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Health and Safety Laboratory

ANALYTICAL BRANCH

A METHOD FOR THE DETERMINATION OF RADON IN WATER

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ABSTRACT

A rapid and simple procedure for the determination of radon in water is presented. The analysis is performed indirectly by scavenging the short-lived daughters with lead precipitated as the sulfide, and counting the alpha radiation from RaC'. Theoretical decay curves for radon daughters and radon are included. The recovery determined from radium-spiked solution is satisfactory and the reproducibility for successive water samples is good. Techniques for the elimination of long-lived interfering nuclides are discussed. Preliminary investigations indicate that the chemical procedure in conjunction with a Samson alpha survey meter is feasible for in-the-field studies.

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The presence of detectable amounts of radioactivity in springs, streams and other bodies of water has been recognized for a number of years. At various sites a large portion of this activity is due to dissolved radon and its short-lived daughter products. In these cases, radon is concentrated by gaseous diffusion and transport by water from its initial position where it was present in the form of radium.

Jacobi(1) and others have described methods for the determination of dissolved radon by deemanation followed by collection and counting with an ionization chamber. This procedure requires expensive custom-made instrumentation. Harley(2) has studied sampling and measurement of airborne daughter products of atmospheric radon for the determination of the radon concentration of air. In a roughly parallel fashion, the daughter products of radon can be removed from solution by chemical means, and after this separation, the activity can be measured and related to the original radon concentration.

(1) Jacobi, Journal of the Chemical Society, S 314, 1949

(2) Harley, Nucleonics, Vol. 11, No. 7

In practice, 1-liter samples of water are collected and stored in polyethylene bottles. Before the bottles are capped, carrier lead and HCl are added. At least 3 hours are allowed to elapse prior to analysis to establish radioactive equilibrium between parent and daughter product activities. The solution is transferred to a beaker and H_2S bubbled through. The PbS is collected on a Millipore filter by vacuum filtration. At least half an hour is permitted to elapse before counting to allow the measurement to be made on the linear portion of the daughter product decay curve. Since at no point in the chemical operation is radon completely and instantaneously removed from the solution, the time between precipitation of the daughter products and completion of the filtration must be short. For a 1-liter sample, this can be accomplished in less than 5 minutes.

In Figure 1 the radon decay scheme is outlined. If an equilibrium condition exists prior to the removal of radon, the overall alpha activity of the daughter products may be expressed by the Bateman Solution:

$$\sum \lambda n = 1.02\ e^{-\lambda_2 t} + 4.27\ e^{-\lambda_3 t} - 3.29\ e^{-\lambda_4 t}$$

where t is the time after removal of radon and λ_2, λ_3, and λ_4 are the decay constants for RaA, RaB and RaC respectively.

This equation is plotted in Figure 2 as fraction of initial activity against time in minutes. The linear portion of the curve corresponds to an effective half-life of 31 minutes. This value and the shape of the initial portion of the curve have been checked experimentally by measuring the activity of the decay products in an alpha scintillation counter(3).

Since low background, high geometry α scintillation counters are available in this laboratory, the α activity of the radon daughters is counted. For most routine measurements, one minute counting periods can be used. Under these circumstances, 200 micromicrocuries of radon may be determined with a 25% error at the 95% confidence level. In the case of low activity samples, the precision of the measurement can be increased by extending the counting period and adjusting the average counting rate by the theoretical count-decay correction.

(3) Graveson, DeGiovanni, Levine, "An Alpha Scintillation Counter for Laboratory Measurements", NYO-1523. The sample mount in the counter chamber employed in the present study has been widened to accommodate sources of various diameter.

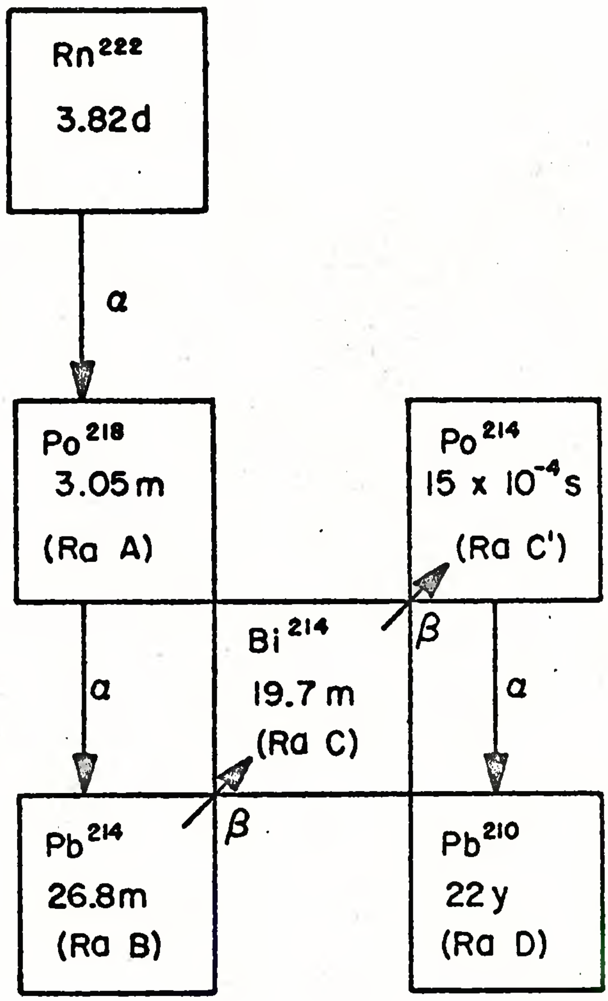

FIG. I PRINCIPAL DECAY SCHEME FOR RADON

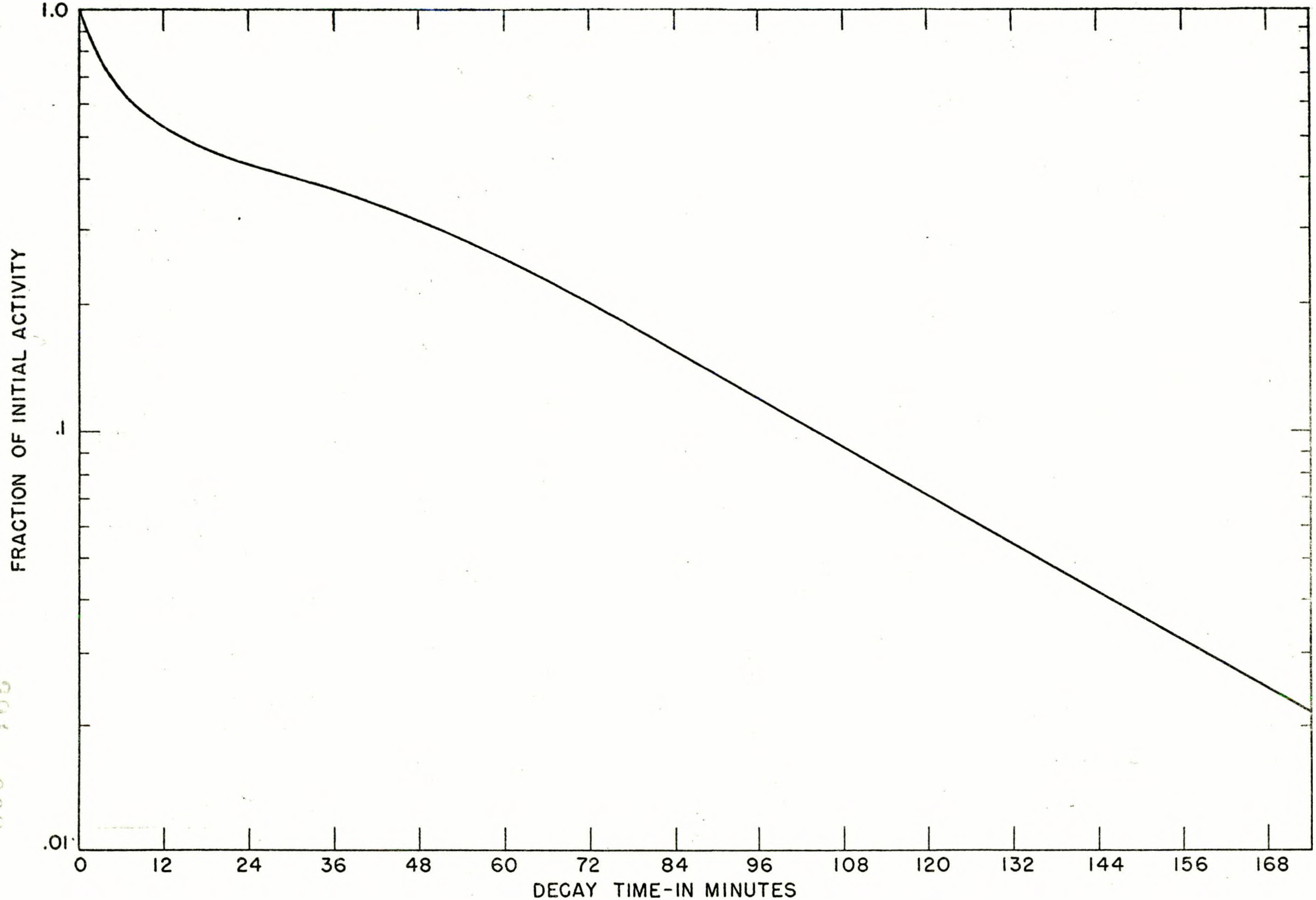

FIG. 2 RADON DAUGHTER PRODUCT α DECAY

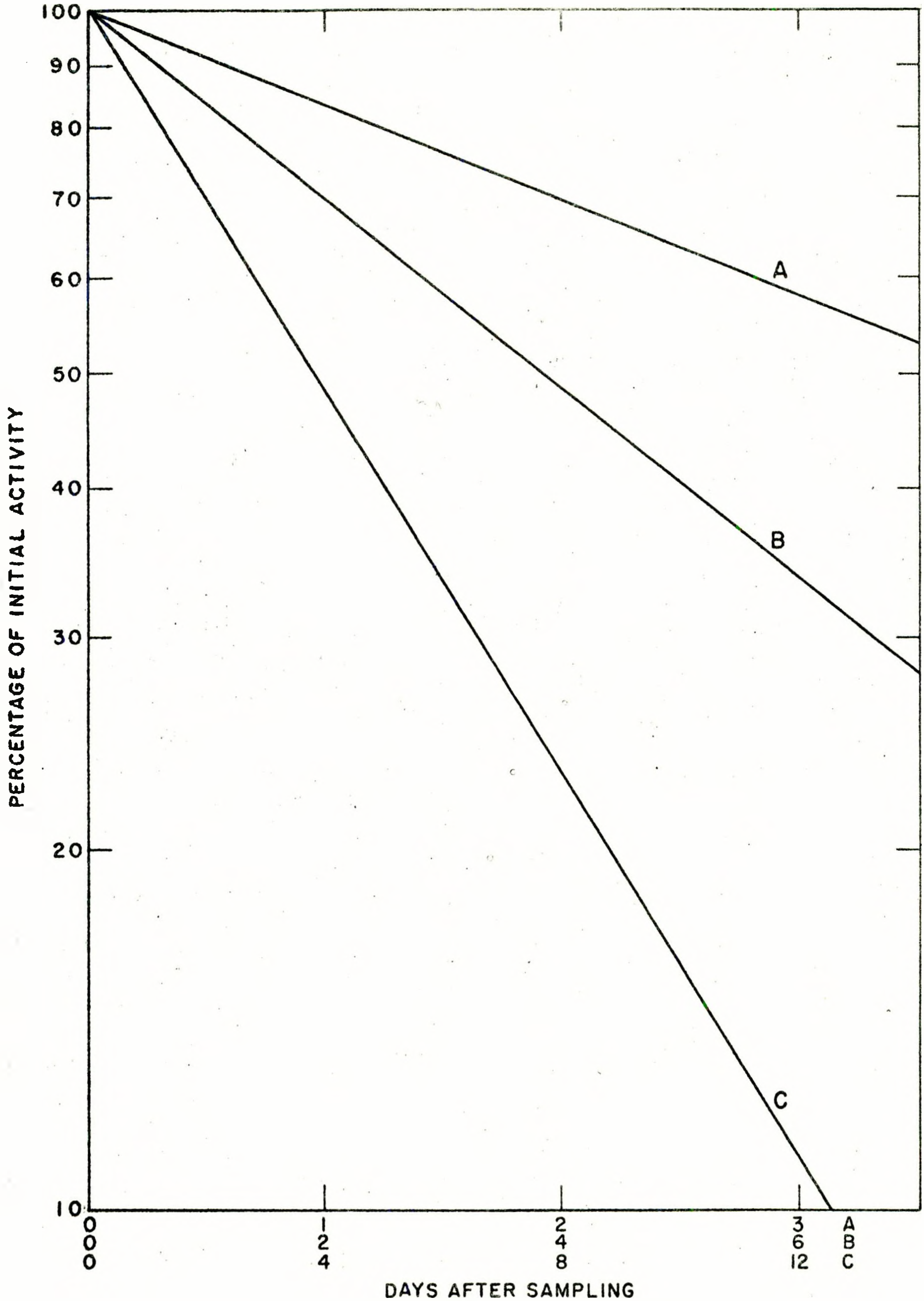

FIG. 3 RADON DECAY

INTERFERENCES

Long-lived naturally occurring radionuclides, i.e., thoron daughter products and RaF, will be coprecipitated with PbS and when present in the sample, will interfere with the activity measurement for the radon daughters. This may be checked by measuring the residual activity after the Rn daughter products have completely decayed. The long-lived activity is extrapolated and subtracted from the initial measurements.

The radon activity in a solution which contains radium will not decay according to the radon half-life. Therefore, the extrapolated value for radon determined at the time of chemical analysis will be in error. The magnitude of the error will depend on the amount of radium present and the time between analysis and extrapolation. The radium may be determined by first boiling the filtrate after the PbS precipitation and returning it to the sample container. Radon is allowed to build up from the radium and the daughter products precipitated and counted. A suitable correction is made on the original radon measurement.

α ABSORPTION

To insure complete precipitation of the radon daughter products, 20 milligrams of inert Pb^{++} are added as a carrier. An experiment was conducted to study the total effect of absorption and scattering of alpha radiation in this mass of lead carrier. Samples of Ra D, E, F in the presence of vanishingly small quantities of macroconstituents were plated on aluminum planchets and compared with Ra D, E, F spikes of PbS. The lead was precipitated as the sulfide from a neutral solution contained in an Atomlab-Ekstein centrifuge tube. Experimental errors such as possibly incomplete precipitation and collection of the PbS and nonuniform distribution of the precipitate on the sample pan were minimized by determination of the alpha-to-beta ratios (see Table 1). The average difference between the two sets of data is 0.80. Since it is true that the energy of Ra C' (7.6 Mev) is greater than that of Ra F (5.7 Mev), the use of an empirical correction factor such as 0.80 represents an approximation.

TABLE 1

ABSORPTION IN LEAD SULFIDE

A. "CARRIER FREE" Ra D, E, F

Sample	α Activity c/m	β Activity c/m	Ratio α/β
1	668.2	233.7	2.86
2	549.9	229.7	2.39
3	494.2	184.6	2.68
4	709.2	215.1	3.30
5	751.2	222.4	3.38
6	472.2	158.9	2.97
AVERAGE			2.93

B. 20 mg Pb^{++} CARRIER ADDED

Sample	α Activity c/m	β Activity c/m	Ratio α/β
7	437.2	177.4	2.46
8	390.9	168.2	2.32
9	326.9	134.2	2.44
10	lost	—	—
11	369.9	181.4	2.04
AVERAGE			2.32

C. 40 mg Pb^{++} CARRIER ADDED

Sample	α Activity c/m	β Activity c/m	Ratio α/β
12	595	351.9	1.69

APPARATUS AND REAGENTS

1 liter polyethylene bottles

1 liter graduate

10 ml graduate

2 liter aspirator flask

500 ml aspirator flask

2 liter beaker

stirring rod

Millipore filtering apparatus*

Millipore filters HA, white, plain .047 mm, Lovell Chemical Co., Watertown, Mass.

forceps

HCl - Assay (HCl) 37.0%

Lead carrier solution 20 mg Pb^{++}/ml
dissolve 31.97 grmas $Pb(NO_3)_2$ in distilled water and dilute to 1 liter.

Mounted cylinder of H_2S "lecture bottle" size cylinder obtained from Fisher Scientific Company.

Samson Survey Meter

α Scintillation counter(3)

*Millipore filter holder - part #3
Millipore filter holder - clamp #3
Millipore filter holder - part #4
} Lovell Chemical Co. Watertown, Mass.

ANALYTICAL PROCEDURE

1. Collect a 1-liter sample of water and transfer to a polyethylene bottle containing 8.5 ml concentrated HCl and 20 mg of Pb^{++}. Fill the bottle to the top, stopper tightly and allow at least 3 hours to elapse before analysis.

2. Transfer the solution to a 2-liter beaker and immediately bubble through H_2S rapidly until the precipitation is complete. Note the time of the commencement of this step.

3. Immediately vacuum filter through a Millipore paper with appropriate apparatus. Note the time at the completion of this step.

4. Allow at least 30 minutes to elapse after the completion of step #3.

5. Measure the alpha activity and note the time.

6. Check for residual long-lived activity.

CALCULATIONS

Determination of micro-micro curies of radon gas at time of sampling:

$$\left(c/m\right)\left(\frac{1}{geom.}\right)\left(\frac{1}{0.8}\right)\left(\frac{1}{A/A_o}\right)\left(\frac{1}{B/B_o}\right)\left(\frac{1}{2.22}\right) = \mu\mu/\text{sample}$$

SYMBOLS

c/m - Net alpha c/m

geom.- Instrument geometry

0.8 - Absorption factor

A/A_o - Fraction of initial daughter product activity counted. The period of radon daughter product decay is the time difference between the midpoint of the chemical separation and the start of the activity measurement.

B/B_o - Fraction of original radon present at time of analysis.

2.22 - d/m/$\mu\mu$c

If the activity is determined by means of counting, the correction factors tabulated in Table 2 may be used to adjust the measured counting rate to the instantaneous rate at the start of the count.

TABLE 2

COUNT DECAY CORRECTIONS

Counting Time Minutes	Count-Decay Factor
1	1.012
2	1.023
5	1.057
10	1.116
20	1.240
30	1.372

DATA SHEET OUTLINE

Column	Description
1	Sample number
2	Volume collected
3	Time of sampling
4	Volume used (in liters)
5	Time at midpoint of chemical separation
6	Time at start of count
7	Column #6 - Column #5
8	A/A_o (from Rn daughter decay curve - Figure 2)
9	Counts
10	Duration of count (minutes)
11	c/m
12	Net c/m (corrected for decay during count)
13	d/m
14	Column #13 ÷ Column #8 (Activity of Rn at time of precipitation
15	Column #5 - Column #3
16	B/B_o (from Rn decay curve - Figure 3)
17	Column #14 ÷ Column #16
18	Column #17 ÷ 0.8 (Activity of Rn at time of sampling
19	Column #18 ÷ 2.22 (μμ Rn at time of sampling)
20	μμc Rn per liter at time of sampling

RECOVERY AND REPRODUCIBILITY

The performance of this procedure has been tested in two ways. Known amounts of standard radium were added to one liter polyethylene bottles, diluted with 0.1 N HCl and stored for two months. The radon daughters were precipitated and the original radon activity was calculated. The results are recorded in Table 3. Satisfactory recovery is indicated for each of the three spiked samples.

It was of interest to test the reproducibility of the procedure under actual field conditions. For this purpose, a body of deep and still water was selected. Successive samples were collected on two different dates and the analysis performed one to two days afterwards. The calculated radon activities are recorded in Table 4. Good agreement is indicated among the replicates collected on the two different dates.

TABLE 3

RECOVERY OF RADIUM SPIKES

Sample	Ra added µg	Ra found µg	Recovery %
a	0.1000	0.1017	102
b	0.0201	0.0195	97
c	0.0214	0.0185	86
AVERAGE			95

TABLE 4

COMPARISON OF REPLICATE SAMPLES

SITE A28

A. Water samples collected 9/16/54

Sample	Radon $\mu\mu c/L \times 10^4$
A28 (1-9)	2.44
A28 (3-9)	2.49
A28 (5-9)	2.28
A28 (7-9)	2.59
AVERAGE	2.45

B. Water samples collected 10/11/54

Sample	Radon $\mu\mu c/L \times 10^4$
A28 (5-10)	1.61
A28 (6-10)	2.05
A28 (7-10)	2.33
A28 (8-10)	2.49
AVERAGE	2.12

FIELD APPLICATION

Perhaps the widest utilization of this technique for radon analysis will be on-the-spot investigations in areas remote from a central chemistry laboratory. The major obstacle in adapting the prodecure for field use has been the need for a rugged, sensitive and self-contained counter. It appears from preliminary studies that a Samson alpha survey meter can satisfy these requirements as a field type of alpha counter. The meter reads from 0 to 500 c/m and can be scaled by factors of 1, 5, and 25.

Calibration Procedure

Since earlier investigations have shown that the response of the Samson meter is strongly dependent on the energy of incident alpha particles, it was necessary to calibrate with Ra C' radiation. This was done in the following manner. Long-lived daughter products were scavenged from a radium solution with lead sulphide. The purified solution was stored for several days and the short-lived daughters were precipitated with lead sulphide. The precipitate was counted at various times during the decay process in the scintillation counter, and then measured immediately afterwards by the Samson instrument. Scintillation counter geometry was determined from plated uranium standards.

For the Samson measurement the sample was mounted under two metal shims, 0.062 inches thick, and the sensitive area of the Samson placed directly over it, resting on the shims. The data for this particular Samson meter is recorded in Table 5, and the calibration curve is shown in Figure 5. The 100 reading was taken as the lower limit of detection for each scale and for the most sensitive scale this is approximately equal to 10^{-10} curies of radon. A schematic drawing of the counting mount is in Figure 4.

Comparison of Field and Laboratory Analysis

Twelve duplicate water samples were collected in an area containing radioactive anomalies. One half of the duplicates were analyzed out-of-doors in the general vicinity of the area sampled. Activity measurements were made with the Samson meter. The other group of water samples were returned to the laboratory and the lead sulphide precipitations were counted in an α scintillation counter. Equipment associated with the analysis was the same in both places with the exception, that in the field the intake of an automobile engine's vacuum manifold was used as a source for the vacuum filtration. These data for this survey are shown in Table 6.

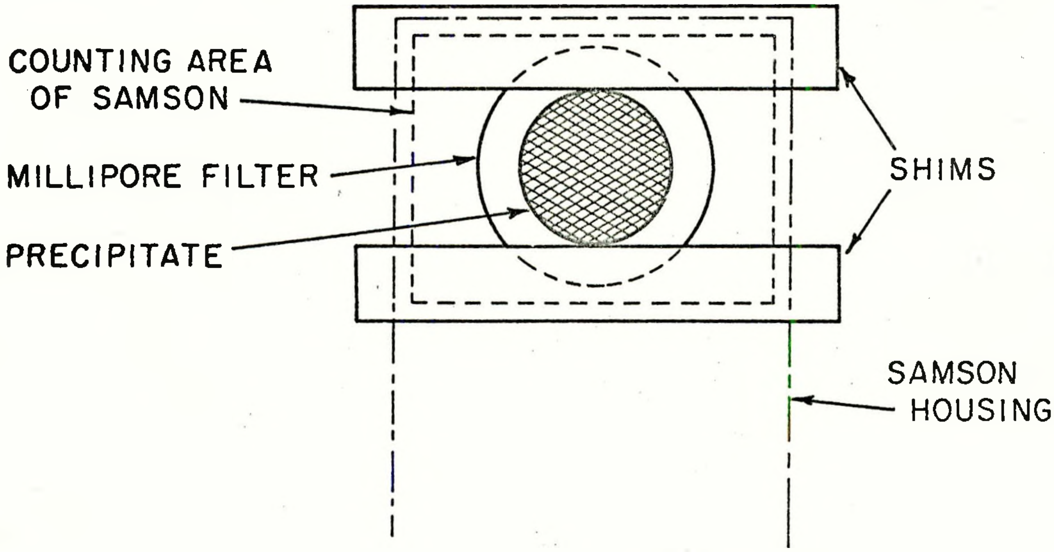

FIG.4 SAMPLE MEASUREMENT WITH SAMSON METER

TABLE 5

SAMSON CALIBRATION FOR Ra C' ALPHA PARTICLES

α d/m	Samson Reading
14,060	11,500
13,534	11,875
10,837	8,750
10,085	8,750
7,891	6,750
7,318	6,500
5,570	5,000
5,333	4,500
4,190	3,250
4,022	3,125
2,789	2,625
2,738	2,500
1,964	1,725
1,902	1,600
1,551	1,125
1,438	1,000
1,102	900
1,037	800

TABLE 5 (continued)

α d/m	Samson Reading
788	625
748	650
584	475
515	450
438	300
365	300

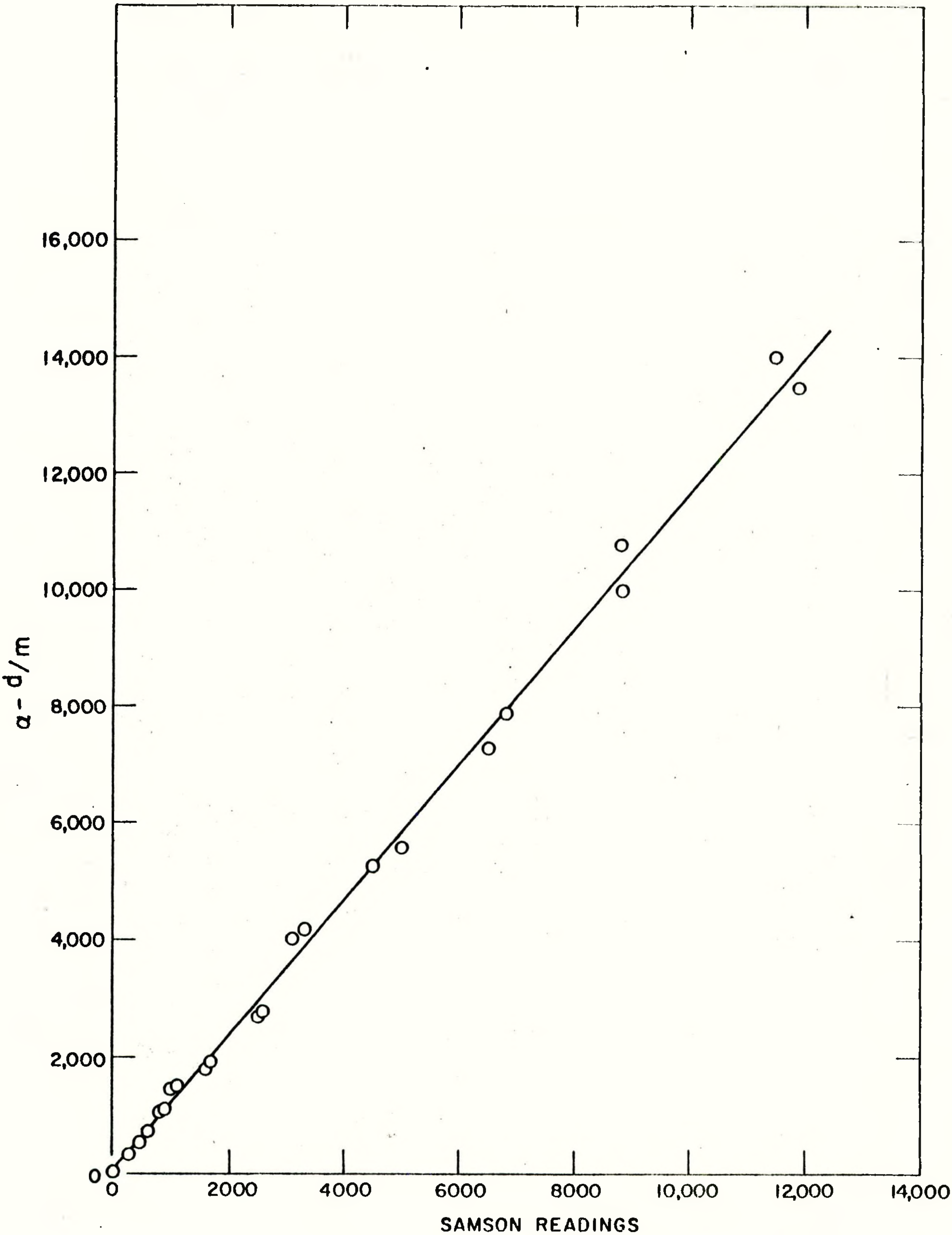

FIG. 5 SAMSON CALIBRATION -Ra C'

TABLE 6

COMPARISON OF FIELD AND LABORATORY RADON MEASUREMENTS

	Rn in μμc/L	
Sample	Field	HASL
A25	30,100	24,600
A28	32,600	24,000
A50	6,500	6,800
A54	11,800	14,900
A30	5,400	4,700
A52	5,200	6,000
A53	15,300	11,000
A55	550	300
A56	1,200	960
A60	6,400	4,900
A63	15,400	17,300
A90	8,500	7,400
B36	190	86

CONCLUSIONS

The method described is sensitive, the procedure simple and suitable for the type of mass production analysis required for a radiological survey. It is in no way intended as a total replacement for the direct emanation procedure where precise and extremely low level concentrations of radon are measured. In the present procedure, care must be exercised to minimize the time required to separate the daughter products completely from the gaseous parent.

ACKNOWLEDGEMENTS

The present study has been considerably advanced by the continuing assistance and interest evinced by the Raw Materials group including Dr. Thomas Walthier and Mr. Jack Kratchmann.