1945/31

C.3

PRELIMINARY REPORT ON
RADIOACTIVITY TESTS ON
RADIUM HILL SAMPLES.

PLAN No. 1233

012635

J.C. Dooley.

DEPARTMENT OF SUPPLY AND SHIPPING.

Mineral Resources Survey Branch.

PRELIMINARY REPORT ON RADIOACTIVITY TESTS ON RADIUM HILL SAMPLES.

Report No. 1945/31.

Plan No. 1233

INTRODUCTION.

The work described in this report forms part of the uranium investigation being conducted by the Commonwealth Government for the British Government. It was carried out at the request of Mr. S.B. Dickinson, Director of Mines of South Australia, who is the delegate of the Controller of Minerals Production and in charge of the investigation.

By arrangement with Mr. Dickinson, 94 samples from the Radium Hill workings, S.A., were submitted to the Mineral Resources Survey for determinations of relative radioactivity, with a view to making estimates of their uranium content. The tests on them were conducted at Canberra between 30th April and 1st June, 1945. After the determinations were made a suite of these samples was selected and submitted to Mr. Dickinson for assay for uranium and thorium by the South Australian School of Mines. Estimates of the uranium content of the remaining samples will depend on the results of these assays.

This report is an interim one pending the completion of the assays.

Similar work was previously carried out by the writer (1945) on samples from Mount Painter, South Australia, and reference should be made to the report on that work for a discussion of the limitations of accuracy involved in making uranium estimates from radioactivity measurements. The particular applications of this discussion to the Radium Hill type of sample are considered below.

The Geiger-Muller equipment used for the determination of the Radium Hill samples differs from that used in the previous work, in that an electrical counter is used to record the number of active particles arriving at the Geiger-Muller tube, instead of a meter measuring the rate of arrival of the particles.

SPECIFIC PROBLEMS ASSOCIATED WITH THE RADIUM HILL ORE.

The primary ore consists of iron oxide minerals with a high content of titanium, and with small amounts of uranium, vanadium, cerium, thorium, etc. Sir D. Mawson (1944) states that the minerals include ilmenite, ilmenite-davidite combination, titano-magnetite, martitised magnetite, titano-hematite, ilmeno-rutile, rutile and rarely minute quantities of davidite. The latter mineral contains oxides of iron, titanium, rare earths, and uranium. Where the remaining minerals are radioactive due to the presence of uranium, Mawson infers that davidite is present in solid solution. The titaniferous iron oxide complex is commonly but erroneously referred to as 'ilmenite' and for convenience this term has been used in the report. As the above minerals are primary ores, they can be presumed to be of sufficient age for the uranium radioactive series to have reached radioactive equilibrium.

From the uranium in the 'ilmenite', the secondary mineral carnotite is formed by weathering and appears as a yellow stain on the primary minerals. Sir D. Mawson (1944) states that the carnotite contains 47.8 per cent of uranium oxide; thus uranium is being removed from the 'ilmenite' while its disintegration products remain, and the equilibrium conditions in the 'ilmenite' are disturbed. As the carnotite ages, the uranium contained in it disintegrates, forming again the radioactive series which reaches radioactive equilibrium in about a million years. Simultaneously the excess disintegration products in the 'ilmenite' disintegrate more rapidly than the uranium itself, restoring the equilibrium conditions in the primary ore in about a million years. It can be shown that the excess of disintegration products in the primary ore at any time exactly balance their deficiency in the secondary ore formed from it. Thus if the primary and secondary ores are taken together, each product is present in the same proportion as in the case of a uranium ore in radioactive equilibrium, and the total activity from the uranium series is proportional to the total amount of uranium present. This depends on the formation of the carnotite in close proximity to the primary mineral from which it was formed.

Thorium occurs in Radium Hill ore, and the activity readings include the radiations from the uranium and thorium series. One analysis of Radium Hill ore quoted by Sir D. Mawson (1944) shows 0.13 per cent ThO_2 in a sample containing 2.25 per cent U_3O_8. This small content of thorium should not seriously affect the results, as the activity of the thorium series is somewhat less than that of the uranium series. Other analyses give thorium grouped with cerium, lanthanum and yttrium, as about 3 per cent. Radium prepared from Radium Hill ore is reported by Sir D. Mawson (1944) and Thomas (1942) to contain very little of its isotope mesothorium I. As the latter is a disintegration product of thorium, and cannot be separated chemically from radium, this would indicate that there is not much thorium present in the ore treated. The South Australian School of Mines has been asked to determine the thorium as well as uranium in the samples selected for assay, in order to give more information on this point.

As far as the uranium in the ore is concerned, the radioactivity measurements are due to total uranium content. The methods of treatment of the ore to recover the acid soluble uranium contained in the carnotite differ considerably from those for the acid insoluble uranium in the 'ilmenite' as described by Thomas (1942). In the past the carnotite was lost and only the 'ilmenite' recovered and treated. Thus it may be desirable to make separate determinations of acid-soluble and acid-insoluble uranium. It is impossible to do this by radioactivity methods without first treating the samples chemically to separate the acid-soluble uranium, which could then be determined by alpha-ray measurements. However, it is comparatively easy to assay the acid-soluble uranium chemically, and this may be simpler than the method outlined above. The chief purpose of the present tests is to reduce the difficult work involved in assaying for the acid-insoluble uranium.

DESCRIPTION OF EQUIPMENT.

The equipment used was made up in the workshop of the Mineral Resources Survey. It has been used previously in the field at Radium Hill by Messrs. J.M. Rayner and C.H. Zelman, and in the laboratory by Mr. Rayner, who made some tests on previously assayed Mount Painter samples, and showed that an approximately linear relation exists between count-rate and uranium content.

The Geiger-Muller tube is supported horizontally inside a wooden box surrounded by a lead-screen 2.6mm. thick, which serves to screen the tube from alpha and beta radiations. All measurements thus depend on gamma rays. The tube in its box and screen is placed in position on a wooden stand. Samples to be tested are held in a rectangular glass container or cuvette which can be placed on the wooden stand in either of two positions fixed relatively to the Geiger-Muller tube.

The amplifying and recording equipment has been modified from a circuit described by Strong (1939). A circuit diagram is attached. Pulses from the Geiger-Muller tube are passed through one stage of amplification using a type 57 valve. The positive amplified pulses are then fed to the grid of a thyratron type 885, with a Cenco electrical counter in its anode circuit. When the circuit components are correctly adjusted, each pulse triggers the thyratron, drawing a surge of current through the counter, which thus records each particle that causes the Geiger-Muller tube to conduct.

When this counting equipment was used in the field at Radium Hill, all voltages were obtained from batteries. In the tests to be described, voltages were obtained through power packs from the A.C. mains.

RANDOM VARIATIONS IN COUNT-RATE.

The arrival of particles at the Geiger-Muller tube causing it to discharge is by no means regular. It has been found that they conform to a purely random distribution; i.e. the chance of arrival of a particle in an interval of time of fixed duration is constant; in particular the chance of arrival of a particle is not affected by the arrival of previous particles. A proof given by Lewis (1942) for these circumstances shows the chance W_n of n particles arriving in a given time t as -

$$W_n = \frac{(\lambda t)^n}{n!} \cdot e^{-\lambda t}$$

where λ is the average count-rate taken over a very long period of time. From this expression the mean deviation D from the true count, of a count taken over t and defined as the square root of the probable value of $(n - \lambda t)^2$, can be calculated; it is found that -

$$D = \sqrt{\lambda t}$$

Thus the mean departure d of the count-rate n/t from the true average count-rate is

$$d = \frac{D}{t} = \sqrt{\frac{\lambda}{t}} = \frac{\lambda}{\sqrt{\lambda t}} \approx \frac{\lambda}{\sqrt{n}}$$

and the percentage error in the count-rate is -

$$100 . \frac{d}{\lambda} = \frac{100}{\sqrt{n}}$$

Thus the probable error in the average count-rate decreases with the square root of the total count, and the accuracy of the measurements can be increased by taking counts over a longer period. In the present work, the count-rate varied from about 90 to 250 counts per minute, and most of the counts were taken over a period of 10 minutes. Thus the mean uncertainty of the count-rates due to random variations would vary from about 3.3 per cent for the count-rate of 90 per minute to 2 per cent for the count-rate of 250 per minute. Table I shows the measurements of the normal count-rate over a typical run, illustrating the random variation.

TABLE I.

Normal readings during one run of the equipment, commencing at 1.30pm. of 17th May, 1945.

Total Count	Time, mins.	Count/min.	Departure from mean d	d^2
985	10	98.5	+6.9	47.5
909	10	90.9	-0.7	0.5
934	10	93.4	+1.8	3.2
915	10	91.5	-0.1	0.0
896	10	89.6	-2.0	4.0
879	10	87.9	-3.7	13.7
942	10	94.2	+2.6	6.8
890	10	89.0	-2.6	6.8
893	10	89.3	-2.3	5.3
	Mean =	91.6	Mean =	9.8

From the preceding table the following values are obtained -

$$\text{Root mean square departure} = \sqrt{9.8} = 3.1$$

$$\text{Theoretical mean square departure (for 10 min. reading)} = \frac{\sqrt{915}}{10} = 3.0$$

PROCEDURE.

Samples submitted for test weighed about ¼ lb. each and had been pulverized. Each sample was quartered, and 100 gm. was weighed out. The 100 gm. sample was placed in a glass cuvette of internal thickness about ⅜ in., internal width about 2⅝ in., and wall thickness about ⅛ in. The sample was packed down to a level indicated by a mark on the cuvette about 2¼ in. from the bottom. The cuvette could be placed on a wooden stand in either of two positions fixed relatively to the Geiger-Muller tube, with its wider face parallel to the axis of the tube. The distance from the centre of the tube to the near surface of the sample was about 2¼ inches in the first position, and about 3⅞ inches in the second position.

The normal or background count-rate, i.e. the count-rate which is measured with no samples near the tube, was found to average 93.0 per minute. The count-rate varied considerably with the voltage applied to the Geiger-Muller tube. Its 'Plateau', or region of minimum variation of count-rate with voltage, was found to be between 1170 and 1250 volts. The voltage during readings was maintained as close to 1200 volts as possible. The equipment was usually run for half-day periods, alternating measurements of the normal count-rate with measurements on samples, each measurement occupying about 10 minutes. The average of all the normal count-rates for each half-day period was calculated, and this was subtracted from the count-rate for each sample tested during that period to obtain a measure of the activity of the sample.

A standard sample was made using 70 gm. of sample A (see section on 'Calibration') in a glass cuvette similar to that used for the samples to be measured. Counts were made with this standard in the second position at the beginning and end of each half-day's run. These were taken as a check on the sensitivity of the instrument. It was found that the ratio of the count-rate with the standard sample in position to the normal count-rate was constant within the limits of random variations. The normal count rate was used in determining the relative sensitivity of the instrument for each run, as more readings were taken of the normal than of the standard, and therefore the normal count-rate gave a better average. A count-rate of 100 per minute was taken as an arbitrary value for the normal, and all samples in a given half-day's run were multiplied by $100/n_o$, where n_o is the average normal count-rate for that run.

When a pulse is registered on an electrical counter, the counter is rendered insensitive for a short interval of time t_o, and any further pulses arriving in this interval are not registered. If N pulses per unit time are registered, the counter is inoperative for a fraction (Nt_o) of the total time for which a reading is taken. Thus the true count-rate is given by $\frac{N}{1 - Nt_o}$. The resolving time of the counter used is not known, but it was found advisable to keep the count-rate below about 250 per minute. Some tests on the addition of two samples showed that there was no appreciable loss of counts at this rate. In order to reduce the count-rate, samples which showed high activity (as indicated in a brief preliminary test) were tested in the second position, while lower grade samples were tested in the first position (closer to the Geiger-Muller tube) to obtain increased sensitivity.

CALIBRATION.

Three samples were prepared from Radium Hill ore and labelled A, B, and C, as follows -

A. Hand-picked 'ilmenite'.
B. 'Ilmenitic' ore containing some country rock.
C. Country rock, comprising massive biotite, black mica schist, and grey gneissic rock.

Each sample was pulverized to pass 30 mesh, and thoroughly mixed, and 100 gm. selected by quartering. Three mixtures were made, one of 50 gm. A with 50 gm. C, another of 50 gm. B with 50 gm. C, and the other containing 5 parts B with 2 parts A. The activity of these samples was measured by the method outlined above. Counts were taken on these samples over intervals of about 10 minutes with an aggregate of about 60 minutes for each sample.

After measurements had been made on about half of the samples submitted for test, five of them (Nos. 3204, 3221, 3229, 3245 and 3247) covering a wide range of activities were selected. Further measurements were made on these samples to a total of about 60 minutes each. These five samples together with the samples A, B and C, were sent to Mr. S.B. Dickinson for assay by Mr. Dalwood, South Australian Government Assayist, for uranium and thorium. Their relative activities and the activities of the mixtures are given in Table II.

TABLE II.

Relative activities of samples to be used as standards.

Sample.	Relative Activity.
A	300.1
5B-2A	234.0
B	208.7
50% A-50% C	162.1
50% B-50% C	115.1
C	9.2
3247	208.3
3221	119.3
3245	97.5
3229	60.4
3204	5.4

Several of these standard samples were tested in both the first and second positions, and the ratio of the count rates was calculated. The average ratio of the count rates in the first position to those in the second position was found to be 1.85. The count-rates of samples which were tested in the second position were therefore multiplied by 1.85 in order to compare them with those tested in the first position.

A considerable variation in density of the samples was found, the ilmenite being much denser than the country rock. Because of this it was not possible to make all the 100 gm. samples occupy the same volume in the cuvette. A few of the denser samples were found to settle down below the mark on the cuvette without any attempt at packing. Therefore a second mark was made on the cuvette about 1¼ inch from the bottom, to which the denser samples were packed for testing. All dense samples were tested in the second position. A 100 gm. sample was prepared mixing samples A and B in the ratio of 2 : 5, and this sample was of such a density that it could be packed to either mark on the cuvette. When this sample was packed to the higher mark, its count-rate in the second position was found to be 1% greater than when it was packed to the lower mark. Hence the count-rates of samples packed to the lower mark and tested in the second position were multiplied by 1.87 instead of 1.85, in order to compare them with the lighter samples tested in the first position.

TESTS OF ORE SAMPLES.

The samples submitted for test were numbered 3201 to 3234, 3236 to 3257, 3301 to 3307, and 3401 to 3431 inclusive. The selected 100 gm. from each sample was tested for 10 minutes, and the count-rate per minute was reduced to the equivalent count for the first position and packing to higher level, as explained above in the section on 'Calibration'. Two lists of the results are given, Table III with the samples arranged in numerical order, and Table IV in decreasing order of activity. The mean uncertainty of the activities is estimated to be about ± 5; thus it cannot be claimed that samples whose activities are less than 5 contain any radioactive material.

After testing, the 100 gm. used was mixed again with the remainder of the sample and the completed samples returned to Mr. Dickinson.

The 100 gm. lots which were used for the detailed measurements of the samples used as standards were not mixed with the rest of the samples, but were forwarded separately for assay. The activities for these samples given in Table II refer to measurements made on the 100 gm. lots only; in Table III and IV, the readings given are the average of all measurements made on these samples.

When the assay results are to hand it is anticipated that if the thorium content is not high it will be possible to convert the activity readings into equivalent uranium percentages.

If the thorium content is appreciable but the thorium/uranium ratio reasonably constant, such a conversion may still be possible.

If on the other hand, the assay results show that the thorium content of the samples is variable and sufficiently high to contribute an appreciable part of the total radiation from the samples, it may be possible by carrying out additional tests, such as perhaps the measurement of the absorption coefficients of the gamma rays emitted by the samples, to determine the relative amount of uranium and thorium present.

J.C. Dooley

CANBERRA.
23rd June, 1945.

(J.C. Dooley)
Geophysicist.

REFERENCES.

Dooley, J.C. (1945). Report on Geophysical Work at Mount Painter. using G.M. Equipment, Comm. Min. Resources Sur. Report No. 1945/30.

Lewis, W.B. (1942) Electrical Counting, Cambridge University Press, Chap.X.

Mawson, Sir Douglas (1944). The Nature and Occurrence of Uraniferous Mineral Deposits in South Australia. Trans. Roy. Soc. S.A., Vol.68 (2).

Owen, H.B. & Thomas R.G. (1943) Uranium Minerals in Australia - joint C.S.I.R./M.R.S. Report; Comm. Min. Resources Sur. Report No. 1943/24.

Strong, J. (1939) Procedures in Experimental Physics, Prentice-Hall Inc., N.Y. p.283.

Thomas, R.G. (1942) Processing of Radium Ores in South Australia. Aust. Chem.Inst.Jour. & Proc., vol. 9, No.6.

TABLE III.

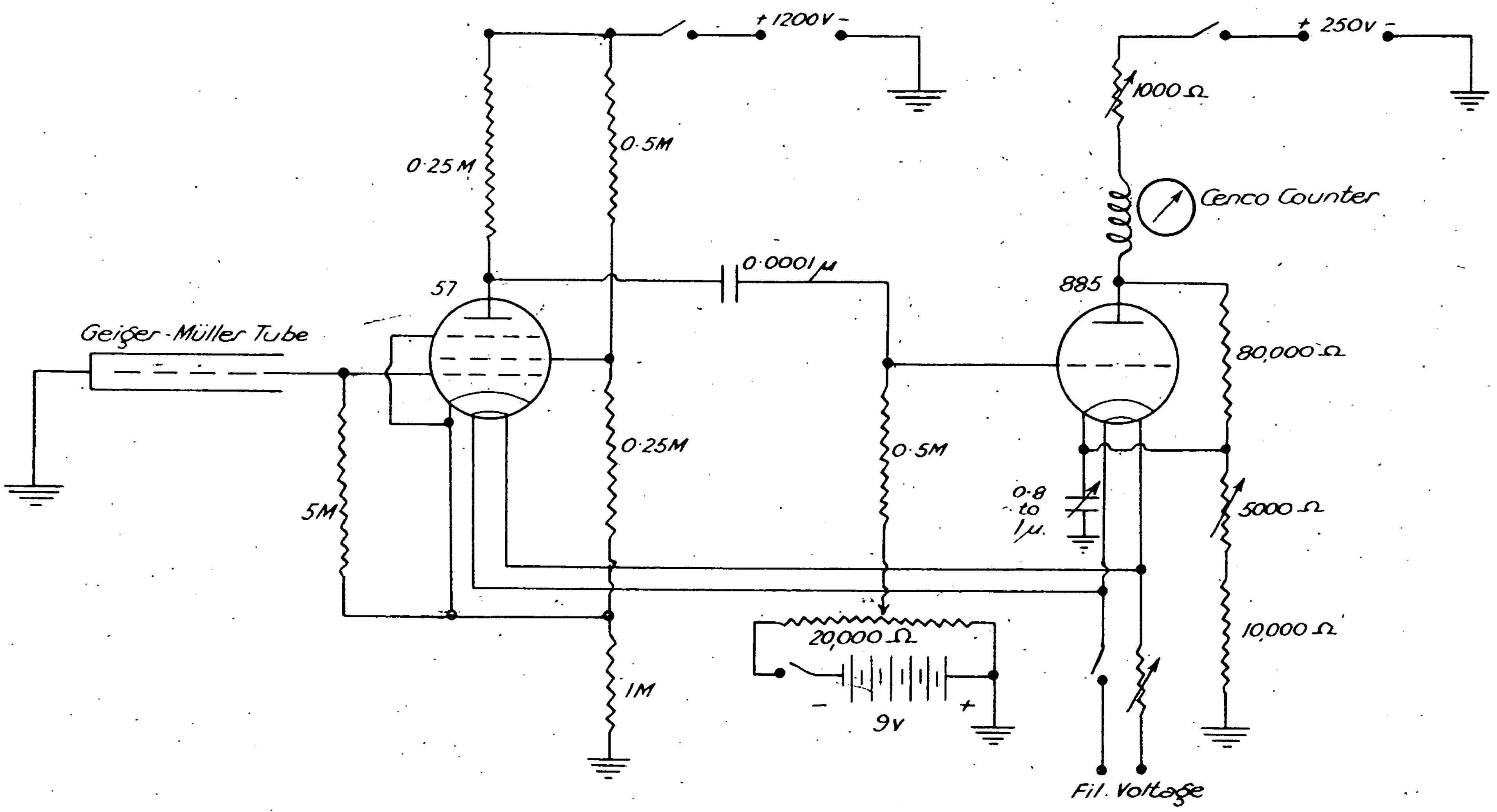
Relative activities of Radium Hill samples, submitted for test.

Sample No.	Relative Activity.	Sample No.	Relative Activity.
3201	0	3251	40
3202	21	3252	149
3203	19	3253	62
3204	5	3254	54
3205	0	3255	37
3206	5	3256	4
3207	4	3257	30
3208	0	3301	56
3209	8	3302	5
3210	4	3303	7
3211	19	3304	18
3212	41	3305	5
3213	17	3306	18
3214	11	3307	30
3215	10	3401	4
3216	11	3402	14
3217	10	3403	60
3218	2	3404	130
3219	28	3405	0
3220	5	3406	10
3221	121	3407	1
3222	129	3408	90
3223	154	3409	3
3224	179	3410	0
3225	174	3411	153
3226	84	3412	108
3227	6	3413	99
3228	39	3414	4
3229	60	3415	35
3230	8	3416	8
3231	8	3417	0
3232	12	3418	45
3233	7	3419	28
3234	8	3420	6
3236	28	3421	92
3237	1	3422	33
3238	2	3423	29
3239	7	3424	15
3240	0	3425	64
3241	48	3426	65
3242	11	3427	45
3243	98	3428	27
3244	17	3429	34
3245	96	3430	22
3246	32	3431	21
3247	207		
3248	0		
3249	18		
3250	10		

TABLE IV.

Relative activities of Radium Hill samples, in decreasing order of activity.

Sample No.	Relative Activity.	Sample No.	Relative Activity.
3247	207	3304	18
3224	179	3213	17
3225	174	3244	17
3223	154	3424	15
3411	153	3402	14
3252	149	3249	13
3404	130	3232	12
3222	129	3242	11
3221	121	3214	11
3412	108	3216	11
3413	99	3250	10
3243	98	3215	10
3245	96	3217	10
3421	92	3406	10
3408	90	3209	8
3226	84	3231	8
3426	65	3416	8
3425	64	3234	8
3253	62	3230	8
3229	60	3239	7
3403	60	3303	7
3301	56	3233	7
3254	54	3227	6
3241	48	3420	6
3427	45	3204	5
3418	43	3302	5
3212	41	3206	5
3251	40	3220	5
3228	39	3305	5
3255	37	3414	4
3415	35	3210	4
3429	34	3207	4
3422	33	3401	4
3246	32	3256	4
3257	30	3409	3
3307	30	3218	2
3423	29	3238	2
3236	28	3237	1
3419	28	3407	1
3219	28	3205	0
3428	27	3248	0
3430	22	3410	0
3431	21	3208	0
3202	21	3201	0
3203	19	3417	0
3211	19	3240	0
3306	18	3405	0



GEIGER-MULLER COUNTER RECORDING
CIRCUIT DIAGRAM

J. C. Dooley
6·6·45.

1233