S **64**. *The Determination of Radon and Radium in Water.*

By R. B. JACOBI.

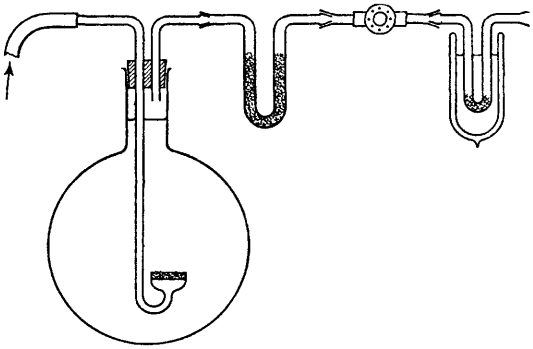
The scheme here described for radon and radium analysis was devised as a compromise between the opposing aims of simplicity and convenience of working on the one hand, and a high order of sensitivity of measurement on the other. The latter arose from the expectation that the waters to be analysed would generally contain appreciably less than a micro-microgram of radium per litre, and, as it was not desired to handle water samples of a volume greater than 1—2 litres, equipment was required which would measure activities of the order of 0·1 $\mu\mu$-curie. The experimental procedure involves the separation of the radon dissolved in the water sample and its transference to the ionisation chamber for measurement, and the concentration of the radium into a solution of small bulk, from which the radon may be allowed to accumulate, the radium being estimated by measuring the amount of radon so obtained.

Separation of Radon.—The method depends on two important points. First, radon may be effectively swept out of aqueous solution at room temperature, provided that the sweeping gas passes through the water as a stream of small bubbles, and the total volume of gas so used is large compared with the volume of the water : it is found that ten volumes of argon will give a loss of radon not greater than 1% (which is generally within the limit of accuracy) for amounts of activity up to about 20 $\mu\mu$-curies, and nitrogen acts similarly. This is in contrast with previously published opinion, *e.g.*, a discussion by Evans (*Rev. Sci. Instr.*, 1933, **4**, 216), referring to papers by Moran (*Trans. Royal Soc. Canada*, 1916, **10**, III, 57, 77) and Boltwood (*Amer. J. Sci.*, 1904, **18**, 378; 1905, **20**, 128), submitting that quantitative removal of radon from water can be achieved only by prolonged boiling, which technique is followed by Evans (*Rev. Sci. Instr.*, 1935, **6**, 99) and his co-workers in the United States, and by workers at the National Physical Laboratory in this country. Secondly, radon is completely removed from the gas phase by silica gel cooled in liquid air, from which it is released at a temperature no higher than that of boiling water, the cycle of operations being 100% efficient within the limits of experimental error. Such a process was utilised by Keevil (*Amer. J. Sci.*, 1938, **36**, 304) and was independently developed by the author (Thesis, London, 1941) in connection with other work. It provides a useful method for separating radon from gases which are not readily condensed on silica gel. Combination of the above steps affords a convenient procedure for transferring radon from solution in a water sample to an ionisation chamber for measurement.

EXPERIMENTAL

The sample of water is contained in a flask, which it fills so as to leave only about half the length of the neck, or a little more, as " dead space " (Fig. 1). The inlet tube reaches nearly to the bottom, and is turned upwards; it carries a sintered-glass plate so as to break up the current of gas into a stream of fine bubbles. The gas then passes through a drying tube containing broken pellets of potassium hydroxide, and on through a valve to a U-tube containing a small amount of silica gel, this tube being immersed in liquid oxygen; the outlet is open to the atmosphere. The rate of flow is such that a volume of gas at least ten times the volume of the water will pass through in 10—20 minutes; a flow rate of several l./min. can be obtained by increasing the pressure at the input end.

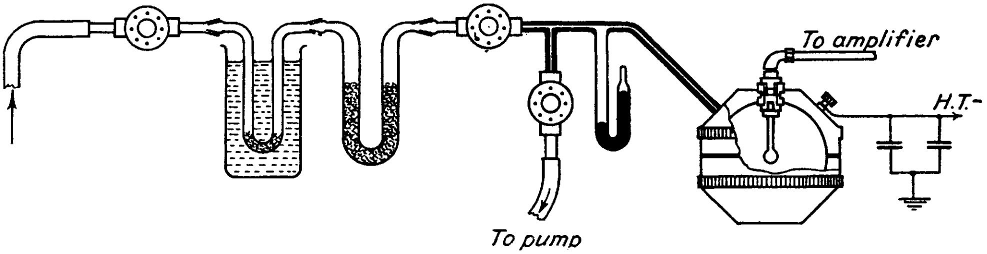
FIG. 1.



Radon in water: collection of radon.

The next step is to transfer the radon trapped in the silica gel into the ionisation chamber (Fig. 2). The drying tube, recharged with fresh alkali, is removed to the output side of the absorption tube (which is still kept in liquid oxygen), and argon is passed through to displace air—if nitrogen was used to sweep the radon out of the water, the nitrogen remaining in the absorption tube will also be displaced by argon. The re-positioning of the drying tube is intended to exclude from the ionisation chamber the small amount of water which will have been carried through into the cooled silica gel and will be released again on warming. The chamber is evacuated, and the radon is swept into it by warming the silica gel tube with boiling water while a slow current of argon passes through; the chamber is in this way allowed to fill to atmospheric pressure, the time taken being about 5 minutes. Counting may begin at once; if sufficient radon is present, the curve will show a rise to a maximum after about 3 hours, owing to the formation of an active deposit, and will then fall according to the normal decay of radon.

FIG. 2.

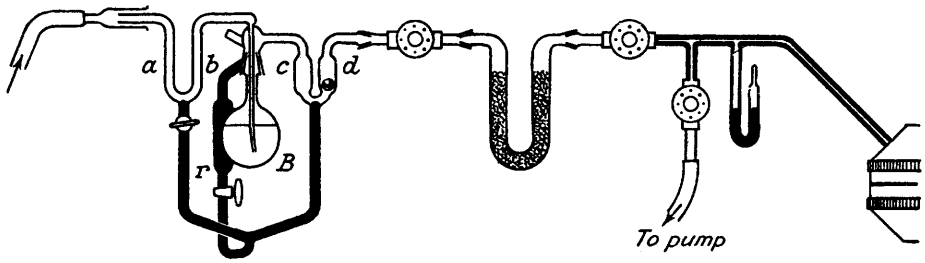


Radon in water: release of radon into chamber.

Determination of Radium.—If the sample of water contains appreciably more than about 10 $\mu\mu$g. of radium per l., no extraction of radium is required, as a small portion can be sealed in a suitable trap, and the radon which accumulates measured without undue difficulty; in cases of somewhat lower activities, a suitable portion may be cautiously evaporated down to about 15 ml., and the concentrate then sealed and handled in the same way; but generally a much larger bulk of water is needed to provide enough radium for a reliable measurement, and an extraction process must be employed to concentrate the radium into a small enough volume of solution.

From Nakai's survey (*Bull. Chem. Soc. Japan*, 1940, **15**, 333) of precipitations which will bring down small amounts of radium from aqueous solution, that of manganese dioxide has been chosen as being a compromise between chemical efficiency and convenience and rapidity in handling. The reaction involved is $2KMnO_4 + 3MnCl_2 + 2H_2O \longrightarrow 5MnO_2 + 2KCl + 4HCl$. To the water sample (say 2 l.) a few drops of hydrochloric acid are added to keep in solution any calcium of temporary hardness, and then the measured amount of manganous chloride solution to yield 0·3 g. of manganese dioxide, according to the above equation. The sample is heated almost to boiling point and a slight excess of permanganate solution is added, to give a permanent pink colour; after about an hour's digestion at just under 100°, the precipitate is allowed to settle, most of the liquid is decanted, and the precipitate collected in a fast filter paper, washed once, and allowed to drain well; it is dissolved in a minimum of hot hydrochloric acid, the solution cautiously boiled free from chlorine and evaporated to a few ml. to remove most of the excess acid. The resulting liquid is transferred, with washings, to a bulb of standard form of 25-ml. capacity, with the neck in the form of a ground glass cone (*B*, Fig. 3) and adjusted to 15 ml.; the bulb is attached to a trap of the form shown on the left of Fig. 3, and a stream of argon blown through for a few moments; the trap is then sealed, and note is taken of the time and date of sealing; the time and date of opening the trap will then give the interval during which radon will have accumulated according to its half-life of 3·825 days, and the percentage of equilibrium attained can be calculated.

FIG. 3.



Radium measurement: transfer of radon to chamber.

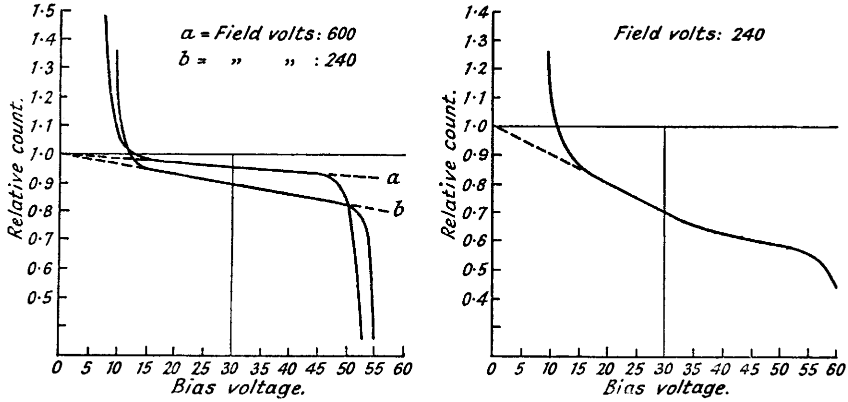
This type of trap is fully described by Arrol (Thesis, London, 1938). When open, gas may pass through the arms (*a*) and (*b*), bubble through the liquid in the bulb *B*, and be carried off through (*c*) and (*d*). By applying pressure to the mercury reservoir (*r*) at the rear of the trap (the two stopcocks being open) mercury is forced up so as to close, at the same moment, the junction between (*a*) and (*b*) and that between (*c*) and (*d*), so cutting off the space from (*b*) to (*c*); the level should be further raised until the steel ball in arm (*d*) is pressing lightly against the constriction at the top of the arm, so giving protection should the pressure in the tubing beyond it accidentally become less than atmospheric. The diameter of (*b*) is to that of (*c*) roughly as the enclosed volume in the narrow tubing, from (*b*) to the level of liquid in the bulb, is to that in the wider parts from (*c*) to the same level, so that as the mercury level is changed the pressure in both sides will change equally, without either bubbling of gas from side (*b*) through the liquid or syphoning of liquid back into (*b*). The stopcock under the junction of (*a*) and (*b*), when closed, prevents mercury swinging from side to side when the trap is handled; it must, of course, be open whenever the mercury level is altered.

After a suitable period, the trap is fitted to the train leading to the ionisation chamber (Fig. 3). It is advisable to have a slight excess pressure of argon to the right of the valve next to the trap. Argon is caused to flow slowly through a tube fitting loosely over the inlet of the trap; and the mercury allowed to fall in both sides together, a little gas being allowed to flow back through the valve mentioned above so as to keep the adjacent limb of the trap at atmospheric pressure and allow the mercury to fall evenly. The chamber having been pumped out, argon is slowly drawn in through the trap, the first valve, the drying tube, and the second valve; the radon is swept out of the bulb and into the chamber, and as the ratio of volumes is so large (about 550 : 15) the transfer of radon is effectively complete; the rate of flow is 100 to 200 c.c./min. When the chamber is filled to atmospheric pressure, counting may begin.

Since radon is liable to be absorbed by greases, the usual lubricants for stopcocks and joints must be avoided; therefore metal needle valves are employed in the admission train to the chamber, and the cone-and-socket joints are lubricated with a solution of powdered sucrose in glycerol; this preparation is not unduly hygroscopic, and is able to hold the slight pressure inside a closed radon trap for several months. The drying agent used at all times is potassium hydroxide; it has been found efficient at comparatively high flow rates of argon saturated with water vapour : calcium chloride was found to be quite inadequate, the gas entering the chamber being so moist that ionisation was drastically reduced, few α-particle discharges giving pulses strong enough to be recorded.

Blank experiments were made to ascertain what correction, if any, was to be applied for radium introduced as impurity with the reagents; fortunately, the batch of reagents used in the current series of determinations showed no perceptible trace of radium, and so no correction is to be made to the figures shown in the tables.

FIG. 4.



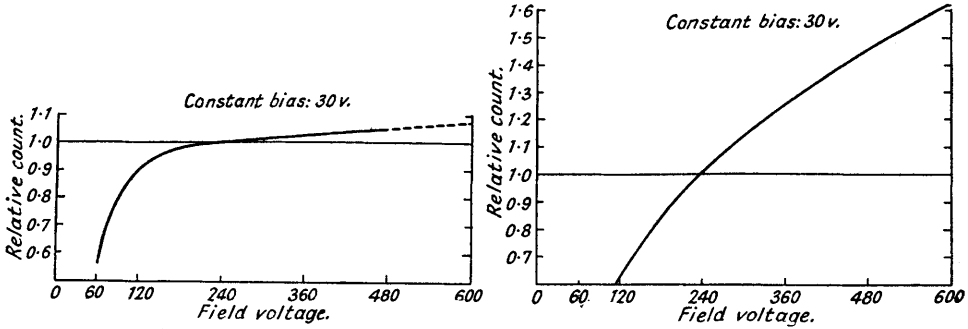
(*a*) *Amplifier bias discriminator curves. Ionised gas: argon.*

(*b*) *Amplifier bias discriminator curve. Ionised gas: nitrogen.*

The Ionisation Chamber.—In order to minimise counting errors, the requirements are a high efficiency of counting α-particles and a low background. Accordingly, in designing the chamber the following points were borne in mind. (1) A spherical chamber, having the lowest possible surface/volume ratio, will keep to a minimum the loss due to " wall effect " whereby a particle emitted towards the chamber wall from an atom situated close to that wall will not produce enough ions to give a recordable pulse; it will also reduce background due to activity on the surface from any α-emitter contaminating the material of which the chamber is made. (2) A small chamber will reduce the background, both for the reason given above and because it presents a small projected area to cosmic rays or other such causes of spurious pulses. (3) A polished nickel-plated inside surface will also help to reduce the background. (4) The use of argon, which is a good ionising gas, improves counting efficiency in that in argon a shorter length of α-particle track is needed to give a recordable pulse, and the bias-voltage plateau is more nearly level at low field voltage than would be the case with many other gases, such as nitrogen. (5) Pulse counting, with a suitable automatic device for recording the counts at regular intervals, allows of easy calculation of probable errors, and also obviates the troubles due to electrometer leakage encountered by Evans, Kip, and Moberg (*Amer. J. Sci.*, 1938, **36**, 241).

The chamber employed is shown partly in section in Fig. 2. It is spherical, of internal diameter 4 inches, and the capacity is about 550 c.c. The insulators are of polystyrene, but an improved version has been built using quartz. The field voltage is applied so that the body of the chamber is negative to earth, the collecting electrode being linked to earth by the input circuit of the amplifier; this means that electrons are collected, the voltage pulse so given having a sharply rising front. The pulse is amplified by a Freundlich linear amplifier which incorporates a discriminating circuit, the bias being variable from zero to well above the saturation output voltage of the amplifier. Curves of the change in recorded count with change of discriminator bias are shown in Fig. 4, the relative count for the extrapolation of the plateau to bias zero volts being taken as unity in each case. The steep slope at low bias is due to amplifier noise producing spurious counts, and the sharp falling off at high bias is due to the fact that the amplifier cannot deliver pulses greater than 50—55 volts, and these are cut off by a larger bias. Extrapolation of the plateau back to zero bias gives the relative count which would be given if the chamber were 100% efficient, *i.e.*, if all pulses, however small, were detected. Fig. 5 shows field-voltage curves, the bias being kept constant at 30 volts in each case, the count at 240 volts field being taken as unity: it must be understood that the actual count given in nitrogen is considerably less than that in argon by the same amount of activity. The slope of the curve for argon is much flatter than that for nitrogen over the same voltage range, and, as we see in Fig. 4, the bias plateau for argon is much more level, hence the superiority of argon stands out markedly. These curves are found to accord closely with calculations of efficiency based on theoretical considerations. In the same way, calibration of the chamber, by the use of a standardised solution of radium, agreed well with the calculated value: at field voltage 240 v. and bias 30 v., it is 4·1 × 10^{-15} curie/α/hour, corresponding to an efficiency of 91%.

FIG. 5.



(*a*) *Field-voltage curve.*
Ionised gas: argon.

(*b*) *Field-voltage curve.*
Ionised gas: nitrogen.

Radon and radium in water.

(Both determinations on the same sample of water in each case.)

Location.	Date of sample.	Radon, μμc./l.	Radium, μμg./l.
River Thames (near Sutton Courtenay)	Sept. 1947	0·26 ± 0·02	<0·1
	Nov. 1947	0·22 ± 0·01	0·02 ± 0·01
	Apr. 1948	0·33 ± 0·01	0·009 ± 0·001
Bath: Pump room	Dec. 1947	166 ± 1	2·3 ± 0·1
Domestic tap (same building)	Dec. 1947	31·0 ± 0·5	0·11 ± 0·01

Radium in raw and tap waters.

(Samples from towns in Devon and Cornwall, Dec. 1948—Jan. 1949.)

	Radium, μμg./l.	
Location.	Raw.	Tap.
St. Ives: Trenwith mine	2·50 ± 0·05	—
Lower Town	—	1·10 ± 0·06
Plymouth: Burrator reservoir	0·07 ± 0·01	—
Newquay: Trewollack shaft	0·11 ± 0·01	—
River at Rialton	0·05 ± 0·006	—
Barnstable	0·0 ± 0·006	0·0 ± 0·005
Falmouth	0·20 ± 0·01	—
Exeter (River Exe ?)	0·04 ± 0·02	0·035 ± 0·005
River at Modbury, near Plymouth	0·17 ± 0·01	—

The tables show some determinations made on samples of water from the River Thames and from Bath for radon and radium, and from various places in the West of England, both tap and raw waters for radium only. The units employed are 10^{-12} curie (μμc.) and 10^{-12} g. (μμg.). It will be seen that, apart from the samples from the Pump Room at Bath and from St. Ives (Cornwall), all the figures for radium are less than 1 pg./l., ranging down to less than the detectable limit in the two Barnstaple samples. Thus the original estimate of the order of magnitude seems to have been correct: it was based on some of the more recently published values for natural waters where, cases of obviously highly active springs being ignored, the figures are distinctly lower than the estimates made in the early years of the century, in particular on the work of Evans, Kip, and Moberg (*Amer. J. Sci.*, 1938, **36**, 241) who give, for determinations on Pacific Ocean water, an average value of 0·1 μμg./l. The radium content of the River Thames appears remarkably low: the third determination (April 1948) was carried out on a 12-l. sample. By contrast, the Bath Spa water and the sample of raw water from St. Ives show the highest radium figures, the former having also an easily measurable radon content; the Bath tap-water sample showed a much lower radium content, and also a lower, though still appreciable, amount of radon.

The above work has been carried out in the laboratories of the Atomic Energy Research Establishment where it is hoped to continue a programme involving many more water samples of natural origin.

ATOMIC ENERGY RESEARCH ESTABLISHMENT,
HARWELL, DIDCOT, BERKS.

[*Read, March* 30*th*, 1949.]