an aluminium disk (containing the grounded source), placed 2 cm. above the lower collecting plate and is mounted on a brass ring to which it can be secured. The brass ring itself is supported by Bakelite blocks and fixed to the brass cylinder supporting the guard ring as shown in fig. 3. The ionising space is the gap between these two electrodes. The lower collecting electrode is secured to a brass rod which passes through an amber cork insulated by ebonite from the main body of the chamber into the said brass housing of the F.P. 54. The brass housing also contains the high leakage resistance $R = 3 \times 10^{11} \Omega$ as shown in fig. 3. The high resistance was constructed in the laboratory by filling a quartz tube of 10 cm. length and 2 mm. diameter with pure Xylol.

The minerals examined were generally in massive forms. They were first broken to pieces and then crushed and mixed well to a fine powder in an agate mortar to assure a uniform sampling and then sieved through 170 mesh sieve which gave a mean diameter of .015 cm. to the powder particles. A weighed quantity of these fine powders were mixed with a weighed quantity of plaster of paris to minimise the strength of the minerals and were deposited in thin layers on the aluminium disks. Thus prepared the source plates which were the upper electrodes of the ionisation chamber described earlier. The final results are shown in tabular form together with the estimated errors in Table III.

The method of α -ray counts to estimate quantitatively U and Th in rocks and minerals has been used successfully for concentrations of 1 part in a million. The difficulties in such estimations are the presence of contaminating radioactivity in the metals of the ionisation chamber of the same order of magnitude and the tedium of having to count over very long periods of time by the eye to obtain a reasonably accurate estimate. The errors involved could be brought down to quite low value by greatly extending the time of counting. It is interesting to compare the values obtained by the method with available data. The analysis of Ceylon thorianite is comparable to the values $U = 20.2\%$, $Th = 62.7\%$ obtained by Honigschmidt (1919b) in his analysis of a similar sample of Ceylon thorianite. The sample of Allanite from Ranchi has been chemically examined by Dr. P. B. Sarkar (1941) and yielded a value of $Th = 2.99 \times 10^{-3}$ gm./gm. of the mineral and compares favourably with our results. It would be useful to develop a continuous recording device to extend measurements over a number of days. It would be necessary to determine the amounts of Th- and U-lead for determination of age unambiguously.

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The figures at the end of each reference, viz. a, b, c, denote the minerals so marked in the tables.

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