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For The Atomic Energy Commission

William A. Peterson

Chief, Declassification Branch

RADIUM DETERMINATION
BY ALPHA COUNTING

(Final Report)

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ABSTRACT

A method is described for the determination of radium by alpha counting. A dilute hydrochloric acid solution of the radium sample is passed through a short column of copper powder to remove polonium. The effluent is mounted on glass slides and alpha counted four to five hours after mounting. Twenty-four hours after mounting, the slides are counted again, and the percentage increase in counts is used to determine a correction factor for the growth of radon and its daughters. Precision and accuracy are within the limits of the counting instrument used.

INTRODUCTION

The determination of radium by alpha counting is complicated chiefly by the fact that radon, the first product of the radium decay chain, is a gas. The classical emanation method¹ takes advantage of the volatility of radon to determine radium indirectly. The method is extremely sensitive, and, if the counter has been properly calibrated and maintained, provides good precision. However, the elaborate apparatus and continual maintenance required make the method unsuitable for the routine analysis of a large number of samples.

A more convenient technique involves the aeration of a radium solution at elevated temperatures to drive off radon and allow the short-lived daughters to decay to insignificance.² This method is restricted to freshly purified samples of radium since the presence of appreciable amounts of radium F (polonium-210) results in an erroneously high counting rate.

Accuracy has been sacrificed for speed in the chloride precipitation method.³ Considerable self-absorption is introduced by the use of barium as a carrier for the radium, and an empirical correction curve is necessary to compensate for this error. The method provides an excellent separation of radium from its daughters as well as from thorium and uranium and, as such, is a useful preliminary step in any radium determination.

The method to be described was developed to reduce the amount of labor and equipment involved in the assay of carrier-free radium and to improve the precision and accuracy of such a determination.

Four basic steps are involved; (a) spontaneous deposition of polonium on metallic copper, (b) expulsion of radon from the sample when the slide is dried, (c) counting the slide after the new radon is again in equilibrium with its short-lived decay products, and (d) counting the slide one day later to determine the percentage of radon retained by the slide.

STANDARD PROCEDURE

1. The end of a small Pyrex funnel is drawn to an opening of approximately one millimeter, and a small plug of glass wool is inserted. Approximately 0.2 gram of hydrogen-reduced copper powder (150-200 mesh) is poured into the funnel to form a column approximately 5 millimeters high and 3 to 4 millimeters in cross section. The copper is washed with dilute (1:5) hydrochloric acid until it appears bright. The size of the tip is adjusted by filing so that the effluent drop size is about 0.05 milliliter. The column is thoroughly rinsed with water and dried with alcohol and ether.

2. The stem of the funnel is filled with a dilute hydrochloric acid solution of the radium sample to be analyzed, precautions being taken against the formation of air bubbles in the stem. The funnel is never filled above the stem.

3. The first two or three drops of the effluent are discarded, and the remainder is collected in a small test tube or vial. The mouth of the collecting vessel is kept small to minimize evaporation. If the sample is not mounted immediately, the vessel is stoppered tightly.

4. Within 24 hours after the copper reduction an aliquot of the polonium-free sample is mounted on a glass disk, the mount being spread over as large an area as possible to reduce self-absorption. The sample is dried under an infrared lamp adjusted to a height of two inches from the sample. Time zero, the time when heating was begun, is noted.

5. The dried slide is placed in a closed container such as a pill box and the container is kept closed except when the slide is being transferred to a counting chamber. The slide is counted in an air-ionization parallel-plate chamber at 4.0, 4.5, or 5.0 hours. The slide is returned to its container until 24.0 hours after time zero when it is counted again.

6. The percentage increase between the two counts is calculated and the correction factor is found from Figure 1. The correction factor is applied to the counts obtained at the earlier time to find the activity due to pure radium.

EXPERIMENTAL

Efficiency of the Copper Reduction Step.

A radium D, E, and F equilibrium mixture (RaD-E-F) was prepared by crushing aged radon capsules under 2 normal nitric acid. A portion of the solution was converted to the chloride by evaporating nearly to dryness with concentrated hydrochloric acid and was then diluted with distilled water to a chloride concentration of approximately 2 normal. When assayed, the solution was found to contain approximately 10 microcuries of polonium per milliliter.

A portion of the RaD-E-F solution was passed through the copper column and samples of the effluent were mounted for alpha and beta counting. The slides were counted periodically for 34 days, and the amounts of radium E and radium F were calculated as percentages of their activity in the original mixture (Figure 2).

Because of the low energy (0.025 Mev) of the radium D beta, it was considered desirable to use an absorber which would screen out all of the weak beta particles rather than risk losing part of them through self-absorption. An aluminum absorber (1.87 milligrams per square centimeter) was used which absorbed 100 per cent of the radium D betas and allowed 98 per cent of the radium E betas (1.17 Mev maximum energy) to pass. The use of an absorber also prevented the counting of backscattered particles. A control sample of the original RaD-E-F was counted with the same absorber.

The amount of radium D present was calculated by the differential-decay method⁴ from the rate of regeneration of radium E and, separately, from the rate of regeneration of radium F. The residual radium D was found to be 94.5 per cent of the original amount. Only 26 per cent of the original radium E passed through the copper column while radium F was completely removed. After five days, less than one per cent of the original radium F had been regenerated.

After the RaD-E-F elution the copper column was washed repeatedly with dilute hydrochloric acid. Beta activity appeared in the effluent (presumably from radium E) and increased to a maximum in successive washes before disappearing. The elution of radium E from the copper column was not studied quantitatively but semiquantitative data indicated that repeated use of the same copper would lead to erroneous results unless the column were first washed completely free of reduced radium E and radium F. Accordingly, the copper was discarded after each run, and a fresh column was prepared immediately before each determination.

Calculation of Radon Retention from 48- and 72-hour Counts.

Because of mechanical failures or because of the intervention of a holiday or weekend, it may be impractical to count slides at 24 hours after mounting. To determine whether it would be equally accurate to obtain the correction factor from the alpha growth after two or three days, a series of three slides was counted at 4.0, 24.0, 48.0, and 72.0 hours after mounting. There was no significant difference among the three correction factors obtained (Table I).

Analysis of a Standard Sample

A gamma-ray standard, certified by the National Bureau of Standards as containing 100 ± 0.7 micrograms of radium and 2 micrograms of inert barium, was diluted to 25 milliliters with 2 normal hydrochloric acid. Two 5-milliliter aliquots of this stock solution were transferred to 25-milliliter volumetric flasks and two milliliters of RaD-E-F was added to one of them. Two more 5-milliliter aliquots were transferred to 50-milliliter volumetric flasks and two milliliters of RaD-E-F added to one of these. All four flasks were filled to the mark with 2 normal hydrochloric acid.

The four dilutions prepared from the standard sample were analyzed by the method already described. Since the painstaking work of Kohman, Ames, and Sedlet⁵ relating counting rate to weight of radium, was carried out with platinum slides, a series of eight platinum slides was prepared. No difference was found between the counting yield on glass and on platinum, so the reported value of 1.1148×10^{12} counts per minute per gram of radium was used directly.

The gamma-ray standard was found to have contained 99.7 ± 0.6 micrograms of radium as compared with the certified value of 100 ± 0.7 micrograms (Table II). No significant difference was found when the analysis was carried out with and without added RaD-E-F.

DISCUSSION

Radium decays according to the following scheme:

Besides radium and radon, only the three polonium isotopes are significant alpha emitters. Three branch chains exist, involving three alpha emitters; astatine-218 (0.04 per cent of the decay of radium A), radium C (0.04 per cent) and radium E (less than 10^{-5} per cent) but these may be neglected since after one hour their contribution to the alpha activity of the main chain is not detectable within the limits of precision of the parallel-plate counter.

It has been shown that polonium can be quantitatively removed from a hydrochloric acid solution by spontaneous deposition on copper and that 75 per cent of the bismuth is removed at the same time. If, at nearly the same time, radon is completely removed from the solution by heating, the radium decay chain will be broken into two coexistent but distinct genetic lines headed, respectively, by radium and radium B.

The alpha activity of each chain can be calculated from the standard equations for the growth of daughter activities.⁶ To simplify calculation, the following assumptions are made: (a) that all new radon produced after its initial expulsion from the sample is retained, together with its decay products, (b) that, just before its expulsion, radon and its short-lived decay products had grown to 50 per cent of equilibrium with radium, (c) that the time between the copper reduction and removal of radon is negligible, and (d) that 100 per cent of the bismuth, instead of 75 per cent, is removed by copper reduction.

These assumptions lead to small errors which become insignificant during the four-hour waiting period prescribed by the procedure.

Using the half-life values compiled by Seaborg and Perlman,⁷ the relative alpha activity (C) of pure radium, taken as 1.0000 at time zero, is given by $C = 4.0000e^{-\lambda_2 t} + 0.0006e^{-\lambda_3 t} + 0.0208e^{-\lambda_4 t} - 0.0118e^{-\lambda_5 t}$ where t is in hours, $\lambda_2 = 0.007549$, $\lambda_3 = 13.633$, $\lambda_4 = 1.5515$, $\lambda_5 = 2.1107$. (All λ values are in reciprocal hours.)

The growth and decay of radium C', the only significant alpha-emitting daughter of radium B, is given by

$$B = 1.8873 (e^{-\lambda_4 t} - e^{-\lambda_5 t})$$

where B is the alpha activity of radium C' relative to that of the radium parent.

Several useful points calculated from these equations are given in Table III (C and B), and a plot of both equations is shown in Figure 3.

Since the loss of radon from a solid sample, whether by recoil or diffusion, is a function of such physical characteristics as sample thickness and crystal size, the percentage loss will be independent of time. This is confirmed experimentally by the data in Table I.

The method of calculating the correction factor is best explained by an example. Suppose that the slides were counted at 4.5 and 24.0 hours and that the counting rates were 10,000 and 10,909 counts per minute, respectively. The increase in counts is 9.09 per cent, while the increase in counts if 100 per cent of the radon had been retained (Table III-C) would have been

$$\frac{1.4892}{1.0922} - 1 = 36.35 \text{ per cent.}$$

Therefore, the actual radon retention is

$$\frac{9.09}{36.35} = 25 \text{ per cent.}$$

At 4.5 hours, the relative activity of the alpha-emitting daughters of radium (Table III-A) would have been 0.0910 if 100 per cent of the radon had been retained. But, since only 25 per cent of the radon was retained, the relative increase is only $0.0910 \times 0.25 = 0.0228$. In addition, if the slides were mounted immediately after the copper reduction, the radium C' which grew from unreduced radium B will not yet have decayed to insignificance (Table I-B). Adding this small contribution, the total relative alpha activity

at 4.5 hours is $0.0228 + 0.0012 + 1.0000 = 1.0240$. The alpha activity directly due to radium is therefore

$$\frac{10,000}{1.0240} = 9,766 \text{ counts per minute.}$$

To simplify the calculation of the correction factor, a graph can be constructed relating the percentage increase in counts directly to the correction factor. For example, it has already been shown that the increase in counts (for 100 per cent radon retention) between 4.5 and 24.0 hours is 36.35 per cent, corresponding to a correction factor of 1.0922 (Table III-C). For zero per cent retention, the correction factor is 1.0012 (Table III-D). Plotting per cent increase on the abscissa and correction factor on the ordinate, draw a straight line between the points having coordinates of (0.00, 1.0012) and (36.35, 1.0922). The correction factor can now be read directly if the increase in counts is known.

Such a plot has been made in Figure 1 for the usual case where the second set of counts is made at 24.0 hours.

It should be noted that a small error in the determination of radon retention will not significantly affect the value of the correction factor applied to the four or five-hour counts. In the example given above, a 10 per cent error in determining radon retention would have been reflected as a 0.2 per cent error in the result.

On the other hand, if the first set of counts had not been made until 24 hours after mounting, a 10 per cent error in determining the radon retention would have caused a one per cent error in the correction factor. Furthermore, the counts at 24.0 hours are likely to be somewhat less accurate than those at 4.0 hours because of the loss of radon during transfer of the slide to the counting chamber. The increased background introduced into the chamber by the escape of radon also contributes to the inaccuracy.

The error which may result from neglecting the 4.0-hour counts can be illustrated by reference to Table I. Using the 24- and 48-hour counts, the average counting rate due to radium is found to be 17,079 counts per minute. From the 24.0 and 72.0-hour counts the average obtained is 16,960 counts per minute. The two values are in error by 2.5 and 3.2 per cent, respectively.

The correspondence between the counts obtained from glass and platinum slides is surprising at first glance since backscattering would be greater from platinum.⁸ However, counting yield depends upon the amount of self-absorption as well as on the composition of the backing plate, and there is evidence to suggest that radium diffuses into a platinum surface to a significant degree:

1. Once flamed, a platinum slide bearing radium can never again be freed of alpha activity by purely chemical means unless some of the surface platinum is dissolved.
2. It was found by Kohman et al.,⁵ and confirmed by the author, that a platinum sample plate which has been ignited can never again be freed of radon by redissolving and reigniting the sample.
3. Radon retention, like self-absorption, is a function of sample thickness. On glass slides, the average radon retention was 23.6 per cent. On unflamed platinum slides it was 47.1 per cent and on flamed platinum slides the average was 70.7 per cent. (Kohman et al., found the recoil-retention factor to vary between 65 and 88 per cent for flamed platinum mounts.)

It seems likely, therefore, that there would be considerable absorption of backscattered particles, particularly those scattered at low angles. Depending upon the depth of penetration this absorption would tend to cancel out the backscattering effect, making the counting yield equal to, or even less than, that of an identical sample on glass.

The method as described is applicable directly only to samples of radium uncontaminated by thorium or other alpha emitters not descended from radium. Where such contaminants are suspected, it is suggested that a preliminary separation of the radium be made by ion exchange⁹ or chloride precipitation. In the chloride method, if five milligrams of barium is used to carry the radium and the precipitate is redissolved in one milliliter or more of solution, the amount of barium transferred to the slide in a 25-microliter sample will introduce no significant self-absorption.³ In this case, too, the copper-reduction step can be dispensed with.

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TABLE I

CALCULATION OF RADON RETENTION

SLIDE NUMBER	COUNTS PER MINUTE AT				CALCULATED RADON RETENTION		
	4.0 HOURS	24.0 HOURS	48.0 HOURS	72.0 HOURS	24.0 HOURS (%)	48.0 HOURS (%)	72.0 HOURS (%)
1	17,903	19,726	21,973	23,512	27.17	29.96	29.03
2	17,900	19,066	20,657	21,942	17.37	20.30	20.92
3	<u>17,831</u>	<u>19,362</u>	<u>20,011</u>	<u>21,477</u>	<u>22.93</u>	<u>16.12</u>	<u>18.95</u>
AVERAGE	17,878	19,385	20,880	22,310	22.49	22.13	22.97

SLIDE NUMBER	CALCULATED CORRECTION FACTOR AT			CALCULATED RADIUM			
	24.0 HOURS	48.0 HOURS	72.0 HOURS	24.0 HOURS (CTS./MIN.)	48.0 HOURS (CTS./MIN.)	72.0 HOURS (CTS./MIN.)	AVERAGE (CTS./MIN.)
1	1.025	1.027	1.027	17,466	17,432	17,432	17,443
2	1.017	1.020	1.020	17,601	17,549	17,549	17,566
3	<u>1.022</u>	<u>1.016</u>	<u>1.019</u>	<u>17,447</u>	<u>17,550</u>	<u>17,499</u>	<u>17,499</u>
AVERAGE	1.021	1.021	1.022	17,505	17,510	17,493	17,503

TABLE II
ANALYSIS OF CERTIFIED SAMPLE CONTAINING
100 ± 0.7 MICROGRAMS OF RADIUM

SLIDES COUNTED	RADIUM PRESENT ($\mu\text{g.}/\text{ml.}$)	RAD.E.F. ADDED ($\mu\text{C.}/\text{ml. of Po}$)	RADIUM FOUND IN DILUTION ($\text{cts.}/\text{min.}/\mu\text{l.}$)	TOTAL RADIUM FOUND ($\mu\text{g.}$)
15	0.800	0.0	884.4 ± 6.3	99.2
14	0.400	0.0	445.5 ± 1.6	99.9
9	0.800	0.8	888.3 ± 4.2	99.6
9	0.400	0.8	448.0 ± 1.8	100.5
8*	0.400	0.8	444.7 ± 1.8	99.7
55			MEAN	99.7 $\mu\text{g.}$
			PROBABLE ERROR OF MEAN**	0.6 $\mu\text{g.}$

* PLATINUM SLIDES

** PROBABLE ERROR = $0.6745 \sqrt{\frac{\sum d^2}{n-1}}$; d = DEVIATION FROM MEAN.

TABLE III
CALCULATED ALPHA ACTIVITY OF THE RADIUM CHAIN
RELATIVE TO THAT OF PURE RADIUM

TIME (HR.)	A	B	C	D
4.0	0.0799	0.0034	1.0833	1.0034
4.5	0.0910	0.0012	1.0922	1.0012
5.0	0.1021	0.0008	1.1029	1.0008
5.5	0.1127	0.0003	1.1130	1.0003
18.0	0.3733	0.0000	1.3733	1.0000
24.0	0.4892	0.0000	1.4892	1.0000
48.0	0.9053	0.0000	1.9053	1.0000
72.0	1.2523	0.0000	2.2523	1.0000

A. RELATIVE ALPHA ACTIVITY OF THE DAUGHTERS OF RADIUM GROWING FROM INITIALLY PURE RADIUM, ASSUMING NO LOSS OF RADON.

B. RELATIVE ALPHA ACTIVITY OF RADIUM C', THE ONLY SIGNIFICANT ALPHA-EMITTING DAUGHTER OF RADIUM B, AFTER REMOVAL OF ALL POLONIUM, BISMUTH AND RADON FROM A RADIUM SOLUTION WHICH WAS INITIALLY AT 50 PER CENT OF EQUILIBRIUM WITH RADON AND ITS SHORT-LIVED DAUGHTERS.

C. CORRECTION FACTOR FOR 100 PER CENT RETENTION OF RADON. (= A + B + 1.0)

D. CORRECTION FACTOR FOR ZERO PER CENT RETENTION OF RADON. (= B + 1.0)

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CALCULATED ALPHA ACTIVITY OF RADIUM