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EQUIPMENT FOR THE DETERMINATION OF RADON AND RADIUM IN WATER.

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ABSTRACT

The design and operation of equipment for the determination of radon and radium in water are described. The results of tests on a few Victorian spring waters are given.

Results indicate that the equipment and technique described are satisfactory and that the spring waters tested contain measurable amounts of radon. A systematic programme of testing Victorian spring waters is being put into effect.

1. INTRODUCTION

Measurements made in various parts of the world show a great variation in the concentration of the naturally occurring radioactive elements, radium uranium, thorium, radon and thoron, in ground waters.

A survey of the literature made by Healy (1952) has shown that the concentrations of these elements may vary over the ranges shown below. These figures apparently refer to radioactivity derived from rocks and not from deposits of radioactive minerals.

'Radium:

Concentrations in springs may be up to 10^{-4} µc/l (microcuries per litre) (Bandish and Brewer, 1939).

Radon:

Concentrations are normally between 10^{-1} and 10^{-5} µc/l, the higher values being found in springs and wells and the lower values in turbulent streams. Tap water may be depleted of dissolved radon because of the turbulence and pressures encountered in pumping. (Delaby et al, 1931 and Latour 1949).

Uranium:

Most natural waters contain 5×10^{-7} to 3×10^{-5} grams per litre (g/l) (Singlevich, Healy and Paaz, 1951).

Thorium:

Concentrations are generally less than 10^{-6} g/l, although significant amounts of Ms. Th. may occur (Duchon, 1940).

Thoron:

No adequate determinations of thoron concentrations had been made prior to the writing of Healy's report.

Concentrations in ground waters in areas of uranium or thorium mineralisation may be much higher than the values given above. Measurements of the radon concentrations in the Hot Springs National Park, Arkansas, have been made by Kuroda, Damon and Hyde (1954). The following extract from their report shows that an appreciable increase was observed in the radon content of springs close to a uranium deposit.

"The hot waters are extremely variable in radon content (10^{-4} to 3×10^{-2} µc/l) possibly because each spring has its own radium bearing tufa - source of radon. The average radon content is about 8×10^{-4} µc/l.

The cold waters are also extremely variable (10^{-4} to 7.3×10^{-3} µc/l) and average about the same as the hot springs.

The spring waters issuing directly from the border of the uranium-vanadium-niobium prospect at Potash Sulphur Springs average about 1.5×10^{-2} µc/l and are more uniform in radon content (6×10^{-3} to 4×10^{-2} µc/l).

The uranium content of selected samples from the prospect area is as high as 0.6% U_3O_8; however, the bulk material averages about 0.02% U_3O_8.

Few, if any, measurements appear to have been made of the radioactivity of ground waters in Australia. Some hundreds of springs have been reported in Victoria, many of which are highly mineralised, and a survey of the radioactivity of these springs appears to be warranted. Deposits of uranium which are too deep to be detected by the usual survey methods could possibly be detected by a survey of this nature if radon emanating from the deposit were carried to the surface by the circulation of ground waters.

In order to measure the small concentrations of the radioactive elements (listed above), sensitive instruments are required. For the uranium measurements some commercially available fluorimeters have sufficient sensitivity (about 10^{-9} grams of uranium).

It has been necessary to construct special equipment for the radon and radium measurements. An alpha scintillation chamber is used as the detector and the smallest amount of radon which can be measured is about 10^{-6} μc. This instrument is described more fully below.

Because of the short half-life of thoron (54.5 secs.) a portable instrument must be used for thoron measurements, so that the determination can be made as soon as the sample is collected, using a continuous gas flow method. No instrument has been constructed for this purpose as yet, but the laboratory instrument made for radon determinations could be modified for field measurements of both radon and thoron, if required.

The determination of small quantities of thorium by radiometric methods is more difficult. The highest reported concentrations (10^{-6} g/l) would produce only 30 alpha particles per hour for a 1-litre sample. Rough determinations could be made using an alpha spectrometer but many hours of counting would be required.

Measurements of the radon and radium concentrations in 12 springs, close to Melbourne, have been made in order to obtain a rough estimate of the activities likely to be found in Victorian springs and to test the equipment. The values obtained for radon and radium and the method of measurement are reported below.

2. DESCRIPTION OF APPARATUS AND METHOD OF MEASUREMENT.

(A) Introduction

The method used for the radon determinations is similar in principle to that described by Damon and Hyde (1952). However, an entirely different method of construction has been used for the scintillation chamber and provision has been made for inserting a constant alpha source into the chamber to check for instrumental drift.

The method used for transferring the radon from the sample to the chamber is similar to that described by Evans (1935) but some simplification has been made possible by the use of a scintillation chamber instead of an ionisation chamber.

(B) Description and operation of the apparatus.

A sketch showing the complete system is shown in Fig. 1 and a more detailed sketch of the scintillation chamber is shown in Fig.2.

The sample for assay is collected in a 500 ml. bottle fitted with a $1\frac{3}{4}$- inch rubber stopper. The sample bottle is connected to the system without loss of radon by forcing two pointed brass tubes through the stopper as shown in Fig.1. The sample is transferred to the flask F1 by evacuating F1 and introducing nitrogen from the jar J2 under the pressure provided by the head of water in the jar J1.

The sample is then boiled for about 10 minutes to drive off the radon. During boiling, more nitrogen is introduced into the system via T1 and T2, sweeping the radon past the acid trap to the scintillation chamber (previously evacuated).

The radon in the chamber decays with the emission of alpha particles of energy 5.49 M.E.V., some of which reach the walls of the chamber (coated with zinc sulphide) causing scintillations which are detected and amplified by the photomultiplier which views the interior of the chamber through a window at one end. The output pulses from the photomultiplier tube are then amplified further and counted on a scaler.

After the radon has been introduced into the scintillation chamber, the count rate at first rises rapidly with the build-up of the first daughter product (RaA), which has a half-life of 3.05mins and emits an alpha particle of energy 6.0 M.E.V. After about 15 minutes, equilibrium is established between Rn and RaA, but the count rate continues to rise slowly with the build up of the next alpha emmitter, RaC, which emits an alpha particle of energy 7.68 M.E.V. If the radon were left in the chamber the count rate would rise slowly until equilibrium was established between Rn and RaC (in about $2\frac{1}{2}$ hours). The count rate would then fall with the decay of radon with a half-life of 3.82 days. In practice, the count is taken about 15 minutes after the radon enters the chamber as the count rate is then changing quite slowly.

When counting is completed it is necessary to remove all radon from the system. This is done by passing a steady stream of air through the apparatus for about 2 hours. It is also necessary to allow the daughter products in the chamber to decay, before another assay is made. A curve showing the fall in count rate after the chamber is opened is shown in Fig 4. This curve shows also the growth of RaA (A to B in Fig. 4) after introduction of the radon, the removal of

radon (B to C), the decay of RaA (C to D), and the decay of RaC (D to E).

In order to make quick checks for instrumental drift, the scintillation chamber is provided with a constant alpha source. The source is attached to the end of a screw passing through the walls of the chamber. When not in use the source may be screwed back into the wall of the chamber, where it is completely shielded from the zinc sulphide phosphor. The source consists of a thin deposit of uranyl nitrate on the surface of a small aluminium collar (see Fig. 2).

To ensure consistent efficiency in the transfer of radon from the sample bottle to the scintillation chamber and to ensure consistent amounts of build-up of the daughter products in the chamber, the assay procedure has been standardised. The procedure which has been adapted is as follows :-
(Refer to Fig. 1 for location of taps, etc.)

1. Close taps T1, T2, T3, T4, T8, T10.
   Open taps T5, T9.
   Set T6 and T7 so that by-pass is closed and acid trap is open.

2. Fill the jar, J2, with water.

3. Connect sample bottle to the system.

4. Turn on water supply to condenser.

5. Turn on vacuum pump.

6. Slowly open valve on nitrogen bottle until most of the water has been lifted from J2 to J1.

7. Close valve on nitrogen bottle.

8. By carefully adjusting T8 evacuate the system slowly to about 10 cm. and close T8.

9. By careful adjustment of T2, slowly bring the system back to atmospheric pressure. Close T2.

10. Take count on Uranium Standard.

11. Take a background count.

12. By means of T8, evacuate slowly to 8 cm. Close T8.

13. By careful adjustment of T1 and T3, transfer the sample to the flask, F1.

14. If necessary, add more nitrogen to the system to increase the pressure to 12 cm.

15. Finally close T1 and T3; turn bunsen to moderate flame and flick the flame over the gauze under the flask a few times. Then heat the flask strongly, starting the stop-watch when the heat is first applied to the flask and noting the time.

16. When boiling point is reached (t = 5 mins. approx), turn down the bunsen to maintain steady boiling. (It will be found that as the pressure in the system is increased it will be necessary to increase

the bunsen flame slowly to keep the sample boiling).

17. When boiling starts, the pressure should be about 30 cm. If necessary, introduce more nitrogen, via T1 and T3, to bring the pressure to this value.

18. Continue steady boiling and raise the pressure at intervals (shown below) by carefully introducing more nitrogen via taps T1 and T3.

At t = 4 mins. raise pressure to 40 cms.

At t = 6 mins. raise pressure to 50 cms.

At t = 8 mins. raise pressure to 60 cms.

At t = 10 mins. raise pressure to 76 cms.

19. Close T9, T1, open T4 and remove the bunsen.

20. Note the time (t^10) when T9 is closed and re-start the stop-watch.

21. Take counts on the sample as follows :-

At t^1 = 10 mins. take a 5 min. count.

At t^1 = 17 mins. take a 5 min. count.

If a larger aggregate count is required for the desired statistical accuracy, take additional counts as follows:

At t = 23 mins. take a 10 min. count.

At t = 35 mins. take a 20 min. count.

At t = 57 mins. take a 40 min. count.

The aggregate count and counting time are then used to determine the count rate.

22. <u>As soon as counting is finished</u> -

Start pumping again and open T9 and T10.

23. Remove the flask and sample bottle and measure the volume of sample remaining in the bottle and the volume of water in the flask. If a radium measurement is to be made, return the sample to a clean bottle, noting the time, date and sample number.

24. Fit a clean flask at F1.

25. Set T6 and T7 to by-pass the acid trap, open T1, T2, T3 and close T4.

26. Leave the pump running and allow the air to circulate through the system until the background has dropped back to the desired level. The next sample may then be assayed.

If a sample is to be assayed when the equipment has not been in use during the previous 6 hours or so, it is desirable to sweep out the system with a stream of air for at least half an hour before starting an assay. This ensures that most of the radon produced by radium

contamination of the apparatus is removed.

(C) Calibration.

The chamber has been calibrated using standard radium solutions prepared at the radiochemical Centre, Amersham, U.K.

In making a calibration, the standard solution is boiled for half an hour to drive off all the radon: the solution is then placed in a sample bottle which is well sealed with a rubber stopper. The sample is left for several days to allow an appreciable, known amount of radon to build up in the sample bottle.

The sample is then connected to the assay apparatus, boiled and several counts taken as described above. The strengths of the standard solutions supplied by the Radiochemical Centre are as follows :-

Standard A:	Volume supplied	250 ml.
	Radium content	2.58×10^{-4} mg. $\pm$ 10%
	Strength	1.03 µc/l $\pm$ 10%
Standard B:	Volume supplied	250 ml.
	Radium content	2.46×10^{-6} mg. $\pm$ 10%
	Strength	0.985×10^{-2} µc/l $\pm$ 10%
Standard C:	Volume supplied	250 ml.
	Radium content	1.90×10^{-8} mg. $\pm$ 15%
	Strength	0.76×10^{-4} µc/l $\pm$ 15%

Standards B and C give radon concentrations within the range of values to be expected in natural waters and Standard A is sufficiently strong to enable large volumes of sub-standard solutions to be made, by dilution.

The following sub-standard solutions have been made up by successive dilution of Standard A. By the use of these sub-standards for calibrating the apparatus, risk of contaminating the primary standards is avoided.

Sub-Standard Solutions.

No. 1. 1.03×10^{-2} µc/l. Made by a hundredfold dilution of Standard A.

No. 2. 1.03×10^{-3} µc/l. Made by a tenfold dilution of Sub-standard No.1.

No. 3. 1.03×10^{-4} µc/l. Made by a tenfold dilution of Sub-standard No.2.

The calibration curves shown in Fig. 5 were obtained from measurements made on these sub-standard solutions.

The calibration values depend to some extent on the time allowed for the build-up of RaA and RaC in

the chamber. The curves of Fig. 5 were prepared according to the counting scheme set out in step 21 of the assay procedure.

It has been found desirable to check the calibration every two or three months, as the efficiency of the apparatus tends to fall off due to deterioration in the zinc sulphide phosphor. It is also necessary to repeat the calibration after laying a new phosphor, as the efficiency depends to some extent on the thickness and uniformity of the phosphor.

(D) Contamination

It has been found that when measurements are made on relatively strong radium solutions (stronger than about 5×10^{-2} µc/l) the glassware becomes contaminated with radium to such an extent that assays of weaker samples may be seriously effected. This contamination, which is very difficult to remove, occurs mainly in the sample bottles and in the 1-litre flask in which the samples are boiled. It has therefore been found necessary to use radium solutions, for calibration purposes, which are no stronger than 10^{-2} µc/l.

(E) Determination of Radium

Clearly this apparatus may also be used for the determination of radium in water samples. This is done by first boiling all radon from the sample to be tested, sealing the sample for a known length of time and then measuring the radon produced by the decay of the radium in the solution. The radium concentration may then be calculated quite simply.

In general, spring waters contain radon which is due in part to the radium in solution and in part to radon which has diffused out of the rocks through which the water has passed. In general, the radon concentrations are found to be in excess of the amount which would be in equilibrium with the radium in solution. Once a sample is sealed into a container the excess radon decays until equilibrium is established (about 28 days). As assays may be made some days after the sample is collected it is necessary to allow for the decay over this period to do this it is necessary to know the radium content. The following example will serve to illustrate how this is done.

Sample collected at time $t = 0$

Radon determined at time $t = 3.8$ days

Radon concentration $= 5 \times 10^{-3}$ µc/l.

After boiling, the sample is sealed for 3.8 days and a second radon determination made (radon concentration $= 5 \times 10^{-4}$ µc/l). At this time the sample would contain half the equilibrium amount of radon, hence the radium concentration $= 2 \times 5 \times 10^{-4} = 10^{-3}$ µc/l.

Hence the excess radon when the first determination was made ($t = 3.8$ d) would be $5 \times 10^{-3} - 10^{-3} = 4 \times 10^{-3}$ µc/l.

Hence the excess radon at time $t = 0$ would have been $2 \times 4 \times 10^{-3} = 8 \times 10^{-3}$ µc/l and the total radon at time $t = 0$ would be $8 \times 10^{-3} + 10^{-3} = 9 \times 10^{-3}$ µc/l.

Times equal to the half-life of radon have been used to simplify the explanation above. In practice, any convenient length of time may elapse between measurements.

3. PRELIMINARY TESTS ON WATER FROM MINERAL SPRINGS.

In order to test the apparatus and to determine what order of magnitude of radon and radium concentration are to be expected in the Victorian mineral springs, several samples were collected from springs near Melbourne. The samples were collected from the eleven sites shown in Fig. 3.

It was found that most of the spring waters were heavily charged with carbon dioxide. It was therefore necessary to fit strong clamps to the stoppers on the sample bottles to prevent leakage of radon under the pressure of the carbon dioxide.

At most of the springs tested, the water flows freely from a pipe set in the ground; at others the water has to be pumped from the ground. It is to be expected that some loss of radon would occur in pumping the water to the surface.

In order to check the reproducibility of the method, five samples were collected at the same time from the Spargo Creek Spring, and assayed.

The results obtained are listed in Table 1 and the distribution of the radon values is shown in Fig. 6.

The radium concentration in most of the springs was found to be too low to be measured directly. Large samples (2½ litres) were therefore collected and concentrated by boiling before assaying. In most instances the concentration was still too close to the limits of sensitivity of the equipment for accurate quantitative results. These results may also have been affected by radium contamination of the apparatus; however, the results are good enough to show that most of the radon in solution is a result of diffusion from rock formations and is not due to radium in solution.

4. CONCLUSIONS

It has been found that fairly high concentrations of radon occur in the mineral springs in the Daylesford area. The values obtained are up to 1,000 times the minimum value which can be detected by this apparatus. The average value is close to that reported by Kuroda, Damon and Hyde (1954) for water from the Hot Springs National Park.

The reproducibility of the measurements is not quite as good as may have been expected but it is adequate for this purpose, in view of the wide range of concentrations observed in these springs. It appears that assays can be repeated generally to within ± 20% of a mean value.

However, the values given for the standard radium solutions used for calibrating the apparatus are accurate to within ± 10 per cent. absolute radon values obtained from a single measurement may therefore be in error by up to about 40% when allowance is made for a possible 10 per cent error in the determination of the calibration constant.

TABLE 1.

Site No. (Ref. Fig.3)	Date Collected	Spring	Whether Pump (P) or Pipe (O)	Radon ($\times 10^{-3}$ $\mu c/l$)	Radium ($\times 10^{-3}$ $\mu c/l$).
1.	8/8/57	Donnybrook	O	1.0	0.0011
2.	12/7/57	Spargo Creek	O	1.7	
	"	" "		1.6	
	"	" "		1.8	
	"	" "		1.9	
	"	" "		1.5	
	31/7/57	" "		1.7	0.0056
	"	" "		2.3	
	"	" "		2.3	
3.	8/8/57	Daylesford	P	1.5	0.0033
4.	8/8/57	Hepburn	P	0.74	0.011
5.	8/8/57	Vaughan	P	0.97*	0.012
6.	23/8/57	Taradale	P	0.35	0.0052
7.	31/7/57	Kyneton	P	0.25	0.0053
8.	31/7/57	Lyonville No.1	O	0.83	(No determination made).
9.	31/7/57	Blackwood-South Spring.	O	1.0	0.0093
	31/7/57	Blackwood-North Spring.	O	3.9	
10.	31/7/57	Glenluce	P	1.2	0.0086
11.	23/8/58	Tylden	P	0.72	0.0014

* Suspected loss of radon due to faulty stopper.

The sensitivity of the apparatus is not quite as good as that reported by Damon and Hyde (1952) but it is adequate for the measurement of the radon concentrations in the springs tested. Sufficient experience has now been gained to enable a more sensitive instrument to be designed if this should be necessary.

5. REFERENCES.

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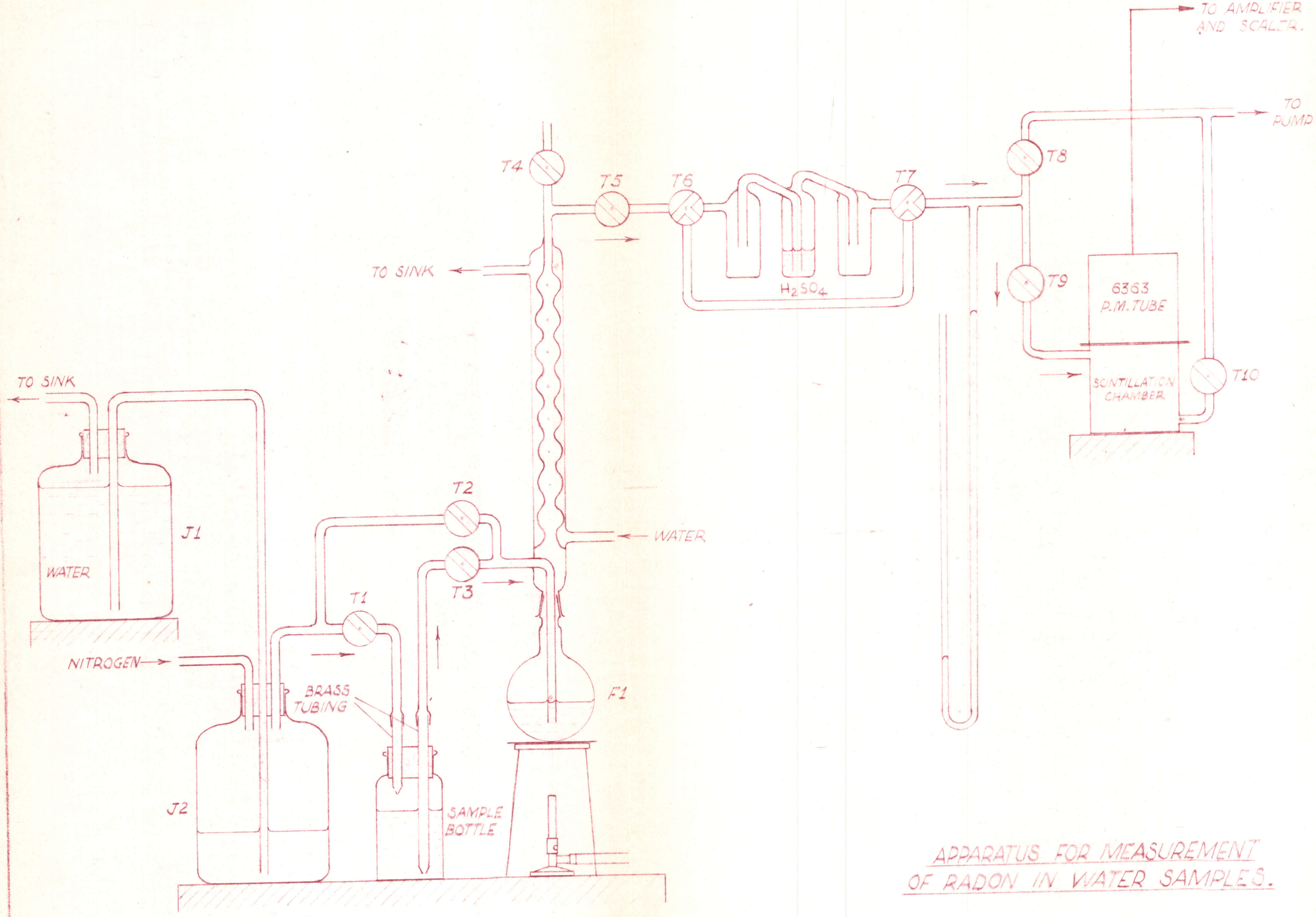
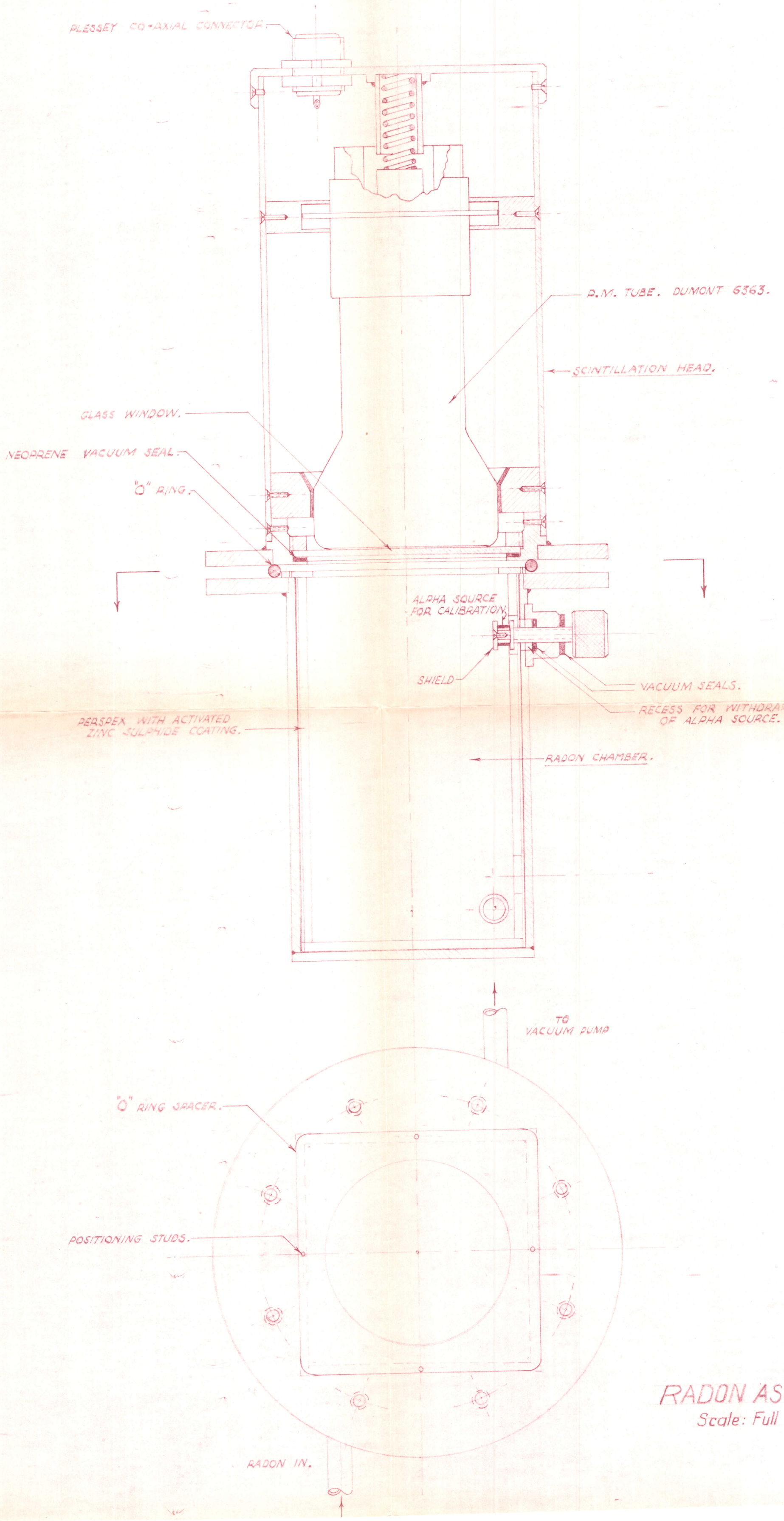
Fig. 1.



APPARATUS FOR MEASUREMENT OF RADON IN WATER SAMPLES.

14-6-57. H/H

Fig. 2.

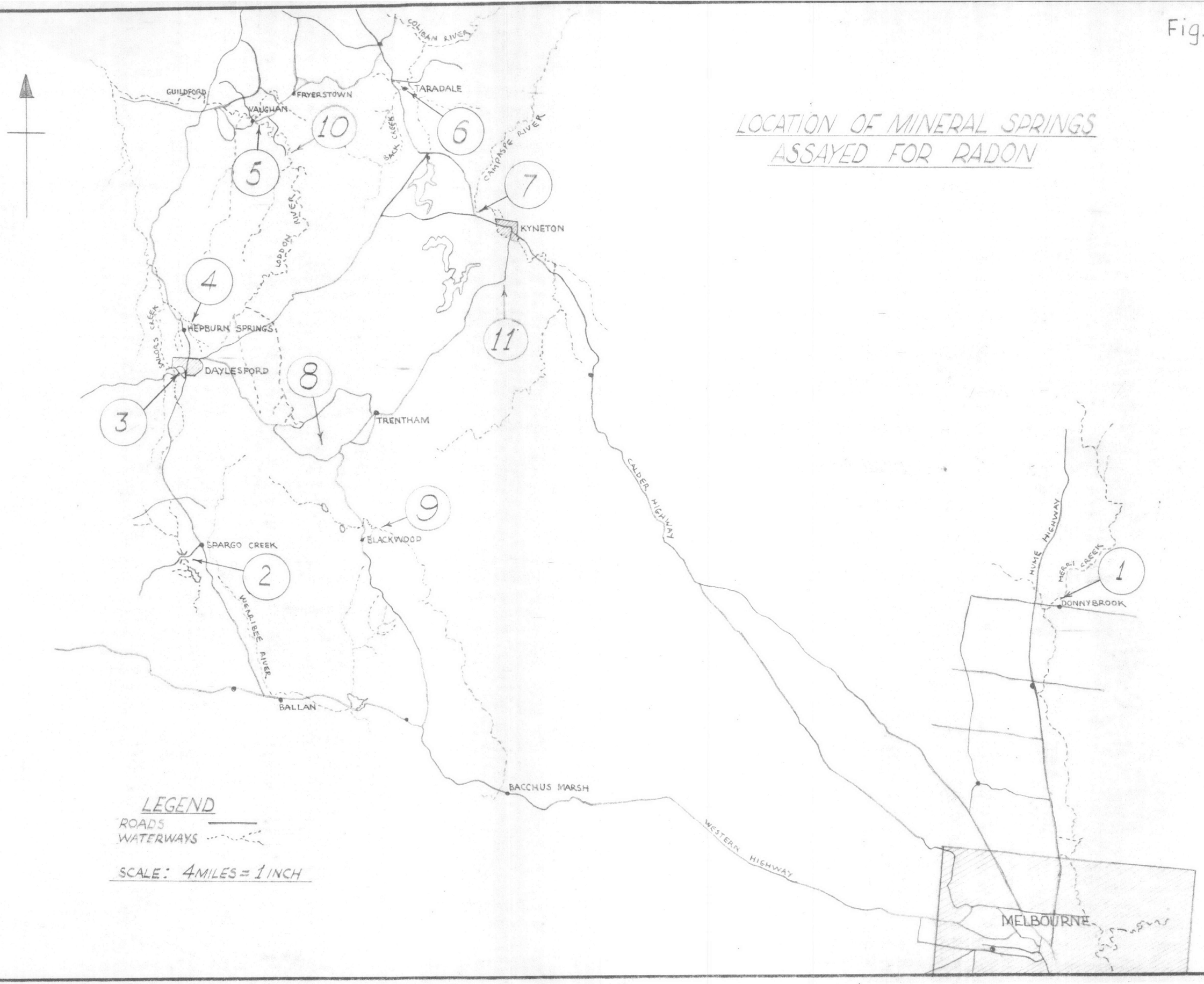


RADON ASSAY UNIT

Scale: Full Size.

Fig. 3.

LOCATION OF MINERAL SPRINGS ASSAYED FOR RADON



LEGEND

ROADS ——

WATERWAYS ·····

SCALE: 4 MILES = 1 INCH

Fig. 4.

DECAY OF RADIOACTIVITY IN RADON CHAMBER.

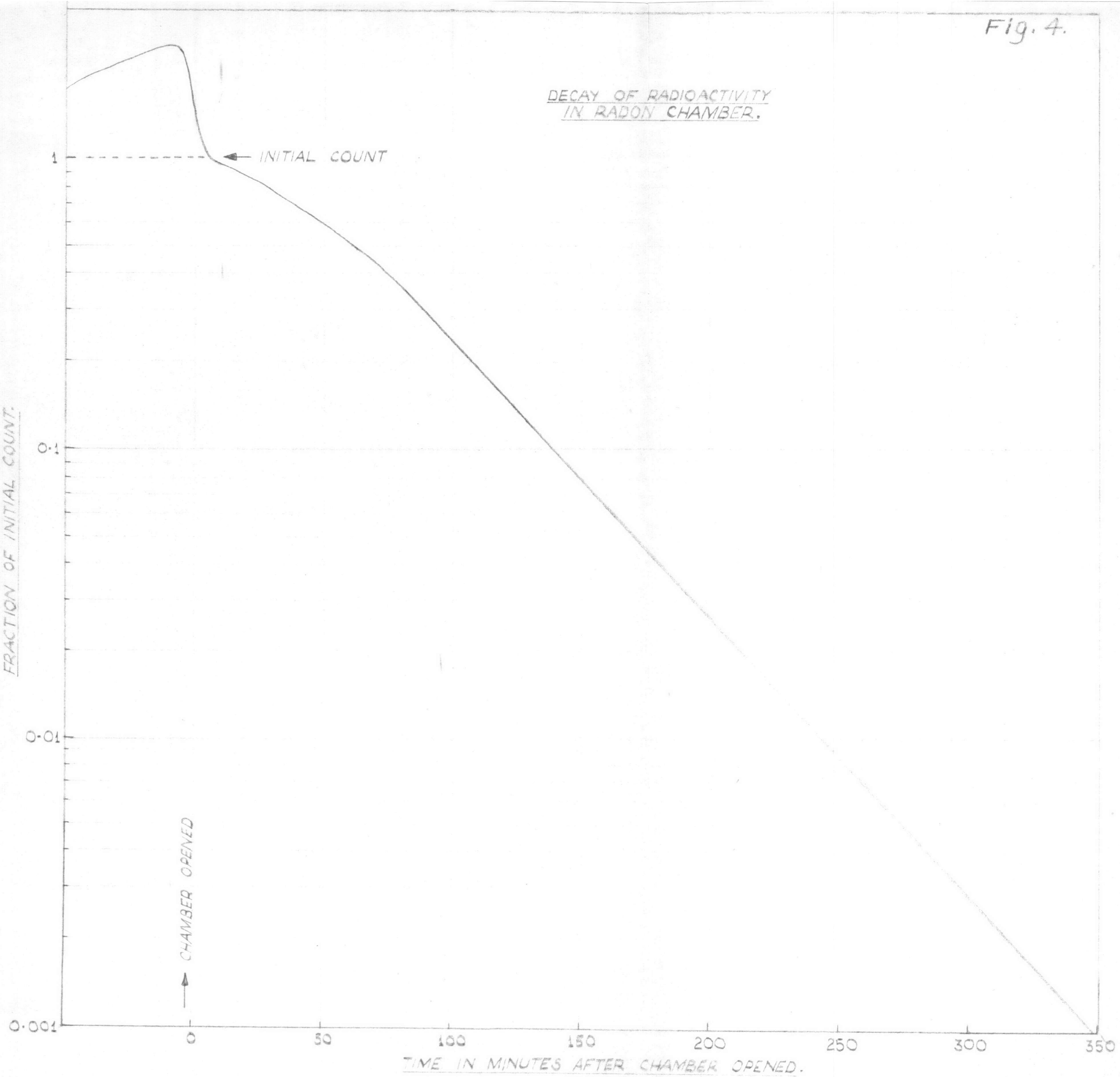


Fig.5.

RADON ASSAY CALIBRATION CURVES

1 - 10 - 57

$E_1 + 10$
$E_1 + 17$
$E_1 + 23$
$E_1 + 35$
$E_1 + 57$

SAMPLE ACTIVITY (COUNTS / MIN / LITRE)

RADON CONTENT (μC / LITRE)

Fig. 6.

CASTLEMAINE

LODDON RIVER

COLIBAN RIVER

CAMPASPE RIVER

TARADALE ⊗ 0·35

VAUGHAN ⊗ 0·97

1·25 ⊗ GLENLUCE

N

0·25 ⊗

KYNETON

TYLDEN ⊗ 0·72

CALDER HIGHWAY

LITHIA ⊗ 1·0

GLENLYON N.E. ⊗ 1·11

HENDERSON'S ⊗ 3·44

GOLDEN SPRINGS ⊗ 1·46

HEPBURN • ⊗ 0·74

TIPPERARY ⊗ 0·81

1·51 ⊗

DAYLESFORD

DEEP CREEK 1·05 ⊗

⊗ 1·09 CORINELLA

LEITCH'S CREEK ⊗ 39·6

WOMBAT CREEK ⊗ 0·74

SAILOR'S CREEK

BORLANDS ⊗ 0·88

LEITCH'S CREEK GULLY 0·86 ⊗ (No 2) 180 ⊗ 0·83 ⊗ (No 1) ⊗ (No 3) 3·35

• LYONVILLE

MINERAL SPRINGS DAYLESFORD AREA

SCALE: 1" = 2 MILES

LEGEND

ROADS

RIVERS

RESEVOIRS

⊗ MINERAL SPRING

1·07 RADON CONTENT — MILLI-μCURIES PER LITRE

GRID CO-ORDINATES REFER TO MELBOURNE SHEET, MILITARY 4 MILE SERIES.

⊗ 3·86 (N)

BLACKWOOD (S) 1·01

LERDERDERG RIVER

SPARGO CREEK

⊗ 1·86

MOORABOOL RIVER

BALLAN

WESTERN HIGHWAY

DONNYBROOK. 23 MILES

1·04

15/8/57

43 42 41 40 39 38 37 36

21 22 23 24 25 26