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UNITED STATES ATOMIC ENERGY COMMISSION

NBL-128

A METHOD FOR THE DETERMINATION OF RADIUM IN ORES AND RESIDUES

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Issuance Date: March 1957

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ABSTRACT

A method for the determination of the radium content of ores and uranium processing residues (K-65) has been developed. Samples were packed into 12 ml. glass vials, the vials sealed and the gamma ray activity of the radium detected after a growth period of 30 days. A high pressure ionization chamber was used as a detector and the gamma rays were filtered through 3/8 inch of lead to minimize the detection of the low energy part of the radium gamma ray spectrum. The large sample size used in the method decreases the importance of sample inhomogeneity.

Corrections are applied for UX and actinium series gamma rays, and for absorption of radium gamma rays in the sample material and in the aqueous radium standard. The magnitude of the correction for the self absorption of radium gamma rays in the sample material was evaluated by using three methods. In the first method, synthetic standards containing known quantities of radium were used. In the second, the slope of the curve for ion current per gram of sample as a function of the number of grams contained in 12 ml. vials was calculated for a large number of samples. In the third, the absorption of radium gamma rays by representative ores and residues was determined by using a radium source and a sodium iodide crystal scintillation counter. The radium content of a homogeneous sample can be established with a precision equivalent to a standard deviation of ±0.1 to 0.4 percent.

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INTRODUCTION

The radium content of ores and other materials is usually measured by the radon method [1,2,3,4] or the gamma ray method [5,6,7].

The radon method [1,2] is capable of greater sensitivity. However, for material of high specific activity, such as uranium ores and processing residues, very small samples are taken with the resulting errors due to variations caused by inhomogenity of the material. The radon method, as used by the National Bureau of Standards*[3] often compares the activity of its sample with a standard of a much different specific activity. Therefore, a correction is required for coincidence loss in the counting apparatus. The radon method also requires close attention to detail and a comparatively large number of manhours per sample.

The gamma ray method, although not as sensitive as the radon method, usually employs a larger sample, between ten and sixty grams of material. The activity of the sample is compared to a standard of nearly similar radium content thus minimizing errors due to non-linearity of the measuring technique. The accuracy of the gamma-ray method depends largely on how accurately the self-absorption correction for the radium gamma rays is determined. This has been evaluated with a large degree of confidence by experimental measurement.

APPARATUS

A high pressure ionization chamber of the type described by Borkowski [8] and others [9] and fabricated from drawings prepared during the Clinton Laboratory days at Oak Ridge [10] is used to measure the radium gamma rays. Tank argon at 30 atmospheres was used in a chamber with a sensitive volume of about 880 cubic inches. A detailed sketch of the instrument is shown in Figure 1. The voltage developed across a 10^{10} ohms resistor by the ion current passing through the resistor is measured using a Vibrating Reed Electrometer and amplifier obtained from the Applied Physics Corporation and a Leeds and Northrup K-2 Potentiometer in a null-type circuit. The circuit is shown in a block-type diagram in Figure 2. A Brown recorder (Minneapolis and Honeywell) is attached to the output of the electrometer. A 2KVA Sorensen voltage regulator is used to stabilize the line voltage input to the instruments. Twelve ml. machine-made glass vials (Kimble Glass Company No. 60910) approximately 19 x 65 mm. are used to hold the sample materials and the standard solution. A lead filter to house the sample and standard vials is used. It is 1.5 inches in diameter by 3.5 inches long with a 3/8 inch wall. A brass connector is used to connect two vials together while filling. The glass vials, brass connector and lead filter are shown in Figures 3A and 3B.

*National Bureau of Standards - NBS

New Brunswick Laboratory - NBL

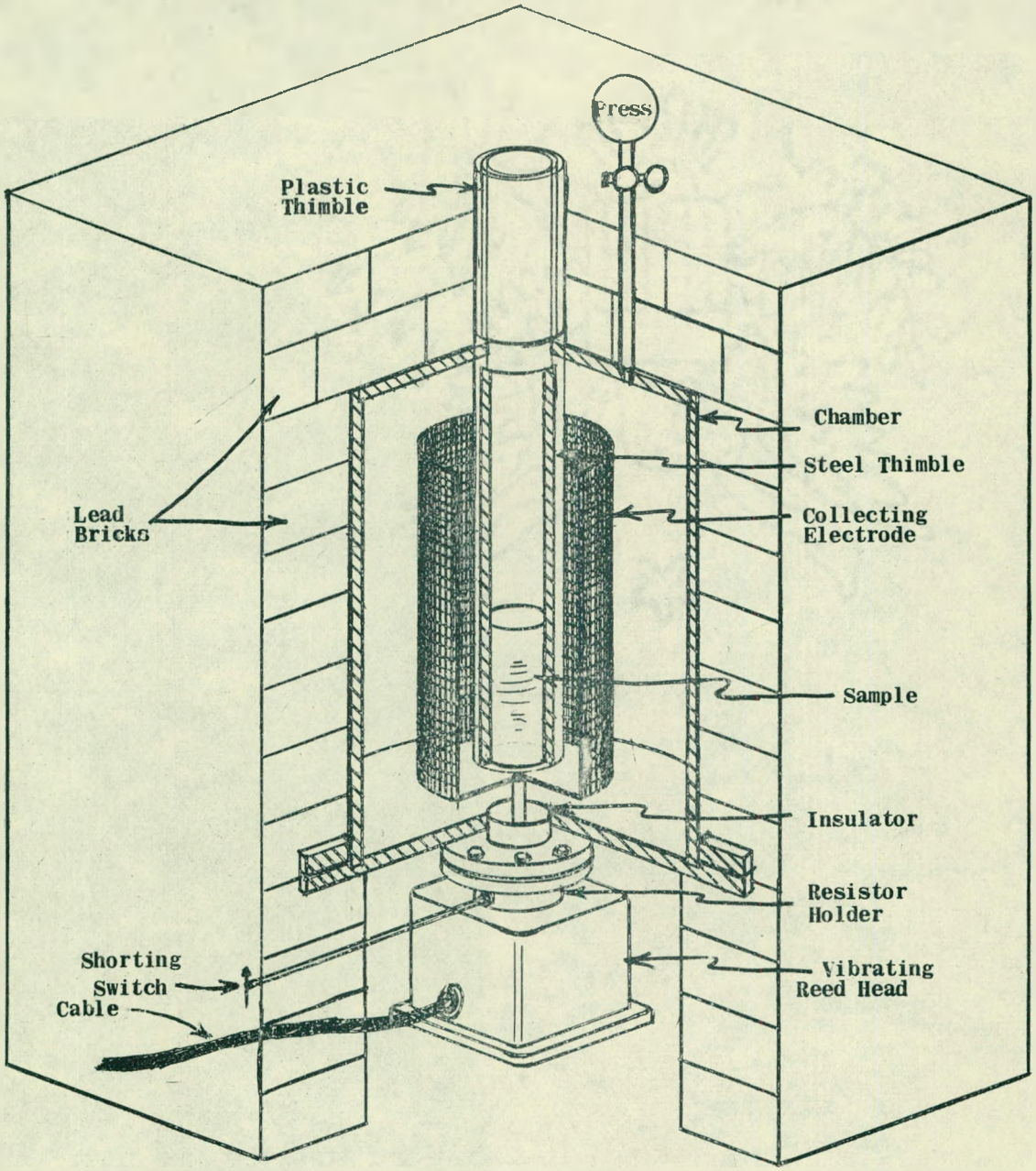

FIGURE 1. CUTAWAY DRAWING OF THE HIGH PRESSURE IONIZATION CHAMBER INSIDE ITS LEAD SHIELD WITH THE VIBRATING REED ELECTROMETER HEAD AND RESISTOR BOX

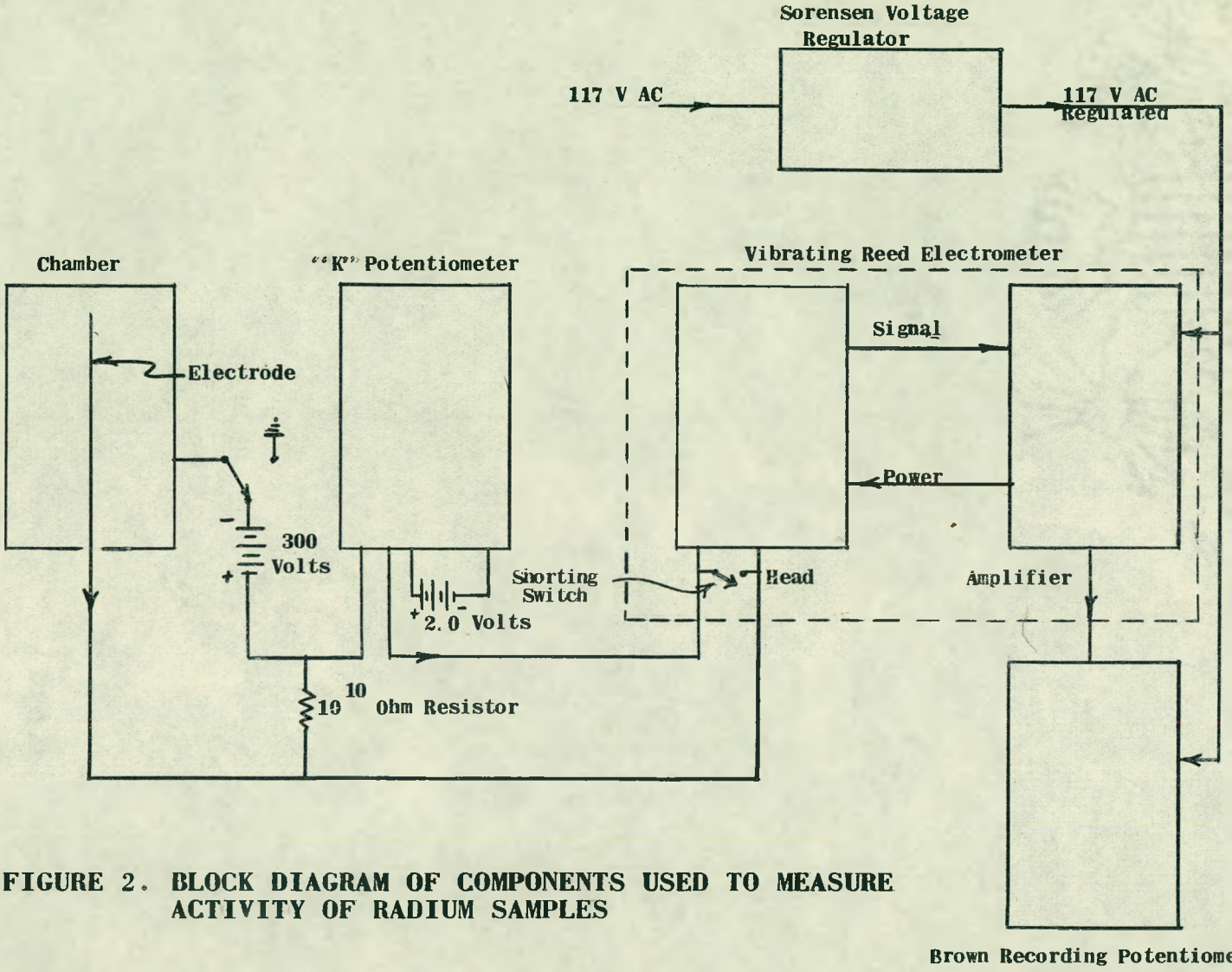

FIGURE 2. BLOCK DIAGRAM OF COMPONENTS USED TO MEASURE ACTIVITY OF RADIUM SAMPLES

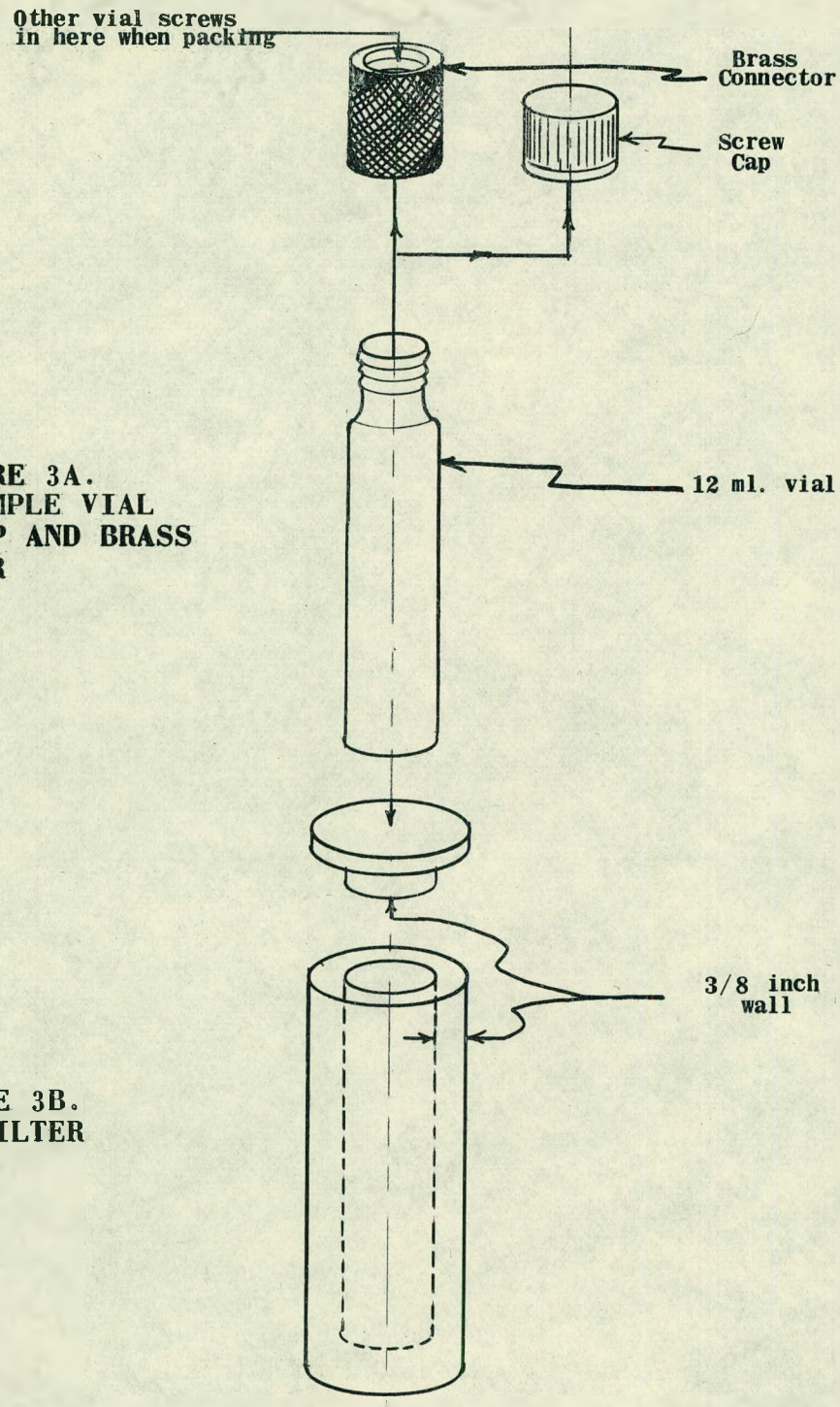

FIGURE 3A.
GLASS SAMPLE VIAL
SCREW CAP AND BRASS
CONNECTOR

FIGURE 3B.
LEAD FILTER

Certified radium standards in solution in flame sealed ampoules prepared in 1947 were obtained from the National Bureau of Standards. The 50 μg. of Ra (in 5 ml. of 5% acid) standard together with the ampoule washings (with 5% acid) were transferred to a 50 ml. volumetric flask and diluted to the calibration mark using a 5% HCl solution containing 2% $BaCl_2$. Suitable aliquots of 2 to 10 ml. of solution as shown below were pipetted and weighed in twelve ml. sample vials so that a set of standards covering the desired range was made. The vials are sealed as indicated below.

NBL Standards

NBL No.	Micrograms Ra in original NBS Std.	Weight of diluted Std.	Wt. taken for NBL Std.	Micrograms of Ra	Millivolts/ microgram Ra
14	2.0	-	entire	2.0	188.5
15	2.0	-	entire	2.0	188.0
19	5.0	-	entire	5.0	189.2
20	5.0	-	entire	5.0	188.7
22	10.0	-	entire	10.0	189.5
30-A	50.0	50.96330g	7.40440	7.26	188.2
30-B	50.0	"	10.21442	10.0	187.4

An indication of the reproducibility of the preparation of these standards has been obtained by the repetition of the above procedure using different flame sealed radium ampoules and by intercomparing the high pressure ionization chamber reading (in terms of millivolts per microgram of radium) for the different concentrations.

The radium content of the ampoules from which the vials were prepared is subject to a gross error estimated to be no greater than ± 1 percent. A part of the uncertainty arises from the fact that an automatic aliquoting device was used in filling these ampoules. The precision of the automatic aliquoting device is ± 0.2%. The uncertainty in the knowledge of the National Primary Radium Standard is ± 0.31%. The precision of the standardization by comparison to the National Primary Radium Standard is estimated to be ± 0.7%.

All standards are corrected periodically for decay. The recent values obtained at the National Bureau of Standards[11] for the United States National Primary radium standards were used to determine the Ra content of the NBL standards.

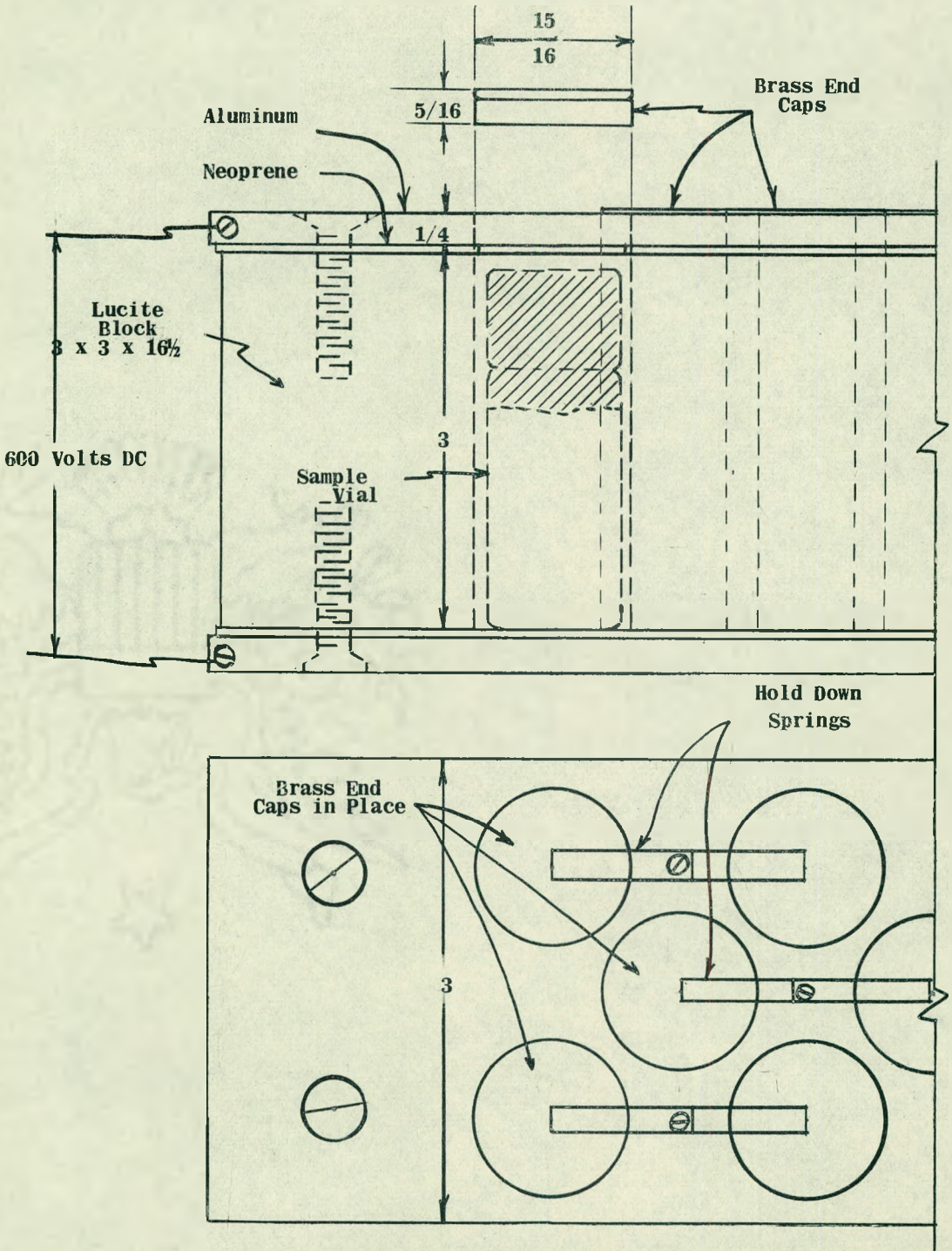

FIGURE 4. RADON LEAK DETECTOR (ALL DIMENSIONS IN INCHES)

PROCEDURE

Filling Sample Vials

Weigh accurately a clean, dry labeled machine-made glass vial with its screw cap. Fill the tared vial and another vial of similar size. Connect the two vials together using the brass connector (Fig. 3A). The above assembly is placed on a mechanical vibrator and shaken until no further transfer into the tared vial occurs. Remove the top vial and connector, level the sample, cap the tared vial with its screw cap and re-weigh the vial. Seal the vial by applying Glyptal paint to the junction between the screw cap and the glass vial. After drying make a second application of the paint by dipping the screw cap into the paint to a point about 1/4 inch beyond the junction of the cap and the vial.

Radon Leak Test

After the paint has dried, the vials are tested for radon leakage. The vials are placed in a cylindrical container with removable brass terminal caps that seal the container. Figure 4.

A potential of 600 volts is applied between the terminal caps. The vial is left in the cylinder overnight, in order that any radium B recoil atoms will be collected. The negative terminal cap is removed and any increase in beta activity deposited on the cap is determined by using a Geiger Mueller counter.

If the above test shows that the seal is leaking it is resealed again and retested. More than two resealings are undesirable since the added material increases the gamma ray absorption in the capped end.

Measurement of Gamma Activity

Allow the radium decay products to grow to equilibrium for at least twenty-five days before determining the gamma activity. Turn on the Vibrating Reed Electrometer and the Sorensen regulator and allow them to warm up. Calibrate the K-2 Potentiometer against a standard cell. After 15 minutes adjust the Vibrating Reed Electrometer, and amplifier dial of which has been set so as to indicate 100 millivolts for full scale response, and the Brown Potentiometer to a zero reference point somewhere in the center of the scale. This is to allow reading of either positive or negative differences from the null position. Remove the shorting connection across the 10^{10} ohm resistor which is mounted in the Vibrating Reed Electrometer head and adjust the K-2 Potentiometer to get a null balance as indicated by the Vibrating Reed Electrometer and the Brown Potentiometer. This is the background activity in millivolts. Place a sample vial in the lead filter, cover with the lead cap and lower the assembly into the thimble of the high pressure ionization chamber. Again adjust the K-2 Potentiometer until a null balance

is obtained. An observation is usually taken for ten minutes and the average millivolts reading of the Brown Potentiometer estimated. The difference between this average and the zero position is added to or subtracted from the K-2 Potentiometer reading to obtain the total "millivolts" activity for the vial. Run the samples at least in quadruplicate. Determine the sensitivity of the ion chamber using the standard vials. Use two standards whose radium content brackets that of the sample and determine their gamma ray activity in "millivolts" as given above for the samples. In practice a sample is run between standards.

DETERMINATION OF CORRECTIONS

Correction for Self Absorption of Samples

The magnitude of the self absorption coefficient, μ, in the equation

$$A = A_0 e^{-\mu x} \qquad (1)$$

where

A = the activity of the sample measured in millivolts per gram,

A_0 = the activity of the sample at zero self absorption in millivolts per gram,

x = the sample weight in grams

has been determined.

First, the activity of a large number of uranium processing residues in millivolts per gram of sample was determined using the high pressure ionization chamber. The measured activity of the standards in millivolts per gram of radium uncorrected for self absorption, was calculated for each standard vial. The amount of radium per gram of sample in a vial was obtained by dividing the above measured activity of the unknown sample in millivolts per gram of sample by the measured activity of the standards expressed in millivolts per gram of radium. Since, for a given sample, different vials did not contain the same weight of sample a relationship for the given sample can be obtained between the specific activity of the sample in millivolts per gram and the weight contained in the 12 ml. vial. Then for each sample the slope of this relationship was estimated using a linear function and a least square analysis. The average value for the slope for 206 samples was calculated to be -0.003, (μ).

Further, for 283 vials of representative samples of different ores the number of grams of radium per gram of sample, uncorrected for self absorption, was measured. In order to obtain the data on a comparative basis the radium to uranium ratio was calculated from the grams of uranium per gram of sample (Chemical Analysis). Then the slope of the relationship between the radium-uranium ratio as a function of grams of sample per 12 ml. vial was determined for this group of samples by linear least square analysis. The slope obtained was -0.003, (μ).

Synthetic samples containing known weights of radium mixed with calcium, strontium, barium and lead as carbonate and a mixture of calcium and lead carbonates were prepared and packed into the vials as described above. The activities of these samples were determined using the high pressure ionization chamber and the specific activity in millivolts per microgram of radium (uncorrected for self absorption) was calculated. The slope was estimated by a linear least square analysis to check the above two determinations. The data gives a slope of -0.003, (μ).

The results of the above three determinations show a small dependence upon sample composition as well as on the average atomic number of the constituents. This dependence is not significant enough to affect the results for samples of the same general type.

An attempt was made to evaluate the self-absorption coefficient, μ, on a fundamental basis.[12] However, the value of μ was too large and resulted in an over correction as indicated by the radical change in the slope.

Correction for Self Absorption of Standard

The actual determination of the radium content of the samples is made by comparison of the activity of the sample against that of an aqueous radium standard. Thus a correction for self absorption in the aqueous radium standard must also be made. This is accomplished by modifying equation (1) thus.

$$\frac{A}{A_0} = e^{-\mu(x-x_1)} \quad (2)$$

where x_1 is the weight equivalent in grams of the standard, and is the correction to be applied to the weight of the sample so as to correct the activity for self absorption. The value of x_1 is determined using equation (1) with the above determined value of μ, substituting x_1 for x and obtaining A/A_0 from experimental measurements. The determination of A/A_0 was done by two methods:

1. Correction using the high pressure-ionization chamber. The activity of the standards was determined using the high pressure-ionization chamber and the specific activity, A, in millivolts per microgram of radium was calculated. Then A_0 was obtained by extrapolating the above data for the synthetic carbonates to a sample weight of zero grams. The value for A/A_0 by this method was found to be

$$\frac{193.0}{199.6} = 0.967$$

2. Correction by absorption measurements using the gamma ray scintillation counter. An independent determination for each of the sample types was done by measuring the transmission, T, of radium gamma rays through representative samples and the aqueous radium standards. A gamma ray scintillation counter and a sodium iodide crystal detector were used. The apparatus, geometrical arrangement and procedure are shown in Figure 5.

The absorption for zero sample weight, T_0, was obtained by extrapolation from the curve.

A standard sample used as a source of radiation was placed on top of two lead bricks. Directly under the standard was a 1/4 inch hole drilled through the lead axial to the sources and detector (Figure 5).

The activity was detected with a NaI (Tl) crystal with the discriminator of the scintillation counter set to detect pulses from 10 to 100 volts.

The sample was inserted from the side into a hole which intersected the gamma ray beam of the standard source. Thus the sample was placed so that it could intercept the gamma rays from the standard and its absorption could be determined.

The formula used to determine the transmission was:

$$\frac{T}{T_o} = \frac{Ct - Cx}{Cs - Bkg}$$

where
Ct = count with standard and sample in place
Cx = count with sample in place
Cs = count with standard in place
Bkg = count with neither in place

This formula gives the fraction of the original count reaching the crystal after the sample is inserted.

It is assumed that A/A_o is equivalent to T/T_o for each sample type. The value for A/A_o by this method was found to be 0.948 for K-65 and 0.969 for Q-11 ore.

In order to obtain the weight equivalent x_1 of the aqueous standard the value of A/A_o for the Q-11 ore was averaged with that obtained from the carbonate samples. Also in a similar manner A/A_o for K-65 concentrate was averaged with that obtained from the carbonate sample. These values are 0.957 for the processing residues and 0.968 for the ores.

The weight equivalent, x_1, for Q-11 ore was found using an expansion of equation (1) to be 10.6 g. and x_1 for K-65 concentrate was found to be 14.8 g.

The weight equivalent correction of the UX series gamma rays in uranium ores has also been determined. The activity of pure $UO_2(NO_3)_2 6H_2O$ was measured in 12 ml. sample vials filled completely using the high pressure ionization chamber. The specific activity in millivolts per gram of uranium was calculated. In a manner similar to that given above the equivalent weight correction becomes 4.4 grams of uranium ore.

The weight equivalent correction of the actinium series gamma rays in uranium ores has been estimated by determining the specific activity of 60 micro-curies of actinium 227 obtained by pile irradiation of radium-226. The irradiation of the radium and the purification of the actinium were done at Argonne National Laboratory. Four months were allowed for the decay products to attain secular equilibrium.

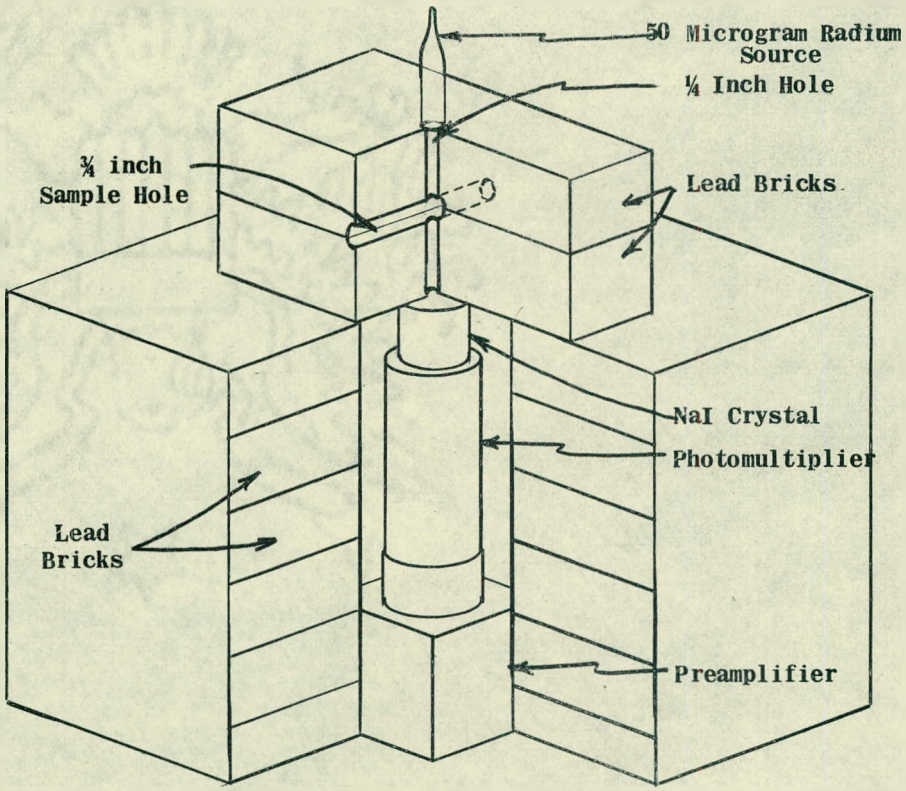

FIGURE 5. CUTAWAY DRAWING OF THE NaI SCINTILLATION DETECTOR USED TO MEASURE THE LINEAR ABSORPTION OF RADIUM GAMMA RAYS

The actinium in aqueous solution was placed in a 12 ml. screw cap vial and its activity measured in the high pressure ionization chamber. The correction is equivalent to 0.6 gram when computed in the above manner.

Corrections Applied to Uranium Processing Residues

Incorporation of the constants pertaining to uranium processing residues into equation (2) and an expansion of the exponential, results in an equation which may be used to correct uranium processing residues, i.e.

$$A_o = A \frac{1}{1-(x-14.8)0.003} \qquad (3)$$

Corrections Applied to Uranium Ores

Incorporation of the above constants pertaining to uranium ores into equation (2) results in the following equation for the correction of uranium ore data.

$$A_o = A \frac{1}{1-(x-16.2)(0.003)} \qquad (4)$$

Corrections for the contributions of ionium and protactinium have not been calculated, since, they are believed to be insignificant. The foregoing correction factors apply specifically to the apparatus and technique used in the method. Any marked changes would require a precise reevaluation for the parameters used.

Calculation of the Radium Content

The true activity, A_o, calculated from the above equation (2) expressed in millivolts per gram of sample is divided by the specific activity of the radium standards expressed in millivolts per gram of radium.

RESULTS

The results of the analyses by NBL of four uranium processing residues and six uranium ores together with the standard deviations (σ) and the percent standard deviations (%σ) are shown in Table 1. In most cases the analyses were done by one operator. However, in the case of A-9748, A-9750 and B-7311 three operators performed the analyses.

DISCUSSION

Table 1 shows that the standard percent deviation of the method is between 0.1 and 0.4 percent. There appears to be no difference in the results on identical samples analysed by each of three operators. This tends to indicate the ease with which the analysis can be done since two of the operators do not perform the analysis on a routine basis.

The accuracy of the analysis is another question. It is dependent on the values of the National Primary Radium Standard, the preparation and standardization in 1947 of the standard radium ampoules and on the evaluation of the correction factors. The latter factor is the only one considered in this determination.

SUMMARY

A gamma ray method for the determination of the radium content of ores and uranium processing residues (K-65) has been developed. The method uses a "4π", high pressure, ionization chamber to compare the gamma activity of the sample, in equilibrium with its decay products, with a standard amount of radium, in equilibrium with its decay products. Corrections are made for UX and actinium series gamma rays and for the self-absorption of radium gamma rays in the samples and standards. The ultimate sensitivity of the method is 10^{-8} grams of radium and the precision is equivalent to a standard deviation of ± 0.1 to 0.4 percent.

ACKNOWLEDGEMENTS

The authors thank the members of the Analytical Chemistry Branch who performed uranium analyses and complete analyses on the various samples as well as to Robert Lanza and Jane Tripp who did the statistical analysis of the data.

TABLE 1.

NBL ASSAYS ON CANDIDATE RADIUM STANDARDS-Q-11 and K-65
(Determinations are in mg Ra/short ton)

A-9745

1	2	3	Avg.	σ	%σ
278.5	277.6	278.0			
278.2	276.9	277.8			
279.1	277.6	278.2			
276.8	276.0	276.8			
277.0	276.6	276.5			
278.6	277.9	278.0			
277.6	277.8	278.2			
279.7	278.5	278.5			
278.2	277.4	277.8	277.8	0.9	0.3

A-9749

1	2	3	Avg.	σ	%σ
125.2	124.8	124.6			
125.0	125.3	124.8			
125.0	125.5	124.7			
125.1	125.2	125.0			
124.9	125.4	125.0			
124.4	125.0	125.2			
124.5	125.1	124.7			
124.8	124.8	-			
124.9	125.1	124.9	125.0	0.3	0.2

A-9747

1	2	3	Avg.	σ	%σ
737.4	737.6	740.0			
736.9	739.0	738.9			
736.7	738.7	740.6			
736.1	738.4	-			
738.1	738.1	739.8			
736.9	739.3	740.0			
736.6	737.1	740.9			
737.0	738.3	740.4			
737.0	738.3	740.1	738.4	1.4	0.2

A-9750

1	2	3	Avg.	σ	%σ
132.7	132.8	132.6			
132.5	132.3	132.3			
132.9	133.1	132.9			
132.9	134.2	133.0			
132.4	132.4	132.3			
132.6	132.0	131.8			
132.9	132.4	132.1			
132.4	132.7	132.2			
132.7	132.7	132.4	132.6	0.5	0.4

A-9748

1	2	3	Avg.	σ	%σ
75.9	75.9	75.7			
75.9	75.8	75.4			
75.9	76.0	75.9			
75.7	76.2	75.9			
76.0	75.8	75.5			
75.6	75.5	75.1			
75.8	75.9	75.4			
75.9	76.4	75.7			
75.8	75.9	75.6	75.8	0.3	0.4

A-9751

1	2	3	Avg.	σ	%σ
95.8	95.5	95.4			
95.6	95.5	95.6			
96.1	95.5	95.9			
95.7	95.9	95.2			
95.2	95.1	95.3			
95.4	95.4	95.7			
95.9	96.1	95.1			
95.6	95.7	-			
95.7	95.6	95.5	95.6	0.3	0.3

TABLE 1 (Cont'd)

MS-240						B-7311					
1	2	3	Avg.	σ	%σ	1	2	3	Avg.	σ	%σ
232.6	232.1					160.0	159.6	159.7			
230.2	230.5					160.3	160.1	160.2			
232.0	231.4					160.2	159.1	160.5			
232.2	232.2					159.5	159.5	159.1			
232.7	231.7					160.3	160.2	160.4			
231.4	230.5					160.0	159.9	159.8			
233.2	232.5					160.4	160.1	159.9			
232.7	232.3					160.1	159.3	160.1			
232.1	231.6		231.9	0.9	0.4	160.1	159.7	160.0	159.9	0.4	0.3

B-4866						
1	2	3	4	Avg.	σ	%σ
273.2	273.2	272.3	273.0			
273.4	272.8	274.1	272.3			
273.8	273.8	273.3	273.2			
273.5	272.7	273.6	272.8			
273.0	272.2	272.6	272.4			
273.4	272.9	273.2	272.7	273.1	0.5	0.2

B-4867						
1	2	3	4	Avg.	σ	%σ
773.6	773.3	773.9	773.4			
773.3	774.8	772.6	773.8			
772.5	773.1	772.8	771.5			
774.5	773.5	773.8	774.2			
774.6	774.4	774.2	773.0			
773.7	773.8	773.5	773.2	773.5	0.8	0.1

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