APPARATUS FOR DETERMINATION OF SMALL QUANTITIES OF RADIUM.

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ABSTRACT. The apparatus here described incorporates the best features of previous designs and has demonstrated its ability to evaluate 1×10^{-14} gram of radium within an observational period of 20 hours. Its advantages include high precision, elimination of fluxes and chemical manipulation, automatic compensation of extraneous ionizations, automatic calibration every hour, and continuous recording over any desired number of hours. The permanent record is made on motion-picture film on which are also recorded all the scales necessary for subsequent calculations. This important feature eliminates the necessity for the use of any external measurement and makes evaluation a mere matter of counting.

INTRODUCTION.

THIS apparatus was assembled for the purpose of determining the radium content of geologic specimens containing the order of 10^{-15} to 10^{-10} gram per gram of sample.

The quantitative measurement of such amounts of radium depends upon the production of ions accompanying the disintegration of the gaseous daughter element, radon, and its products. The radium may be computed from the radon measurement.

All techniques for this purpose require the accomplishment of two things: (1) the quantitative extraction of the radon from the specimen and (2) the measurement of the ionization produced by the alpha-particles from that radon and its products.

Early forms of apparatus to accomplish these things consisted of an ionization chamber in conjunction with an electroscope which was observed visually.[1] The historical background of the introduction of balanced ionization chambers and the use of various types of electrometers for these measurements has been previously outlined.[2] Photographic recording was introduced to increase the accuracy of the measurements by prolonging the period of observation.[a,3] In the early measurements the radon was released from chemically prepared solutions of the specimens, or by fusion, sometimes without, but usually with, a flux.[4, 5] More recently, the specimens have been subjected to extremely high temperatures whereby the

[a] See reference to F. A. Paneth's apparatus in: Urry, Wm. D.: 1936, J. Chem. Phys., 4, 41.

radon is quantitatively removed without the addition of a fluxing medium.[3]

The apparatus described here incorporates the successful developments referred to above as well as some new features, so that now amounts of radium of the order of 10^{-13} gram may be determined with a probable error of a few per cent. It has proved satisfactory in the evaluation of the radium contained in specimens that are of geologic significance, more particularly rocks, ocean-bottom sediments, and water.

The apparatus performs the following functions:

1. Complete removal of the radon from a specimen.
2. Its complete transference, without contamination, to an ionization-measuring mechanism.
3. Evaluation of the ionization produced by the alpha-particles from the radon and its products in radioactive equilibrium with a known amount of radium, i.e., calibration of the apparatus.
4. Evaluation of the ionization produced by an unknown amount of radon.
5. Automatic elimination of extraneous influences.
6. Automatic instrumental calibration every hour, and continuous recording of the relation of ionization to time.

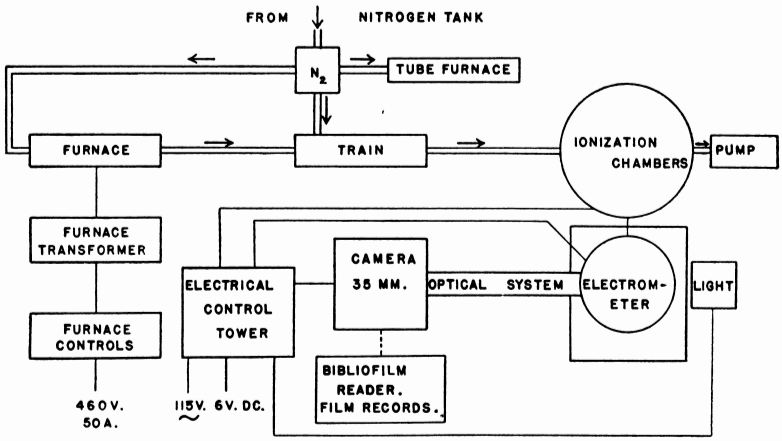


Fig. 1. Radium apparatus units.

APPARATUS.

The constituent parts are shown arranged diagrammatically in Text Fig. 1 and are described in detail below.

Radon-free Nitrogen. This is obtained by storing compressed nitrogen for more than thirty days, by which time any

radon has disintegrated. The nitrogen is used as a carrier gas to transport the minute quantities of radon from the material to be analyzed.

Tube-Furnace. In a 12 inch by 1¼ inch combustion furnace, solid specimens containing water, carbonate or organic matter, may be preheated to remove these substances, the presence of which is undesirable at the time of decomposing the sample in the high-temperature furnace.

An air-dried sample, or one previously dried at 110° C. for ten hours, is accurately weighed into a tube that is drawn out as shown in Text Fig. 2 and then heated in the tube-furnace to

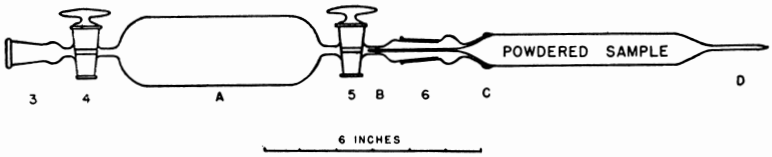


Fig. 2. Radon gas pipette.

600° C. for one to two hours in a stream of dry radon-free nitrogen. The tips are then sealed as indicated. After an interval of thirty days the accumulated radon is in radioactive equilibrium with the radium in the sample.

Gas Pipette. The gas pipette (Text Fig. 2) is used to collect the radon that escaped from the sample during storage and to transfer it to the ionization chamber. The storage tube is sealed, with picëin, into the flange C. The pipette A is evacuated and the eccentric tip of the storage tube is broken against a projection at B, by twisting the ground glass joint 6. The free radon in the storage tube is swept into the pipette with nitrogen. From here it is ultimately swept through the furnace and train into the ionization chamber.

Decomposition Furnace. This is a high-temperature, graphite-resistance, vacuum furnace (Text Fig. 3), which is used to free the radon that is retained by the solid sample. The resistor-heating-element is also the container for the material being heated.[b] The graphite resistor-trough is supported

[b] This ingenious arrangement dates from the experiments of Acheson and others prior to 1900. Many variations have been used since. This furnace was purchased from the Pantechnical Mfg. Co. of Berkeley, California, who built it to designs of R. D. Evans. (Evans, R. D.: 1933, Rev. Sci. Instr., 4, 223.)

between water-cooled clamps of massive copper (A and B) and is surrounded by graphite shields, and is enclosed in a water-cooled, evacuated cylindrical case J. The case is mounted on a sliding carriage in such a manner as to facilitate access to the resistor-trough and electrodes, and so that it may be tipped up for inspection and cleaning. When closed, it is held together by the yoke S and the screw T and a vacuum-tight seal is thus maintained between Q and E. Heavy electric leads from the transformer are soldered to massive blocks of copper H and G which are bolted to the water-cooled terminal supports. Shellacked fiber provides insulation.

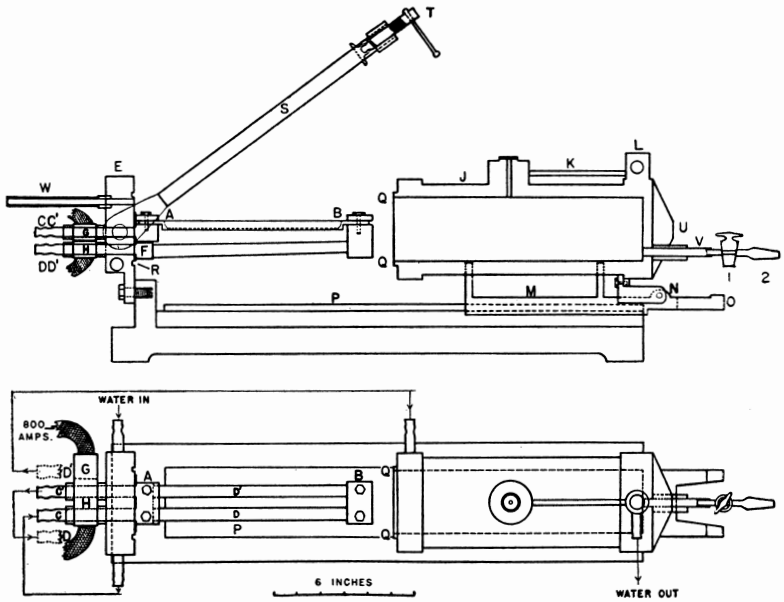


Fig. 3. Decomposition furnace.

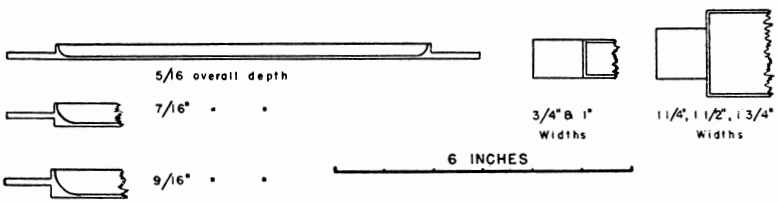


Fig. 4. Graphite resistor troughs.

Four hundred and sixty volts a.c. is applied across any one of the five primary stages of a step-down transformer,[c] the characteristics of which are given in Table I.

TABLE I.

Furnace Transformer Ratings.

Primary volts 440 Tap No.	Secondary volts	Maximum KVA output
1	6	1.4
2	10	4.5
3	15	8.9
4	20	14.5
5	25	20.0

The graphite troughs may be of various dimensions and capacities, as shown in Text Fig. 4, but all have the same length and wall thickness. The troughs, of five different

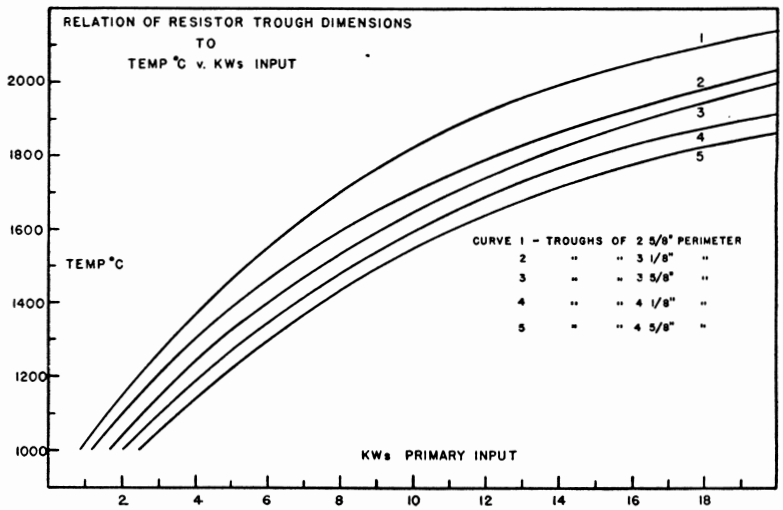


Fig. 5. The approximate equilibrium temperature as a function of the transformer primary energy for various sizes of troughs.

widths, of each of three depths, shown in Text Fig. 4, were tested to determine the relation of power input to temperature. The resulting data are summarized in the curves of Text Fig. 5.

[c] General Electric transformer No. 63 G 839. 20 KVA. The choice of the highest available potential supply in the laboratory reduces the current capacity requirements of the conductors from the main switchboard.

An optical pyrometer determined the temperature, at approximate equilibrium, of the resistor-trough which was sighted through the observation window in the furnace cover and a small hole in the upper graphite radiation shield.[d] Text Fig. 5 shows that troughs having the same transverse perimeter give

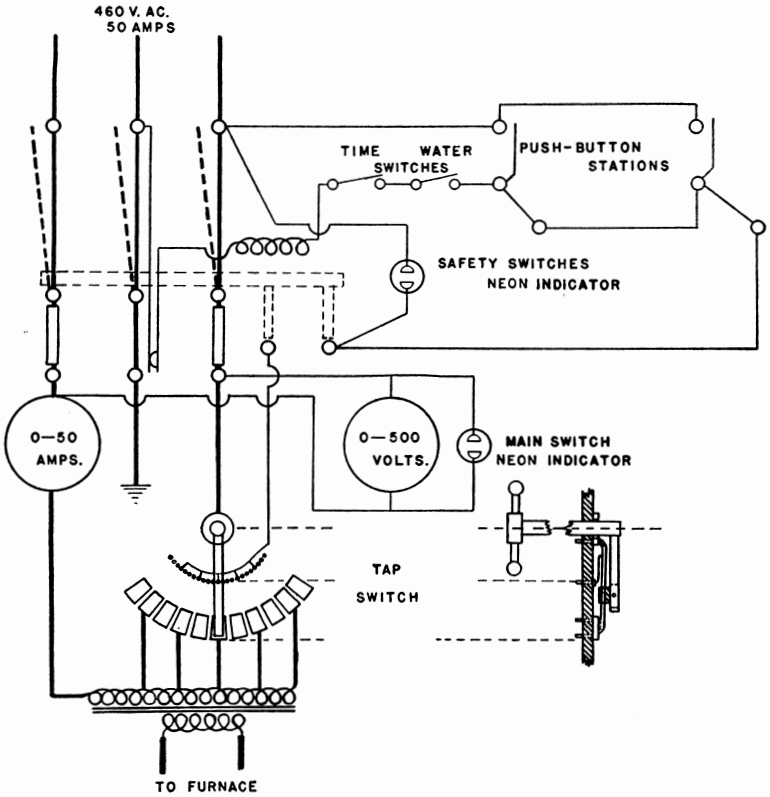


Fig. 6. The control circuit for the furnace transformer.

essentially the same curve of temperature vs. Kws primary input. The selection of trough dimensions from Text Fig. 5 is guided by the attainment of at least 1800° C., and by the most suitable cubic capacity between troughs of similar characteristics. Satisfactory sizes are a 5/16″ by ¾″ trough of 14 cc. capacity (curve 1), suitable for 3 to 4 gram samples of medium to high radium content, and a 7/16″ by 1″ trough of

[d] The correction for the diaphragm effect of these holes on the optical pyrometer reading was established by observing a standard lamp both inside and outside the furnace.

30 cc. capacity (curve 3) for basic rocks and similar material. A 7/16″ by 1¼″ trough of 38 cc. capacity (curve 4) is the maximum that can be employed without overloading the present transformer.

Furnace Controls. The main switch is of the remote-control type[e] with controls located both at the switch panel and at the furnace. The control circuit (see Text Fig. 6) contains two safety devices, one of which is a delayed-time switch that opens the main switch after an interval of five minutes, and the other prevents closing the main switch if water is not flowing through the cooling system, and opens it if this flow should diminish.

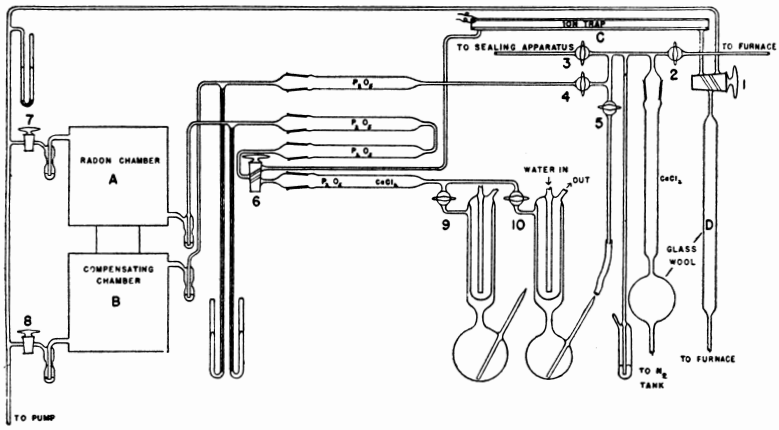


Fig. 7. The train connecting the decomposition furnace and standard radium solutions with the ionization chambers.

The tap switch is controlled from a position near the furnace. It is provided with a series of auxiliary contacts in the magnet circuit of the main switch, so arranged that a movement from one tap to the next first opens the main switch and prevents changing taps under load (see Text Fig. 6).

Train. This consists, in sequence from the furnace, of a dust-trap D, containing glass wool, and an ion-trap C, which collects any ions produced in the furnace. The trap is made of two concentric brass cylinders, 22 inches long, having an annular space between of 1/16 inch, sealed at the ends into a hard-rubber spacer. The outer tube is grounded and the inner one charged to about 800 volts. The remainder of the train

[e] General Electric, three wire, magnetic switch (No. 4383301 G 103).

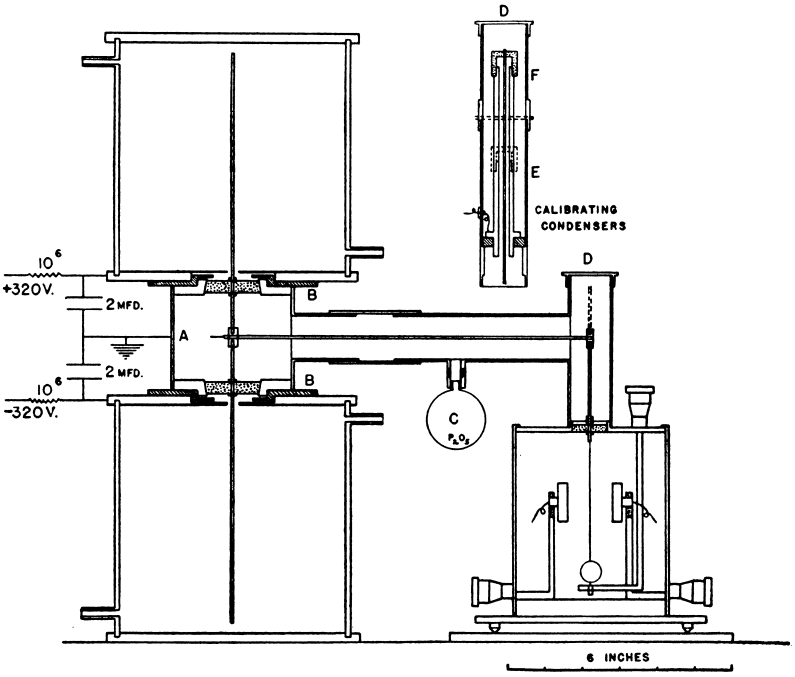


Fig. 8. Ionization chambers and electrometer.

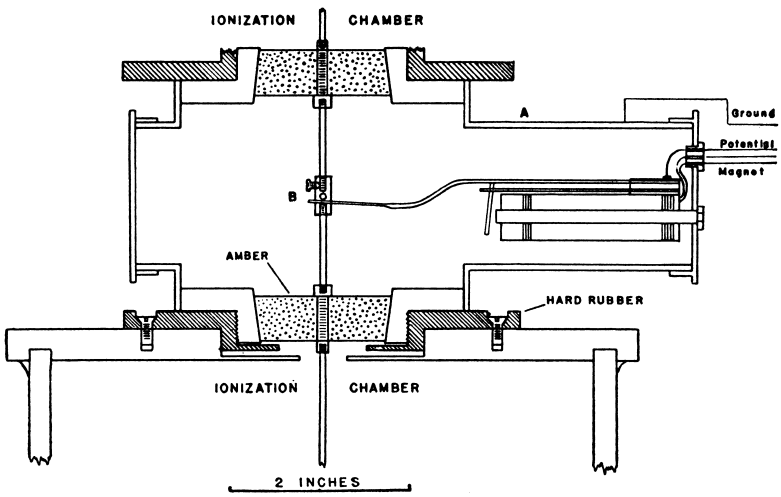


Fig. 9. The insulation system between the ionization chambers.

comprises drying tubes, manometers (to balance the pressure in the two ionization chambers) and mercury gas-traps at the entrances and exits of the chambers, which prevent a diffusion of the radon back into the train and avoid a prolonged contact of the radon with the greased stopcocks 7 and 8 (Text Fig. 7). The ionization chamber may be filled through a flask and condenser which is used to store liquid samples from which the radon may be boiled out. Several flasks with their condensers are provided, two of which are shown permanently sealed to the train (9 and 10, Text Fig. 7). These two flasks contain the standard radium solutions used for calibration.

Pump. The ionization chamber, train, and furnace are evacuated with a Hyvac pump. After decomposition of the sample in the furnace, the radon so liberated is swept into the ionization chamber by filling the system with nitrogen. The compensating chamber (B, Text Fig. 7) is likewise evacuated and filled with radon-free nitrogen.

Ionization Chambers. By connecting the electrodes of two identical ionization chambers,[6] the background ionization, due to radioactive contamination and extraneous radiations, is automatically compensated. One chamber is charged positively and the other negatively with about 320 volts to ground (Text Fig. 8). Therefore negative ions collect on the electrode in one chamber and positive ions on that in the other, resulting in an approximately nett zero charge on the electrometer when no radon is present. Owing to inequalities of contamination between the two chambers and to the statistical fluctuations, this automatic compensation is only approximate; nett background measurements are necessary before and after each radon determination. This differential method is essentially the same as if the background were being eliminated during a measurement, and it permits the entire electrometer scale to be devoted to measuring the charge due to the radon alone. The effects of variations of potential, occurring in the various potential sources, are also removed.

The range of the alpha-particles from radium C′ (6.97 cm.) establishes the dimensions of the chambers, which should be at least 14 cm. in diameter by 14 cm. high to provide for the most efficient ionization. The collecting electrode is made as small as possible in order to minimize the electrostatic capacity. The chambers were cut from one brass tube and are 15 cm. in diameter by 15 cm. high. They are held apart by the brass

cylinder A which bears on the hard-rubber insulations BB (Text Fig. 8). The cylinder A, which is grounded, is provided with three side tubes, one of which is the shielding for the connection to the electrometer. Another side tube (A, Text Fig. 9) contains a relay which establishes various potentials on the electrode system through platinum contacts (B, Text Fig. 9). The third side tube provides access for adjustments. All this system is kept dry by means of phosphorus pentoxide. The collecting electrodes are brass wires, 1/16 inch in diameter, threaded into ⅛ inch screws that in turn are threaded through amber cones into the ionization chambers. These cones, whose larger diameter is 1½ inches, are coated with shellac and seated by evacuating the chambers. The walls of the chambers are recessed into the brass plates forming the tops and bottoms in order that none of the soldering material may reach the inside (see Text Fig. 9). They are "soldered" on the outside only with pure tin instead of the usual lead-tin solder. The same precaution is observed in fastening the brass outlet and inlet tubes, into which the glass connections are fastened with wax.

Electrometer. A Lutz-Edelmann single-fiber electrometer is operated with the unknown potential on the fiber and equal and opposite potentials on the plates. It is mounted on a soapstone base that is supported on three adjusting screws. The highest practical sensitivity is first secured by the mechanical adjustments and thereafter the sensitivity is altered, as required, by changing the potential applied to the plates. Thermostatic control at $30.0 \pm 0.1^\circ$ C. insures constancy of sensitivity, zero point, and focus of the fiber for continuous photographic recording. The focusing and traversing screws of the microscope are extended through the thermostat wall.

Optical System. The field of the electrometer microscope ($\times 28$ magnification) is illuminated by a lamp and reflector located outside the thermostat wall. The light beam passes through a water cell, 2½ inches long, built into the wall of the thermostat.

The central portion of the eyepiece scale, corresponding to 40 divisions, gives a voltage calibration that is very close to linear. The optical system (Text Fig. 10) was designed to project an image of these 40 divisions so as to occupy 22 mm. of a standard 35 mm. motion-picture film. The film advances 22 mm. in one hour, so that an ionization record for each hour occupies a square "frame" 22 mm. on a side. The wall of the

thermostat is indicated at A (Text Fig. 10), the microscope of the electrometer at B, the eyepiece at C. At a distance from the eyepiece of about twice its focal length is located a glass plate, at 45° to the optical axis, in the tube D, which can be adjusted by the lever E. The glass plate reflects sufficient light for visual observation into a vertical tube containing a diaphragm F, a scale G, and a lens H.

The transmitted light passes through a diaphragm K and a timing yoke L (Text Fig. 10). This yoke is moved in a plane

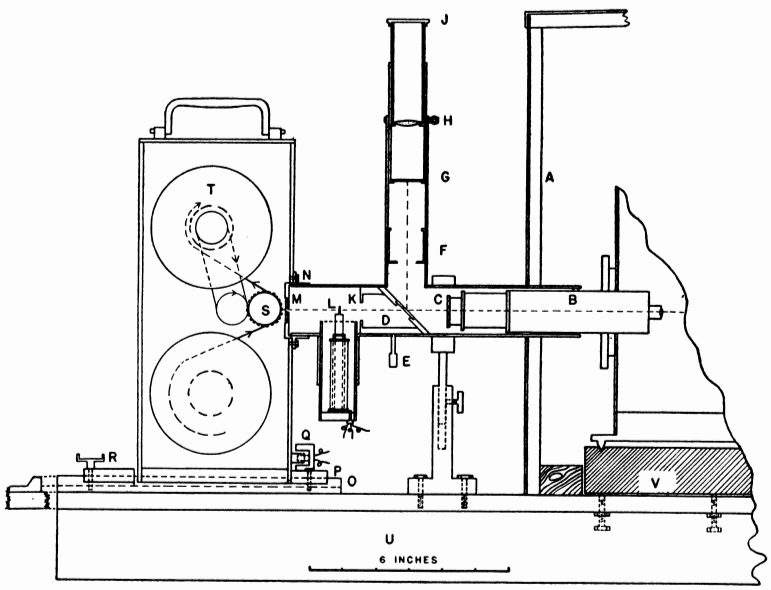


Fig. 10. Optical system.

perpendicular to the optical axis by two magnets, controlled by a master clock, and establishes the position of the image of the camera slit on the recording film, thus providing a time record on the margin of this film (see Text Fig. 11 and Plate I). The Laboratory master clock transmits two independent 5-minute signals spaced 2½ minutes apart, one of which actuates the first magnet and the other the second, thus recording 24 time intervals per hour.

Camera. The horizontal slit defining the width of the light beam projected onto the moving film is located in the camera at M (Text Fig. 10). The removable camera fits the optical

tube at N forming a light-tight system. The camera is aligned by the guide track O. The fore-stop P carries a plug Q to supply current to the telechron motor that drives the film over the geared sprocket S. Since the film rate is fixed, the time of exposure is determined by the width of the slit. The slit is cut as narrow as possible so as to retain a good definition of the image of the electrometer fiber. A slit about 30μ wide was made by cutting a thin platinum foil with a razor-blade. This

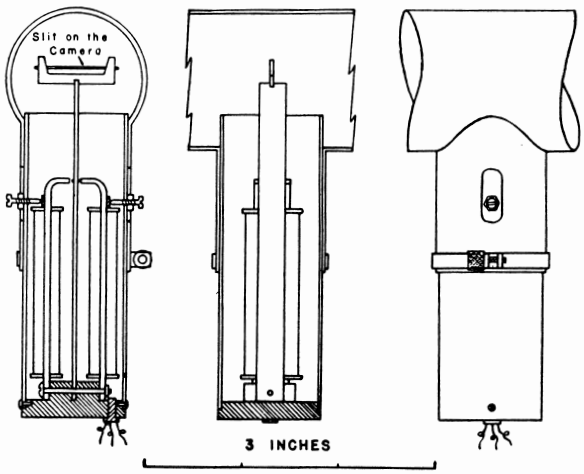


Fig. 11. A magnetic control to obtain optical time signals from electrical time pulses.

was mounted between two microscope cover-glasses, on one of which a millimeter scale was etched, the projection of which produces a reference scale on the film record.

The electrometer, optical system, and camera are mounted on a channel iron, 12 by 36 by 3 inches, to insure stability.

Control Tower. The units necessary for supplying current and potentials to the various parts of the apparatus as well as for automatically calibrating and controlling the record are assembled in a standard radio frame.

A telechron motor rotates once an hour three pairs of cams which actuate three relays that perform the operations necessary for calibration. One relay establishes contact with the electrode system of the ionization chambers at B (Text Fig. 9) for three minutes. During this period the other two relays

connect the electrode system with a predetermined potential, ground it, and connect it with the original potential but of opposite sign. The first relay then opens and isolates the electrode system which is now charged to the final calibrating potential. The ionization in the chamber containing the radon accumulates an excess nett charge on the electrode system, of

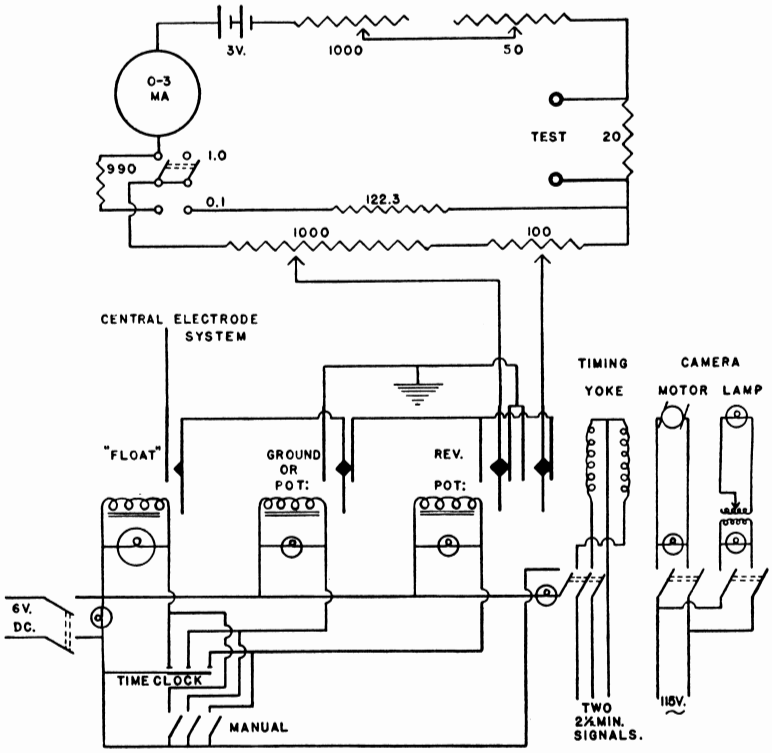


Fig. 12. Potentiometer and automatic calibrating circuit.

the opposite sign, causing the electrometer fiber to move back through the ground position to that of the initial calibrating potential. The calibration potential required to accomplish this in one hour is estimated by a short visual observation at which time the sensitivity of the electrometer is adjusted so as to utilize as much of the recording "frame" as possible. All the clock operations may be performed manually. The calibrating circuit is shown in Text Fig. 12.

A potentiometer supplies calibrating potentials from 0.005 to 2.2 volts. The potentiometer circuit is also shown in Text Fig. 12.

The electrometer plates require a potential difference which is variable between 0 and 140 volts, center-tapped to ground. The ionization chambers each require about 300 volts to ground to yield 90 per cent saturation current.

Many circuits have been developed to transform, rectify, and stabilize the a. c. potentials of laboratory lines. The circuit in Text Fig. 13 is a development from an analysis of voltage

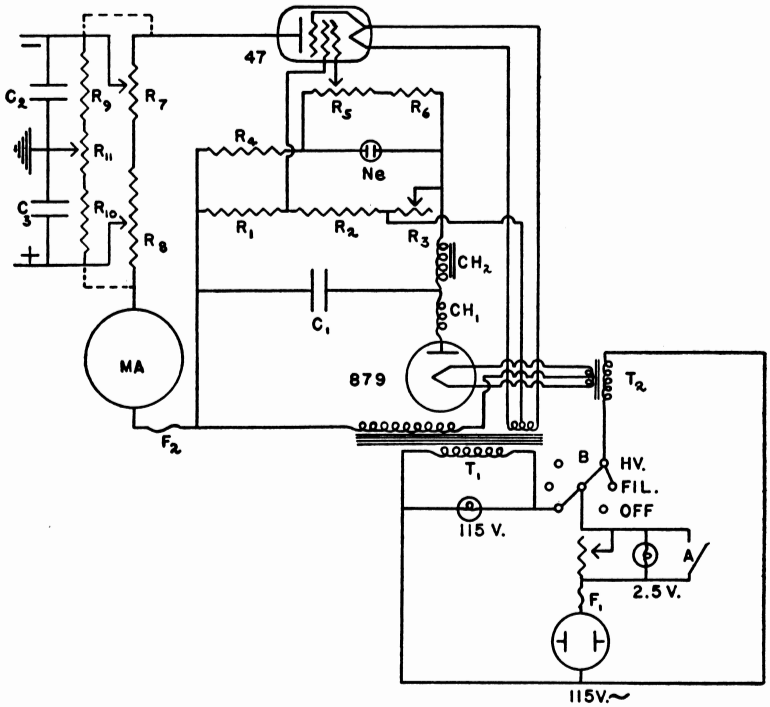


Fig. 13. The circuit values for the potential supply for the ionization chambers, where they differ from those for the electrometer plates, are given in parenthesis.

T_1, 650V. 70MA. 2.5V.Ct. 3A (870V. 250MA. 2.5V.Ct. 3A); T_2, 2.5V.Ct. 3.5A.; CH_1, RF choke; CH_2, 15H. 85MA.; F_1, 1.5A. fuse; F_2, 1/16A. fuse; MA, 0-5 milliammeter (0-10 milliammeter); Ne, 1/4 watt neon lamp without base resistance; C_1, 2mfd 1000V. Dykanol; C_2C_3, 2mfd 600V. Dykanol; R_1, 0.175 meg (0.5 meg); R_2, 15,000 ohms (50,000 ohms); R_3, 5000 ohms variable (20,000 ohms variable); R_4, 0.5 meg (1 meg); R_5, 0.5 meg variable; R_6, 0.5 meg; R_7, 1000 ohms potentiometer (omitted); R_8, 20,000 ohms potentiometer (omitted); R_9R_{10}, 0.10 meg; R_{11}, 10,000 ohms potentiometer.

stabilizers by Evans.[7] The unit to supply the potential for the electrometer plates differs from a second unit to supply the ionization chambers only in the circuit values and the addition of two potentiometers, R_7 and R_8, with which the potential may be varied. Ripple currents picked up in the line between the source of the charging potential and the ionization chambers are eliminated by adding a second filter close to the chambers, as shown diagrammatically in Text Fig. 8.

A potential of 800 volts, for the ion-trap, is supplied with a conventional power-pack using half-wave rectification.

PROCEDURE.

The resistor-trough of the decomposition furnace is preheated in accordance with the time-temperature scheme decided upon for a particular specimen, and the gases evolved are pumped off. Where the radium content of a specimen is known to be very low, this procedure is repeated after cooling and filling the furnace with nitrogen.

The specimen is removed from the storage tube, after the free radon has been swept into the gas pipette as previously described, and transferred to the cold resistor-trough. The furnace, train, and ionization chamber are evacuated and the specimen heated to a succession of temperatures appropriate to the five primary taps of the transformer. The specimen is held at any one temperature for 15 to 75 seconds, depending upon the rate of evolution of the gases, and at the highest temperature for at least 30 seconds.

The pressure in the whole system is now usually between 100 and 250 mm. for 5 g. samples, and the greater portion of the radon is already in the ionization chamber. After cooling, the radon remaining in the furnace and train, together with that in the gas pipette, is swept into the chamber with a slow stream of nitrogen. The whole system is filled to the prevailing atmospheric pressure. The compensating chamber is meanwhile evacuated and filled to the same pressure with nitrogen.

During the three hours required for the radon to reach transient equilibrium with its products, the electrometer sensitivity and the calibrating potential are determined. Thereafter the camera records the rate at which the electrode system accumulates charge for periods of between 3 and 48 hours. At the conclusion of the run, both chambers are evacuated and filled

with nitrogen. The small nett charge due to the back-ground ionization is then recorded over a period of at least 10 hours.

Portions of the film records taken with various electrometer sensitivities are reproduced as positives in Plate I. The film record is read accurately and rapidly by means of a Bibliofilm Reader.[f] The use of 35 mm. "Microfile" film with projection for reading, in preference to that of recording paper with direct measurement, results in a more compact optical system and camera, less fatigue to the observer, less chance for errors in reading, a continuity of recording in excess of 1000 hours if necessary, and small storage requirements for records.

CALCULATION.

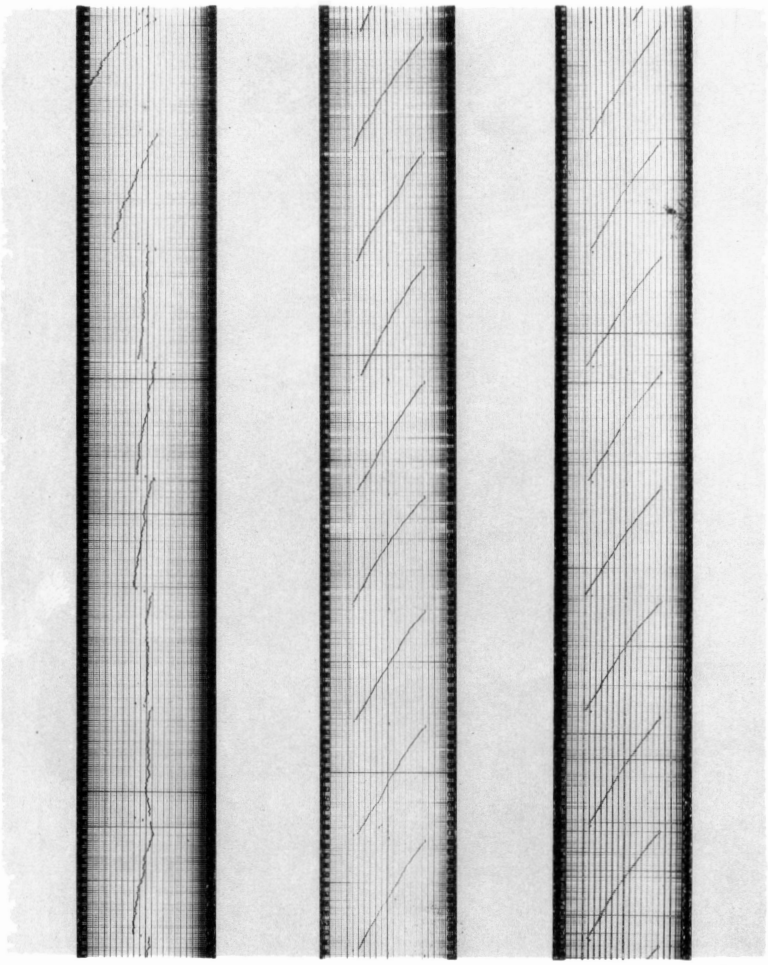
Since the electrostatic capacity of the electrometer changes with its sensitivity, the observations must be reduced to some standard condition by determining the relation between the electrometer sensitivity and the capacity of the electrometer and electrode system. While it is not necessary to determine the absolute value of the capacity, it is convenient to measure this and express the observations in e. s. units of current.

The cylindrical condenser used for calibration (Text Fig. 8) consists of two sections, each being 0.635 cm. I. D. and 6.40 cm. long, and having a calculated capacity of 2.3 cm. A brass wire 0.159 cm. in diameter connects with the electrometer and forms one electrode of the condenser and is held concentric to the cylinder by an amber guide (Text Fig. 8).

To eliminate the unknown end-effects of the cylindrical condenser, readings are taken, first with the lower section and then with the upper section added. By manipulating the shields E and F (Text Fig. 8) and the amber guide, and by replacing the electrode for the first section with one of the same diameter but of appropriate length for the two sections, the geometrical disposition of all the parts surrounding the condenser is identical with one or both sections.

When a potential ΔV_c is applied to the calibrating condenser, an electrometer deflection is obtained which can be converted into volts ΔV_e, with the measured volt-sensitivity of the electrometer. Let $\Delta V_c/\Delta V_e = \mu$. Further, let μ_1 and μ_2 be values

[f] Since an integral number of 2½ minute intervals is chosen, the reading of a record is a counting operation except for the measurement of the fractions of the arbitrary scale units at the beginning and end of each hour. Thus, no error is introduced due to projection distortion.



(a) (b) (c)

FIG. 1

Positives of portions of the electrometer film record showing the marginal time scale, the arbitrary deflection scale, the calibrating points, and the charging of the electrometer. (a) is from a background record at a sensitivity of 7.8 x 10^{-4} e.s.u. of charge per division and shows the decay of the deposit from the preceding radon-run down to the normal background. (b) is from a radon determination at 55 x 10^{-4} e.s.u. per division. (c) is from another radon measurement at 114 x 10^{-4} e.s.u. per division.

of this function for one and both sections of the calibrating condenser. The following equation can be derived:

$$C = \frac{c_2(\mu_2 - 1)(\mu_1 - 1)}{(\mu_1 - \mu_2)} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where C is the capacity of the system without the calibrating condenser and c_2 is the calculated capacity of the second section of the calibrating condenser. C was determined at six sensitivities covering the complete range from 2 to 100 divisions per volt.

In the second method, a change of charging potential ΔV_i on one ionization chamber, e.g. produced by a potentiometer in series with the usual charging potential, while that on the other is held constant, gives an electrometer deflection ΔV_e. No calibrating condenser is added. In this case

$$\frac{\Delta V_i}{\Delta V_e} = \theta = \frac{C}{c_i} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where c_i is the capacity of the ionization chamber. θ was determined for the complete range of electrometer sensitivities with each chamber in turn.[g] The calibrating condenser is now added. If a_1 and a_2 are the values of $\Delta V_i/\Delta V_e$ in the above experiment with one and both sections of the calibrating condenser at ground potential, it can be shown that

$$c_i = \frac{c_2}{(a_2 - a_1)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

c_i is independent of the electrometer sensitivity but three sensitivities were used and the capacity of each chamber was measured, resulting in a value for the radon chamber of 2.1 ± 0.1 cm. and for the compensating chamber of 2.0 ± 0.1 cm. Values of C are obtained by substituting these results in equation 2. Text Fig. 14 shows the variation of the capacity of the system with electrometer sensitivity expressed in divisions per volt and the reciprocal.

In calculating the radium content from the observations, the following symbols will be used:

D = the deflection of the electrometer due to the charge accumulated from the ionization, in arbitrary film divisions.

[g] The relation of θ to the electrometer sensitivity is a measure of the change of capacity of the system with electrometer sensitivity in arbitrary units. These measurements are independent of the calibrating condenser.

t = the number of minutes required to produce D (usually 55 minutes).

S = the sensitivity of the electrometer in volts per division, this being the mean of the calibration before and after each hourly observation.

C = the e.s. capacity of the electrode system determined from S.

E = the calibrating potential in volts.

B and B′ = the positive and negative calibration deflections measured from the ground position in arbitrary film divisions.

T = the time in hours elapsed between the introduction of the radon into the chamber and the middle of a given hourly observation.

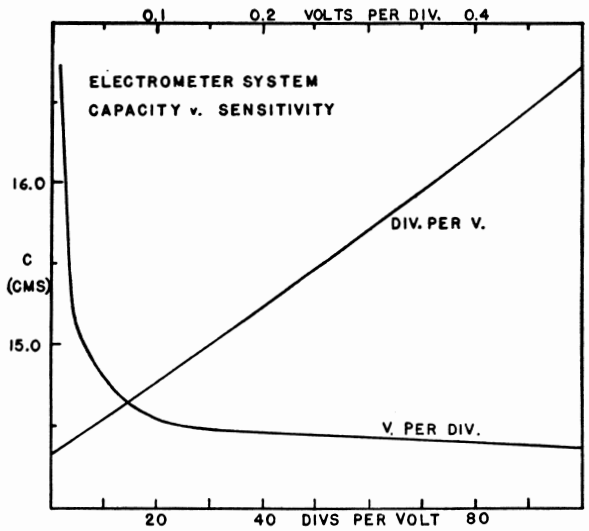


Fig. 14. The e.s. capacity of the electrometer, leads, and electrodes of the ionization chambers, plotted as a function of the sensitivity of the electrometer.

λ_{Rn} = the disintegration constant of radon in reciprocal hours.

i = the ion current in e. s. units from each observation.

$\bar{i}_B$ = the mean differential background ion current, being the mean of background runs preceding and following the radium determination. This is to be added with respect to sign.

i_R = the ion current due to the radon and its products alone.

$u = e^{\lambda_{Rn} T}$

n = the number of observations.

Ra = the radium in grams per gram of the material measured.

K = the apparatus constant in curies of radon (grams of radium) per unit of ion current.
W = the weight of the sample.

The ion current from each observation is given by

$$i = \frac{D}{60t} \cdot S \cdot \frac{C}{300} \text{ where } S = \left[\frac{2E}{B+B'}\right]_{mean} \quad \ldots\ldots\ldots (4)$$

The mean ion current due to the radon and its products, with each observation reduced to the value for T = O, is a measure of the radon present and is given by

$$\overline{i_{Ru}} = \frac{\Sigma(i_{Ru})}{n} = \frac{\Sigma[(i+\bar{i}_B)e^{\lambda_{Ru}T}]}{n} \quad \ldots\ldots\ldots (5)$$

In computing $\bar{i}_B$ from the background observations, equation 5 reduces to

$$\bar{i}_B = \frac{\Sigma(i)}{n} \quad \ldots\ldots\ldots (6)$$

The radium content is given by

$$Ra = \frac{\overline{i_{Ru}} \times K}{W} \quad \ldots\ldots\ldots (7)$$

Observations made prior to 3 hours after the radon is admitted to the chamber are used only to identify the ion current as due to radon, by virtue of the characteristic build-up curve of RaA and RaC′. In background runs, a similar period must be allowed for the decay of the deposited RaA and RaC′ from the previous radon determination.

Probable Error. The probable error in these determinations is especially significant since the quantity measured is itself subject to random fluctuations. This is the prime source of error in the results, and the magnitude of this source can only be decreased by increasing the number of observations. The probable error r, due to random fluctuations observed in the ion current, is calculated from the data with the Bessel formula

$$r = \pm 0.67\left[\frac{\Sigma(\overline{i_{Ru}} - i_{Ru})^2}{n(n-1)}\right]^{1/2} \quad \ldots\ldots\ldots (8)$$

If the values of r for the radium determination, the background

determination, and the algebraic sum of these quantities, be r_1, r_2, and r_3, respectively, then

$$r_3^2 = r_1^2 + r_2^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

A constant probable error of 0.8 per cent is contributed by the errors of the remaining factors in equations 4[h] to 7, which are propagated in the usual manner for products and quotients. Consequently there is a negligible increase in the over-all accuracy, once a sufficient number of observations are made to decrease r_3 to a value corresponding to about 0.6 per cent. The over-all probable error is then 1 per cent. In most cases a value of n of less than 24 hours and a sample of less than 10 grams are sufficient to maintain this order of accuracy. It must be emphasized that this includes no contributions of any unknown systematic errors and merely states that there is a 50 per cent chance that the true value lies within this probable error r_3. The probability that the true value lies within $m \times r_3$ where m is an integer, can be ascertained by reference to probability tables.[8]

An expected value of r_3 can be calculated from an analysis of a large number of background determinations. Such a value is particularly useful in determining the number of observations (n) necessary to obtain a given degree of accuracy for a particular radium content. The radium content can be roughly estimated from the preliminary visual observation. A comparison of the value of r_3 from equation 9 with this expected value has been used to detect departures of the distribution of the fluctuations from the normal law indicating an instrumental error in the measurements, usually due to insulation leakages. The average number of alpha-particles emitted per hour X_2 from the radioactive contamination in each ionization chamber is calculated from the background observations by means of a procedure previously described.[2] If X_1 is the effective number of alpha-particles emitted per hour by the radon and its products in equilibrium, the expected probable error is given by

$$r_3 = \pm 0.67 \left[\frac{X_1 + 4X_2}{n}\right]^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

[h] It is immaterial whether C in equation 4 has the value of the absolute e. s. capacity or only some arbitrary value. Therefore the error involved is that of dC/dS. This can be determined to ±0.2 per cent and is far more accurately known than C itself.

When the result of a radium determination becomes equal to the probable error of the background, the observational limit of the apparatus has been reached. This is given by

$$x_1 = r_2 = 0.67(2X_2/n)^{1/2} = 0.0036\times10^{-12}(2X_2/n)^{1/2} \text{ curies of radon} \qquad (11)^{j}$$

The accuracy of the measurements and the magnitude of the observational limit are therefore, in a large measure, dependent upon the precautions taken to prevent radioactive contamination during the construction of the apparatus. The present value of X_2 is 100 ± 6 alpha-particles per hour in each chamber, corresponding to the low value of 9 alpha-particles per 100 cm.^{2} per hour.

CALIBRATION.

The apparatus constant K is determined by measuring $\overline{i_R u}$ in equation 7 for the radon removed from a standard solution of radium. The temporary standard solution now in use contains 3.30×10^{-9} gram of radium per milliliter.[k] Sub-dilutions of this standard containing 13.2×10^{-12} and 1.32×10^{-12} g. Ra were sealed into the storage flasks previously described (see Text Fig. 7). Various amounts of radon may be obtained from one standard solution by accumulating the radon over accurately known periods.[l]

Prior to the introduction of the radium solutions, the storage flasks were tested for any possible extraneous source of radon by filling them with nitrogen. This nitrogen was transferred after 60 days to the ionization chamber under the same conditions of time and temperature as pertain to the determination of K. In one case the result was negative; in two other cases

[j] Equations 10 and 11 are derived frem equations given in reference 2, namely 11 and 8. X_1 has the value of 250 alpha-particles per hour per 10^{-12} curie of radon. Since the half-life of RaA (3.05 minutes) is short compared with one hour, its disintegration cannot be considered as an independent random process and X_1 in equations 10 and 11 above is therefore given the value of 187.

[k] Standard radium solutions of 10^{-9} and 10^{-11} g. Ra have been prepared by the National Bureau of Standards. This apparatus is being used in a collaborative check on these standards. The final value of K will be determined with these standards.

[l] In routine work, K is determined about every two months. In this interval the radon has reached a state of equilibrium with the radium and the value of K is not subject to a possible error due to an incomplete deemanation of the radium solution at the commencement of any given period of accumulation.

a value of 0.006×10^{-12} curie of radon was found. These values are below the observational limit of the apparatus for a 15-hour run and therefore it is possible to state only that such an extraneous source, e.g. the glass walls, contributes $<0.013\times10^{-12}$ curie of radon to the radon from the standard.

Three hundred ml. of the water used in preparing sub-standards was found to contain $0.006\pm0.002\times10^{-12}$ g. Ra per ml. By the substitution of this value in the equations for the dilution processes the true radium content of a sub-standard is determined. The present correction for the radium content of the diluting water is about 2 per cent.

It was found that a few glass splinters are capable of lowering the radon output of a standard solution, apparently by adsorption of the radium. [9, 10] Thus in Table II the values of K have been obtained from the same sub-standard over comparable periods of time, but it appears that roughly 4.5 and 8.5 per cent of the radium have been removed in 61 and 174 days, respectively, from the one solution, into which about 0.2 cc. of freshly broken glass splinters was accidentally introduced.[m] From equation 7 it is obvious that removal of radium from the standard solution will cause an apparent increase in K.

TABLE II.

Values of the apparatus constant K demonstrating the removal of radium by glass splinters from standard solutions containing 13.2×10^{-12} g. radium.

Time in days		K
After introducing the solution into the flask	After introducing glass splinters	curies of radon per 10^{-5} e. s. u.
4	—	$2.00\pm0.02\times10^{-12}$
10	—	2.01 0.02
12	—	1.98 0.02
18	—	2.05 0.02
134	—	1.94 0.03
	mean	2.00 ± 0.01
10	0	2.00 ± 0.02
71	61	2.09 0.02
184	174	2.17 0.02

[m] Normal values of K were obtained after removing the glass splinters and replacing the solution with a new portion of the same sub-standard in the same flask.

Many of the specimens to be examined, particularly the ocean-bottom sediments, produce considerable quantities of carbon dioxide in the decomposition furnace, so that the gases in the ionization chamber may contain up to 30 per cent carbon dioxide. A determination of the apparatus constant was made with carbon dioxide instead of nitrogen. The compensating chamber was filled with nitrogen as usual. A value of $K_{CO_2}/K_{N_2}=1.02\pm0.02$ was obtained, which indicates that no error is introduced by the presence of carbon dioxide in the ionization chamber.

RESULTS.

Details of the many specimens examined and the results of the radium analyses with their implications will be presented elsewhere. A few analyses have been selected here to indicate their bearing on the technique.

Sampling. The variability of analytical results due to the circumstances of sampling geological material in the field constitutes a difficulty that can only be remedied by more analyses than exist at present, but the effect of small-scale sampling from powders, consisting of 20 to 200 grams of a specimen, has a direct bearing on the laboratory procedure. Specimens of cores[11] of ocean-bottom sediments are easily pulverized and in this condition exhibit little or no inhomogeneity, as can be seen from Table III. The analyses of the limestone (P-193 in Table III) are taken from the results of a suite of rocks which was examined for the effect of various modes and degrees of grinding. This suite was analyzed as one part of a collaborative program to establish primary standards for radium determinations.[12] Differences as large or larger than those given in the fourth column might be expected to occur once in about P occasions (shown in the final column) if these differences are due to the random errors of measurement. With the possible exception of P-126-279, the final preparations of the laboratory specimens are essentially homogeneous.[n]

Loss of Radon from Specimens. If the radon diffuses out of a specimen and is lost to the atmosphere, the calculated radium content will be lower than the true value. This may be

[n] There is reason to believe that the radium has been introduced into the ocean sediments in such a manner as to produce a more uniform distribution for a given horizon than is found in the continental rocks. This will be discussed elsewhere.

TABLE III.

Significance of Sampling.

Specimen	Weight g.	Radium content in 10^{-12} g. per g.	Difference	P No. of occasions
P-126-23	3.15	1.08±0.02		
Ocean-sediment	3.14	1.06±0.03	0.02±0.035	2
P-126-211	3.21	1.38±0.02		
Ocean-sediment	3.00	1.36±0.02	0.02±0.03	2
P-126-279	4.70	1.04±0.02		
Ocean-sediment	2.06	1.14±0.03	0.10±0.035	23
P-135-36	3.10	2.22±0.03		
Ocean-sediment	3.07	2.18±0.03	0.04±0.04	2
P-135-109	3.02	2.27±0.03		
Ocean-sediment	3.24	2.35±0.06	0.08±0.07	2
P-193	10.00	0.13±0.004		
Limestone	5.00	0.14±0.003	0.01±0.005	6

obviated as previously described and Table IV illustrates the reason. The values of P, which have the same significance as

TABLE IV.

The loss of radon from specimens.

Specimen and treatment*		Radium content in 10^{-12} g. per g.	Difference	P No. of occasions
P-124-0	s	1.21±0.02		
Ocean-sediment	ns	1.06±0.02	+0.15±0.03	1400
P-124-207	s	1.85±0.02		
Ocean-sediment	ns	1.22±0.03.	+0.73±0.04	$>10^{12}$
P-75	s	5.53±0.06		
Granite	ns	5.65±0.05	−0.12±0.08	3
P-83	s	1.13±0.01		
Granite	ns	1.07±0.02	+0.06±0.02	23

* s denotes sealed specimens; ns denotes specimens not sealed.

P in Table III, show that with the exception of the granite P-75, the differences in the fourth column can be attributed only to a loss of radon from those specimens which were not sealed and which were merely stored in specimen vials for thirty or more days after being powdered. It is possible that coarse material might show smaller differences but the question of a homogeneous sample would be re-introduced.

This apparatus has functioned continuously for periods of three months, and in the course of 5000 hours of recording has required but two vacuum tube replacements and three phosphorus pentoxide refills. No difficulty has been encountered from the excessive humidity prevailing in the summer months at Washington, D. C.

Radium measurements have been made which range from 0.003×10^{-12} to 25×10^{-12} gram of radium per gram or cc. of a variety of solids and liquids.

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REFERENCES.

1. Meyer, St., and v. Schweidler, E.: 1927, Radioactivität. Teubner, Berlin, pp. 302-312.
2. Urry, Wm. D.: 1936, J. Chem. Phys., 4, 40.
3. Evans, R. D.: 1933, Rev. Sci. Inst., 4, 223.
4. Joly, J.: 1912, Phil. Mag., 6, 22, 134.
5. Ebler, E.: 1912, Z. Elektrochem., 18, 532.
6. Steinke, E.: 1930, Physik. Z., 31, 1019.
7. Evans, R. D.: 1934, Rev. Sci. Inst., 5, 371.
8. Bond, W. N.: 1935, Probability and Random Errors. Edward Arnold & Co., London.
9. Starik, I. E., and Gurevich, A. M.: 1937, Proc. State Radium Institute Leningrad II, 241.
10. Nikitin, B., and Wdovenko, V.: Ibid., p. 256.
11. Piggot, C. S.: 1938, Sci. Monthly, 47, 201.
12. Curtiss, L. F., et al.: 1940, Rev. Sci. Inst., 6, 205.

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