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DEVELOPMENT OF SOLID RADIUM-226
REFERENCE MATERIALS

November 1983

U.S. DEPARTMENT OF ENERGY
ASSISTANT SECRETARY FOR NUCLEAR ENERGY

MASTER

Division of Remedial Action Projects
Technical Measurements Center
Grand Junction Area Office, Colorado

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DEVELOPMENT OF SOLID RADIUM-226 REFERENCE MATERIALS

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with
APPENDIX A
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November 1983

Prepared for
U.S. Department of Energy
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Remedial Action Program
Technical Measurements Center

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1.0 INTRODUCTION

Radium-226 reference materials having a matrix similar to soil or tailings samples are not available in sufficient quantity for use by remedial-action contractors to calibrate their laboratory gamma-ray spectrometers. Such reference materials are needed to provide uniform standardization among measurements made by remedial-action contractors. A task, therefore, was undertaken to prepare about 200 pounds each of three different concentrations of radium-226 reference materials by diluting tailings with high-purity silica. Target values for radium-226 content were 50, 15, and 5 pCi/g.

The radium-226 content of the reference materials was measured by C. W. Sill of EG&G Idaho, Inc., Idaho Falls, using a high-resolution alpha spectrometry technique standardized with National Bureau of Standards (NBS) standard 4961 [1]. A summary of this technique is provided in Appendix A of this report. An independent measurement of the radium-226 content was conducted by Bendix Field Engineering Corporation (Bendix), Grand Junction, Colorado, using a high-resolution Ge(Li) detector, which was calibrated using the New Brunswick Laboratory (NBL) 100-A Series standards [2]. The Ge(Li) detector has also been used to determine the radium-226 content in the calibration models at the Grand Junction facility; these models are used by remedial-action contractors for calibration of borehole logging gamma-ray probes.

2.0 PREPARATION AND SAMPLING

2.1 Tailings Preparation

A large tailings sample from the Monticello, Utah, east tailings pile was selected for use in making the radium-226 reference materials. This sample had previously been crushed and pulverized to minus-28 mesh. This crushed material was screened through a minus-325-mesh screen until about 200 pounds of material was obtained. The minus-325-mesh tailings material was dried at 110°C for 3 days and then blended in a 3-ft³ cross-flow blender for 28 hours. Since this almost completely filled the 3-ft³ blender, the material was transferred to a 10-ft³ cross-flow blender to ensure proper mixing and was blended for an additional 23 hours. After blending, the minus-325-mesh tailings material was placed in 1-gallon glass jars, each jar containing approximately 6 pounds.

2.2 Tailings Sampling

Before the reference materials could be prepared, the radium content of the tailings had to be estimated. The minimum number of samples needed to estimate the mean concentration of radium-226 is calculated from the equation (modified from Natrella [3])

$$CV = \frac{D}{S} \quad (2.1)$$

where

CV = critical value (parameter needed to estimate minimum sample size)

D = maximum allowable deviation

S = estimated standard deviation gained through previous experience

In this case, S = 1 percent, D = 2 percent, and CV = 2. Using Table A-8 given in Natrella [3], the minimum sample size for estimating the mean within 2 percent with 95 percent confidence is six. The number of samples was increased to eight in order to acquire a reasonably good estimate of the mean. The sampling arrangement consisted of two samples from each of four jars.

The four jars were selected at random and each jar split into two approximately equal parts using a Jones splitter. Each of these two parts was progressively split on a randomly selected basis. The splitting process continued until two samples of approximately 10 grams each were obtained for each jar. Ten-gram samples from a predetermined side of the Jones splitter were sent to C. W. Sill, EG&G Idaho, Inc., Idaho Falls, for the determination of radium-226 content.

2.3 Diluent

Minusil No. 218, a high-purity silica purchased from Whittaker, Clark, and Daniels,* and Aerosil No. 200, a surfactant purchased from American Chemical Enterprises, Inc.,** were used to dilute

*Whittaker, Clark, and Daniels, 1000 Coolidge St., South Plainfield, New Jersey 07080.

**American Chemical Enterprises, Inc., 1923 Delman Blvd., St. Louis, Missouri 63103.

the minus-325-mesh tailings material to make three different levels of radium-226 reference materials. The procedures for mixing the Minusil No. 218, Aerosil No. 200, and the tailings are similar to the procedure used by New Brunswick Laboratory [4] in preparing their 100-A Series standards.

Fifty pounds of Minusil No. 218 were blended with 1 pound of Aerosil No. 200 for 15 minutes in a 3-ft³ blender. The blender was stopped for 15 minutes to allow settling of the silica dust, and then an additional 50 pounds of Minusil No. 218 were added and the mixture blended for another 15 minutes. The blended material was removed from the blender and dried at 110°C for 24 hours. The sequence was repeated eight more times to give about 800 pounds of Minusil No. 218 with a 1 percent content of Aerosil No. 200. The 800-pound mixture was split in half and each half separately blended in a 10-ft³ blender for 1 hour. The two 400-pound blends were each split in half, and two halves, one from each of the 400-pound blends, were combined and blended together for an hour. This was repeated for the other two halves. The blended diluent material was then stored in plastic-lined barrels until needed to dilute the tailings. Approximately 30 grams of the diluent material was sent to C. W. Sill for the determination of Ra-226 content.

2.4 Reference Material Preparation

For each of the reference materials (50, 15, and 5 pCi/g radium-226), ten jars of tailings were randomly selected and split into quarters on randomly chosen splits using a Jones splitter. One-quarter of each jar was taken until the calculated weight of tailings needed for the appropriate level of reference material had been collected. The appropriate weight of reference material was dried at 110°C for 24 hours, allowed to cool, and weighed. For each of the reference materials, approximately one-quarter of the calculated amount of diluent and the appropriate amount of tailings were added to a 10-ft³ blender and blended for 45 minutes. The blender was stopped for 30 minutes to allow the dust to settle and another portion of the diluent added and blended. After all the diluent had been added, the mixture was blended for 48 hours. During the 48 hours, the blender was periodically stopped, carefully opened, and the material brushed off the sides and top of the blender.

The reference material was allowed to settle in the blender overnight; then it was removed from the blender and placed in 1-quart jars. The reference material was removed by opening the butterfly valve on the blender and allowing the reference material to flow into the jars.

2.5 Reference Material Sampling

Once the reference materials were prepared, the radium content of these materials had to be estimated. The minimum number of samples needed to estimate the mean concentration of radium-226 and the variability of these materials is calculated from equation (2.1). Since the variability, as well as the mean, is to be estimated, a larger number of samples must be taken. As shown on page 4-11 in the National Bureau of Standards Handbook 91 [3], the minimum sample size for estimating the mean and standard deviation within 2 percent with 95 percent confidence is 27. The sampling arrangement consisted of three samples from each of nine jars.

The nine jars to be sampled were randomly selected. For each of the nine jars, three samples, each consisting of approximately 30 grams, were taken at randomly selected times while the jar was being filled. An additional 700-gram sample was taken at randomly selected times during the filling of each of the nine jars. The twenty-seven 30-gram samples were sent to C. W. Sill for analysis using high-resolution alpha spectrometry, and the nine 700-gram samples were retained by Bendix for analysis using the high-resolution gamma-ray spectrometry system.

3.0 RESULTS

3.1 Tailings

Table 1 shows the radium-226 results obtained by C. W. Sill on the original tailings. A procedure for detecting outliers, as described by Dixon and Massey [5], indicates that the 944 pCi/g radium-226 result obtained on the second aliquot of bottle 29 is an outlier. Another measurement on a sample taken from the second aliquot from bottle 29, however, gave a result of 889 pCi/g radium-226. The results on aliquot 2 of bottle 29 indicate the possibility of a sample homogeneity problem. The tailings material had a tendency to "ball up" when blending, and it was believed that a small ball was sampled that may not have been homogeneous. It was also believed that dilution and blending of the tailings with the high-purity silica mix would break up these "balls" and minimize any homogeneity problems in the actual reference materials.

The radium-226 content of the diluent was found to be 0.153 ± 0.005 pCi/g.

Table 1. Results from C. W. Sill of High-Resolution Alpha Spectrometry Analysis for Radium-226: Original Tailings (0.2500-gram sample size)

Bottle Number	Aliquot No. 1* (pCi/g)	Aliquot No. 2* (pCi/g)
9	888 $\pm$ 6	899 $\pm$ 5
13	895 $\pm$ 6	887 $\pm$ 5
23	883 $\pm$ 5	893 $\pm$ 5
29	880 $\pm$ 5	944 $\pm$ 5** (889 $\pm$ 5)

Mean (without first run of outlier but with repeat run): 889 pCi/g.

Experimental standard deviation: ± 6 pCi/g.

Standard error: ± 2 pCi/g.

*Uncertainties are standard deviations resulting from propagating all random uncertainties incurred anywhere in the measurement process. Estimates of systematic uncertainties are excluded.

**Considered an outlier. Rerun gave 889 pCi/g.

3.2 Reference Material

Using the estimated mean of 889 ± 6 pCi/g radium-226 for the tailings and 0.153 ± 0.005 pCi/g radium-226 for the diluent, the analyzed tailings were diluted gravimetrically (as described in Section 2.4 of this report) to give three diluted reference materials containing 50.2 ± 0.1 , 15.15 ± 0.04 , and 5.15 ± 0.01 pCi/g radium-226, respectively. The uncertainty expressed in the numbers is the standard error associated with the tailings propagated through the dilution calculation. Because all weight measurements made in the gravimetric dilutions were better than a few hundredths percent, they do not affect the statistical uncertainty of the calculated values.

The radium-226 results obtained by C. W. Sill for the three concentrations of reference material (50, 15, and 5 pCi/g) are presented in Tables 2, 3, and 4, respectively. An analysis of these results for extreme values, as given by Dixon and Massey [5], shows that there are no outliers in these data.

Table 2. Results from C. W. Sill of High-Resolution Alpha Spectrometry Analysis for Radium-226: 50 pCi/g Dilution (3.000-gram sample size)

Bottle Number	Aliquot No. 1* (pCi/g)	Aliquot No. 2* (pCi/g)	Aliquot No. 3* (pCi/g)
20	50.9 ± 0.3	50.5 ± 0.3	49.5 ± 0.3
39	51.9 ± 0.3	50.2 ± 0.3	50.5 ± 0.3
52	50.5 ± 0.3	49.8 ± 0.3	50.7 ± 0.3
58	50.1 ± 0.3	49.9 ± 0.3	51.1 ± 0.3
69	50.6 ± 0.3	51.6 ± 0.3	48.5 ± 0.3
79	51.1 ± 0.3	48.8 ± 0.3	49.5 ± 0.3
83	49.5 ± 0.3	50.0 ± 0.3	50.3 ± 0.3
91	50.0 ± 0.3	49.4 ± 0.3	51.0 ± 0.3
117	50.0 ± 0.3	51.1 ± 0.3	49.7 ± 0.3

Mean: 50.2 pCi/g.

Experimental standard deviation: ±0.8 pCi/g.

Standard error: ±0.15 pCi/g.

*Uncertainties are standard deviations resulting from propagating all random uncertainties incurred anywhere in the measurement process. Estimates of systematic uncertainties are excluded.

Table 3. Results from C. W. Sill of High-Resolution Alpha Spectrometry Analysis for Radium-226: 15 pCi/g Dilution (6.000-gram sample size)

Bottle Number	Aliquot No. 1* (pCi/g)	Aliquot No. 2* (pCi/g)	Aliquot No. 3* (pCi/g)
4	15.09 ± 0.09	14.80 ± 0.09	15.05 ± 0.10
32	15.09 ± 0.09	14.90 ± 0.09	15.40 ± 0.10
36	14.90 ± 0.09	14.87 ± 0.09	15.13 ± 0.10
54	15.08 ± 0.09	15.29 ± 0.09	15.46 ± 0.10
56	14.98 ± 0.09	15.22 ± 0.09	15.01 ± 0.10
71	15.26 ± 0.09	14.97 ± 0.09	15.11 ± 0.10
96	15.48 ± 0.09	15.21 ± 0.09	15.10 ± 0.10
104	14.84 ± 0.09	15.32 ± 0.10	14.59 ± 0.10
113	15.50 ± 0.09	15.03 ± 0.10	15.44 ± 0.10

Mean: 15.12 pCi/g.

Experimental standard deviation: ±0.23 pCi/g.

Standard error: ±0.05 pCi/g.

*Uncertainties are standard deviations resulting from propagating all random uncertainties incurred anywhere in the measurement process. Estimates of systematic uncertainties are excluded.

Table 4. Results from C. W. Sill of High-Resolution Alpha Spectrometry Analysis for Radium-226: 5 pCi/g Dilution (12.000-gram sample size)

Bottle Number	Aliquot No. 1* (pCi/g)	Aliquot No. 2* (pCi/g)	Aliquot No. 3* (pCi/g)
4	5.23 $\pm$ 0.03	5.09 $\pm$ 0.03	5.09 $\pm$ 0.03
25	5.27 $\pm$ 0.04	5.18 $\pm$ 0.03	5.10 $\pm$ 0.03
41	5.04 $\pm$ 0.03	5.01 $\pm$ 0.03	5.08 $\pm$ 0.03
68	5.18 $\pm$ 0.03	5.05 $\pm$ 0.03	5.05 $\pm$ 0.03
77	5.01 $\pm$ 0.03	5.25 $\pm$ 0.04	5.26 $\pm$ 0.03
81	5.02 $\pm$ 0.03	5.21 $\pm$ 0.04	5.14 $\pm$ 0.03
106	4.99 $\pm$ 0.03	5.04 $\pm$ 0.04	5.18 $\pm$ 0.03
115	5.34 $\pm$ 0.03	5.14 $\pm$ 0.03	5.11 $\pm$ 0.03
137	5.20 $\pm$ 0.03	5.09 $\pm$ 0.03	5.02 $\pm$ 0.03

Mean: 5.12 pCi/g.

Experimental standard deviation: ± 0.10 pCi/g.

Standard error: ± 0.02 pCi/g.

*Uncertainties are standard deviations resulting from propagating all random uncertainties incurred anywhere in the measurement process. Estimates of systematic uncertainties are excluded.

4.0 STATISTICAL ANALYSIS

In order to test for homogeneity, the reference materials were examined with respect to the mean values and the variation between, as well as within, the bottles. Several tests were conducted, results of which are presented below.

4.1 Test for Equality of Means

An assessment of the null hypothesis, "the means are statistically equal," was accomplished by performing the equality of means test described by Natrella [3]. This test involves selecting two sample means, calculating the difference between them, and comparing this difference with a critical value. If the calculated difference exceeds the critical value, the null hypothesis is rejected and the reference materials must be considered nonhomogeneous. Conversely, if the calculated difference does not exceed the critical value, the homogeneity of the reference materials cannot be disproved.

Details for the test for equality of means (notation by Natrella [3]) are presented below:

Given

the mean of the two subsamples	$\bar{X}_A$	$\bar{X}_B$
the variance of these subsamples	S_A^2	S_B^2
and the number of observations for each	N_A	N_B

then the value for the degrees of freedom (f) is calculated from the equation

$$f = \frac{(V_A + V_B)^2}{\frac{V_A^2}{N_A + 1} + \frac{V_B^2}{N_B + 1}} - 2 \quad (4.1)$$

where

$$V_A = \frac{S_A^2}{N_A} \quad \text{and} \quad V_B = \frac{S_B^2}{N_B} \quad (4.2)$$

The t value (cf. Table A-4 in Natrella [3]) is found using degrees of freedom (f) and $1 - \alpha/2$ where α , the significance level, is assumed to be 5 percent.

The critical value (U) is calculated from the equation

$$U = (t_{1-\alpha/2}) \sqrt{V_A + V_B} \quad (4.3)$$

The critical value (U) is compared with the calculated difference where

$$D = |\bar{X}_A - \bar{X}_B| \quad (4.4)$$

Results of the test for equality of means are presented in Table 5. Samples having the largest difference in mean were selected for this analysis, thereby increasing the likelihood of a statistically significant difference. Two types of comparison were performed, one being an examination of between-bottle means (called "Between" in Table 5) and the other an examination of

within-bottle means (called "Within" in Table 5). The former comparison was accomplished by calculating the overall mean using three aliquots for each of two selected bottles. In order to verify these results, the test was repeated using two different sets of bottles at each of the three dilutions, for a total of six tests. As shown in Table 5, results of all of the between-bottle comparisons indicate that the null hypothesis cannot be rejected because the calculated difference (D) is less than the critical value (U) at the 95 percent confidence level.

Comparison of within-bottle means was accomplished by calculating the overall mean using nine bottles for each of two selected aliquots, and comparing these aliquot means with one another. This test was performed for each of the three dilutions, for a total of three tests. As shown in Table 5, this test also fails to reject the null hypothesis because the calculated difference is less than the critical value at the 95 percent confidence level.

Results of the test for equality of means demonstrate that the calculated difference is less than the critical value for all cases examined. Therefore, insufficient evidence exists to dispute the null hypothesis that these means are equal in a given dilution of reference material at the 95 percent confidence level. Results of these analyses are used to infer that the entire reference material at a specified dilution can be characterized by a single mean value.

Table 5. Results of Test for Equality of Means

Test	Calculated Difference (D)	Critical Value (U) (95% level)	Finding
5 pCi/g, Between (Try 1)	0.16	0.23	D < U
5 pCi/g, Between (Try 2)	0.13	0.22	D < U
15 pCi/g, Between (Try 1)	0.31	0.35	D < U
15 pCi/g, Between (Try 2)	0.40	0.67	D < U
50 pCi/g, Between (Try 1)	0.94	1.58	D < U
50 pCi/g, Between (Try 2)	1.07	2.09	D < U
5 pCi/g, Within	0.03	0.12	D < U
15 pCi/g, Within	0.07	0.21	D < U
50 pCi/g, Within	1.42	0.78	D < U

4.2 Bartlett's Test for Homogeneity of Variance

Another null hypothesis, "the standard deviations are statistically identical," was evaluated using Bartlett's test for homogeneity of variance, described by Dixon and Massey [5]. This test involves calculating a "variance," hereafter called a statistic, and comparing it with a critical value. As with the test for equality of means, if the statistic exceeds the critical value, the null hypothesis is rejected. Conversely, if the statistic does not exceed the critical value, the null hypothesis cannot be rejected.

Details for Bartlett's test for homogeneity of variance (notation modified from Dixon and Massey [5]) are presented below:

Given that
the number of sample groups is k,
each with size n_i ,

where

the total number of samples is $N = \sum n_i$,
the variance of the i th sample group is S_i^2 .

The critical value (M) is cited in Table 6 of Crow, Davis, and Maxfield [6] using the two values, C_1 , and k, where

$$C_1 = \sum \frac{1}{(n_i - 1)} - \frac{1}{A} \quad (4.5)$$

and $A = \sum(n_i - 1)$.

The calculated value (V) is determined from the equation

$$V = (N - k) \ln S_p^2 - \sum [(n_i - 1) \ln S_i^2] \quad (4.6)$$

where

$$S_p^2 = \sum \frac{(n_i - 1) S_i^2}{N - k} \quad (4.7)$$

The critical value (M) is then compared with the calculated value (V).

Results of Bartlett's test for homogeneity of variance are presented in Table 6. For this analysis, two types of comparison were made for each of the three dilutions of reference materials. One comparison involved an examination of between-bottle "variance" (called "Between" in Table 6), and the other involved within-bottle "variance" (called "Within" in Table 6). To accomplish the between-bottle comparison, the statistic was calculated using the variance from each of the nine bottles. As shown in Table 6, results of all of these comparisons indicate that the null hypothesis cannot be rejected because the calculated statistic (V) is less than the critical value (M) at the 95 percent confidence level.

Examination of within-bottle variance was accomplished by calculating a statistic using the variance from each of the three aliquots. This test also fails to reject the null hypothesis since the calculated statistic is less than the critical value at the 95 percent confidence level.

Table 6. Results of Bartlett's Test for Homogeneity of Variance

Test	Calculated Statistic (V)	Critical Value (M) (95% level)	Finding
5 pCi/g, Between	3.82	17.85	V < M
15 pCi/g, Between	4.18	17.85	V < M
50 pCi/g, Between	5.65	17.85	V < M
5 pCi/g, Within	3.23	6.31	V < M
15 pCi/g, Within	0.48	6.31	V < M
50 pCi/g, Within	0.83	6.31	V < M

Results of Bartlett's test for homogeneity of variance demonstrate that the calculated statistic is less than the critical value for all cases examined. Therefore, insufficient evidence exists to dispute the null hypothesis that these standard deviations are equal in a given reference material at the 95 percent confidence level. Results of these analyses are used to infer that the entire reference material at a specified dilution can be characterized by the same amount of variation.

4.3 Analysis of Variance

A test of the null hypothesis, "the variation at different levels (between or within bottles) is statistically equal," was conducted using a one-way analysis of variance. This test compares the within-bottle and between-bottle variation simultaneously, and was performed using a computer program provided by Dixon and Brown [7]. One example of the results of this analysis of variance is presented in Table 7. To accomplish this test, a calculated F value is compared with an F Table [7] to determine whether or not the critical value has been exceeded. The F value, a variance ratio, is calculated by dividing one mean squared error by another mean squared error, where the denominator is an unbiased estimate of the population variance [8]. This test fails to reject the null hypothesis because the calculated F value is less than the critical F value, as indicated by the probability cited in Table 7.

Table 7. Typical Example of Analysis of Variance for the Radium-226 Reference Material (one-way analysis of variance, 50 pCi/g dilution)

Source of Variance	Degrees of Freedom	Sum of Squares	Mean Squared Error	F Value	Probability
Between Bottles	8	2.161	0.270	0.336	0.940
Within Bottles (error)	18	14.467	0.804		

Results of the analysis of variance demonstrate that the mean squared error at the between-bottle level is not significantly different from the mean squared error at the within-bottle (error) level. Therefore, insufficient evidence exists to dispute the postulate that the variation at the different levels is statistically identical, unbiased, and thus homogeneous at the 95 percent confidence level within a given dilution of reference material.

4.4 Discussion of Statistical Results

All of these statistical tests show that, at the 95 percent confidence level, there is no statistically significant difference with respect to either mean or variance when making comparisons using the reference material samples. By inference, this conclusion is extended to the entire reference material because of the random sampling procedures utilized throughout the preparation and testing. One might criticize the conclusions drawn by these tests because of the limited number of samples utilized. However, each of these tests was performed using small-sample statistics, which compensates for the variation based on the number of samples taken.

As shown in Tables 2, 3, and 4, the relative experimental standard deviations range from about 1.5 percent to about 2 percent. By propagating random uncertainty for a single measurement, the estimated relative standard deviation is about 0.6 percent. This difference indicates the possibility of a slightly higher amount of variation in the reference materials than predicted by random uncertainties. This variation might be attributed to systematic errors, a small amount of inhomogeneity, or both. Prior to the

preparation of the reference materials, 2 percent was the acceptable limit placed on variation. This acceptable limit determined the number of samples that were to be selected for testing purposes as shown by equation (2.1). If the variation measured in the samples exceeded this limit, the material would be considered nonhomogeneous. Since the measurements did not exceed the 2 percent limit, the materials are considered to be homogeneous within the 2 percent limit. In lieu of qualifying statements, the only observation that can be made with certainty is that any subsequent measurement of radium-226 in these reference materials will be within 1.5 to 2 percent of the estimated means cited in Tables 2, 3, and 4 sixty-eight percent of the time, which is equivalent to plus-or-minus one standard deviation from the mean.

5.0 COMPARISON OF HIGH-RESOLUTION ALPHA AND GAMMA-RAY SPECTROMETRY RESULTS

Each of the 700-gram samples of the reference materials was packed under 1-ton pressure into a seamless stainless steel can, measuring approximately 2 inches high and 4 inches in diameter. Each can containing reference material was placed in an oven and heated at 110°C for about 4 hours. The cans were removed from the oven and immediately sealed while hot. The cans remained undisturbed for 20 days to allow radium-226/bismuth-214 equilibrium to be established; then the radium-226 content was determined by Bendix using a Ge(Li) detector calibrated with NBL 100-A Series standards. A report describing the gamma-ray spectrometry system and procedures used by Bendix is in preparation [2]. Tables 8, 9, and 10 show the gamma-ray spectrometry results obtained by Bendix from analysis of the three levels of reference material.

Table 8. Results of Bendix High-Resolution Gamma-Ray Spectrometry Analysis for Radium-226: 50 pCi/g Dilution (approximate sample size--550 grams)

Bottle Number	Ra-226 (pCi/g)*
20	51.4 $\pm$ 0.7
39	52.1 $\pm$ 0.7
52	51.3 $\pm$ 0.7
58	48.6 $\pm$ 0.7
69	50.1 $\pm$ 0.7
79	50.1 $\pm$ 0.7
83	50.7 $\pm$ 0.7
91	51.8 $\pm$ 0.7
117	49.8 $\pm$ 0.7

Mean: 50.7 pCi/g.

Experimental standard deviation: ± 1.1 pCi/g.

Standard error: ± 0.04 pCi/g.

*Uncertainties are standard deviations resulting from propagating weighing, sample positioning, and counting random uncertainties in the measurement process.

Table 9. Results of Bendix High-Resolution Gamma-Ray Spectrometry Analysis for Radium-226: 15 pCi/g Dilution (approximate sample size--550 grams)

Bottle Number	Ra-226 (pCi/g)*
4	15.3 $\pm$ 0.4
32	15.1 $\pm$ 0.4
36	14.8 $\pm$ 0.4
54	15.0 $\pm$ 0.4
56	14.6 $\pm$ 0.4
71	15.5 $\pm$ 0.4
92	15.1 $\pm$ 0.4
104	15.0 $\pm$ 0.4
113	15.4 $\pm$ 0.4

Mean: 15.1 pCi/g.

Experimental standard deviation: ± 0.3 pCi/g.

Standard error: ± 0.1 pCi/g.

*Uncertainties are standard deviations resulting from propagating weighing, sample positioning, and counting random uncertainties in the measurement process.

Table 10. Results of Bendix High-Resolution Gamma-Ray Spectrometry Analysis for Radium-226: 5 pCi/g Dilution (approximate sample size--550 grams)

Bottle Number	Ra-226 (pCi/g)*
4	4.9 ± 0.2
25	5.0 ± 0.2
41	4.9 ± 0.2
68	5.2 ± 0.2
77	5.0 ± 0.2
81	4.9 ± 0.2
106	5.1 ± 0.2
115	5.2 ± 0.2
137	5.5 ± 0.2

Mean: 5.1 pCi/g.

Experimental standard deviation: ±0.2 pCi/g.

Standard error: ±0.1 pCi/g.

*Uncertainties are standard deviations resulting from propagating weighing, sample positioning, and counting random uncertainties in the measurement process.

The high-resolution alpha spectrometry results obtained by C. W. Sill (Tables 2, 3, and 4) and the high-resolution gamma-ray spectrometry results obtained by Bendix (Tables 8, 9, and 10) for radium-226 were compared using the test for equality of means described by Natrella [3]. This test compares the means of the results of the two methods to determine if there is any measurable difference. As can be seen by the results of this test (Table 11), the calculated difference (D) is less than the critical value (U) for each of the three reference materials. For each reference material, there is no statistically significant difference at the 95 percent confidence level between the experimental results obtained by the two measurement methods; thus, these two methods yield the same result.

Table 11. Comparison of Radium-226 Results Obtained by High-Resolution Alpha Spectrometry and High-Resolution Gamma-Ray Spectrometry

Reference Material	Alpha Mean	Gamma-Ray Mean	Calculated Difference (D)	Critical Value (U) (95% level)	Finding
50 pCi/g	50.2	50.7	0.4	0.9	D < U
15 pCi/g	15.12	15.1	0.03	0.22	D < U
5 pCi/g	5.12	5.1	0.05	0.15	D < U

6.0 RECOMMENDED VALUES OF REFERENCE MATERIALS

The recommended values for the three levels of radium-226 reference materials are presented in Table 12. These values are the means and uncertainties obtained by C. W. Sill using high-resolution alpha spectrometry (Tables 2, 3, and 4). Even though the two measurement methods described herein yield results that are statistically the same, the authors prefer to use the high-resolution alpha spectrometry results to establish the recommended values because the alpha spectrometry procedure was calibrated with a NBS standard.

Table 12. Recommended Radium-226 Values (in pCi/g)

Reference Material	Recommended Value (mean)	Uncertainty*
50 pCi/g	50.2	±0.8
15 pCi/g	15.12	±0.23
5 pCi/g	5.12	±0.10

*Uncertainties are the associated experimental standard deviation obtained by high-resolution alpha spectrometry.

7.0 SUGGESTIONS FOR USE OF REFERENCE MATERIALS

A dry sample of the reference material was opened to the atmosphere for 3 days when the relative humidity was about 40 percent. The reference material picked up less than 0.1 percent moisture. Even though the moisture buildup was small, it is recommended that the reference material be dried to a constant weight at 110°C before use.

In determining the radium-226 content of the reference materials, no attempt was made to determine the emanation. Consequently, use of these reference materials to calibrate gamma-ray spectrometers that measure radium-226 indirectly by using one or more daughters of radium-226 will require sealing the reference material in an appropriate container and allowing the equilibrium between radium-226 and the appropriate daughters to be established.

Although the determination of potassium and thorium in the reference materials was not included in the scope of this task, an estimate of these values may prove useful to remedial-action contractors who use gross gamma instruments. Nine samples of the 50 pCi/g radium-226 reference material were counted for 8 hours by Bendix using high-resolution gamma-ray spectrometry. No gamma-ray peak was found for either potassium-40 (used to measure potassium) or thallium-208 (used to measure thorium). Conservative estimates, therefore, of the potassium and thorium concentrations are less than 1 percent and 3 µg/g, respectively.

8.0 ACKNOWLEDGMENTS

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Appendix A

DETERMINATION OF RADIUM-226 BY HIGH-RESOLUTION ALPHA SPECTROMETRY: A SUMMARY*

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The determination of radium-226 by alpha spectrometry has been investigated critically to determine experimental conditions under which high resolution and accurate and reliable results can be obtained. The procedure recommended involves dissolution of the sample, precipitation of lead sulfate to concentrate and separate barium and radium sulfates from the sample, dissolution of the lead sulfate in alkaline diethylenetriaminepentaacetic acid (DTPA), and reprecipitation with acetic acid to separate barium and radium from the lead carrier and other interferences, and filtering the barium sulfate on a membrane filter for determination by alpha spectrometry. Although this procedure is superficially similar to others using the same combination of steps, the details are markedly different and lead to profound differences in the resolution of the subsequent alpha spectra, and in the recovery, precision, accuracy, and reliability of the results. Each of the individual steps will be discussed separately.

Sample Dissolution

Solid samples are dissolved by fusion with anhydrous potassium fluoride in the presence of barium-133 tracer to ensure complete dissolution of all silicious or refractory materials. Concentrated sulfuric acid is added and the fluoride cake is transposed to a pyrosulfate fusion with simultaneous volatilization of both silica and fluorides. A small additional quantity of potassium fluoride is added after the original fluoride cake has been transposed to volatilize a small quantity of silica that is precipitated rather than volatilized. Because there is no place in the entire procedure at which insoluble materials can be filtered off safely without danger of losing radium, it is mandatory that residual insoluble materials be kept to less than a few micrograms if the best resolution of the subsequent alpha spectra is to be obtained.

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Lead Sulfate Separation

The radium and barium present in the sample are precipitated with lead sulfate at room temperature in the presence of a high concentration of potassium without addition of barium carrier. There is already more barium indigenous to soils than should be present for optimum resolution, even on moderately sized samples. The lead sulfate produced is more finely divided than that produced by hot precipitation and digestion, or in the absence of potassium ion, giving more efficient precipitation without mechanical stirring and in much shorter time, is much easier to transfer quantitatively to a centrifuge tube, gives better packing on centrifugation, and dissolves much faster in alkaline DTPA. The concentration of the lead perchlorate added has been adjusted to delay the onset of precipitation for a few seconds so that the precipitation will occur from essentially homogeneous conditions. After centrifuging, the supernatant liquid is counted in a gamma well counter. If more than about 0.1 percent of the barium-133 tracer is present, an additional portion of lead solution is added to avoid larger losses of radium due to the differences between barium and radium to be discussed below. A small controlled quantity of hydrochloric acid must also be present to provide some preliminary decontamination from polonium-210 which will otherwise result in serious contamination of the detector.

Barium Sulfate Precipitation

The washed lead sulfate is dissolved in only 3 ml of 0.1 M alkaline DTPA, and 3 ml of filtered 40 percent sodium sulfate is then added to keep the total volume as small as possible to keep the concentrations of barium, radium, and sulfate as high as possible to facilitate rapid and complete precipitation of barium-radium sulfate. Three drops of 1-to-1 acetic acid are added while swirling the solution at room temperature vigorously, followed as quickly as possible by 200 μ l of a seeding suspension of barium sulfate injected into the swirling solution. A turbidity much greater than that present in the seeding suspension forms instantaneously. After standing for 30 minutes in a cold water bath, the precipitate is mounted for alpha spectrometry.*

Obviously, if maximum resolution of alpha spectra is to be achieved, the barium carrier must be kept at a minimum, and the acid-insoluble impurities from reagents and sample must be eliminated. However, even when these requirements are met,

*C. W. Sill and R. L. Williams, in Analytical Chemistry 1981, v. 53, p. 412-415.

resolution of alpha spectra of barium sulfate precipitates has not been as good as the actinides on a comparable quantity of cerium fluoride. For example, radium-226 has a 5.55 percent branch that is almost never observed except from specialized carrier-free deposits, even though its energy is separated from the main branch by 183 keV. It can now be demonstrated that the poor resolution generally obtained in the presence of minimal absorber is caused by the way in which the barium sulfate lattice itself is formed, i.e., by self-absorption within the crystal. If the individual crystals are allowed to become very large, the alpha particles will be degraded severely in getting out the lattice, regardless of how small a quantity of carrier is used, the average thickness of the deposit, or the source-to-detector distance.

Electron micrographs at 10,000 diameters magnification of barium sulfate precipitated under different conditions will be shown to support the following facts. When 100 μg of barium is precipitated from hot solutions of alkaline DTPA, the most widely used conditions, the few individual crystals formed are very angular and relatively large, at least 1 μm on a side, and have a great tendency to form much larger clusters. The aggregates are relatively uniformly distributed over the 360- mm^2 area, but the fraction of the total available filter area actually covered is about one-third. Consequently, the effective thickness of the deposit is much larger than it would have been with smaller crystals covering the available area more completely. In other words, the resolution is more determined by the aggregate size than by the quantity of carrier present or by the average thickness of the deposit. Clearly, precipitation from hot solution must be avoided to minimize the crystal growth that occurs through recrystallization. The alpha resolution was 130 keV, full-width-half-maximum (FWHM).

However, when the precipitation was made at room temperature to minimize recrystallization, the size of the individual crystals increased by several-fold, although the aggregates were not much larger, and the alpha resolution decreased further to a FWHM of 270 keV. The obvious reason for this unexpected result is that the reaction rate at room temperature was so slow, even at such high sulfate concentrations, that several minutes were required before precipitation began, and several more minutes before precipitation was complete. The slower rate allows more time for crystal growth to occur, more than offsetting that from recrystallization that occurs in short periods at high temperature. Surprisingly, an increase of fivefold in the quantity of barium carrier present decreased the resolution only to a FWHM of 319 keV. The clusters are of approximately the same size but more closely packed, thus utilizing a much larger fraction of the total

area available. Consequently, the effective thickness of the deposit is not much greater, and the resolution is still determined largely by the aggregate size rather than by the quantity of carrier present or the average thickness of the deposit.

When precipitated from a solid pyrosulfate cake on dissolution in water, barium sulfate shows a milky-white opalescence indicative of a very small particle size. Newly forming crystals of barium sulfate follow closely the habitat of crystals already present. Consequently, if a few drops of a suspension of barium sulfate prepared from sulfate cakes is added to seed a supersaturated solution of barium sulfate in acidic DTPA, precipitation of barium sulfate is immediate and complete, and in the finely divided form characteristic of the seeding crystals. The resolution obtained with larger quantities of barium is also now more related to the quantity of carrier present. The FWHMs obtained for barium sulfate from pyrosulfate cakes were 58 and 166 keV for 100 and 525 μg of barium, respectively. The FWHMs for precipitates formed from cold acidic DTPA solutions with seeding were 68 and 155 keV, respectively. Using this technique, the minor branch of radium-226 separated from samples of soils, ores, etc., is resolved almost completely when the proper quantity of carrier is present.

Chemical Inequality of Barium and Radium

The assumption that barium-133 is a suitable tracer with which to determine the chemical yield of radium-226 is a poor one. The ratio of radium to barium remaining unprecipitated in the barium sulfate filtrate is 40 percent lower than that in the barium sulfate filtered off, while that in the lead sulfate filtrate is 144 percent higher than that in the lead sulfate removed. The smaller losses of radium than barium in the barium sulfate filtrate can be explained easily by the lower solubility of radium sulfate, the lower stability of the radium-DTPA complex, and, particularly, the much larger number of atoms of barium available to carry the radium isomorphously in the barium sulfate lattice. The larger losses of radium than barium in the lead sulfate separation can be explained by the greater disparity in the crystal radii of radium than barium relative to the lead ion in a process involving isomorphous replacement in the lead sulfate lattice. Clearly, barium-133 tracer should be used to correct only for physical and mechanical losses. Chemical losses must be kept to a minimum and a correction determined empirically if desired.

Precision and Accuracy

In preparing standards for the Technical Measurements Center, Division of Remedial Action Projects, U.S. Department of Energy, eight aliquots of a well-blended sample of tailings gave a mean and experimental standard deviation of 889 ± 6 (± 5) pCi/g of radium-226. The uncertainty given in parentheses is one standard deviation of a single measurement from all random uncertainties incurred anywhere in the entire measurement process. The analyzed sample of tailings was then diluted gravimetrically with high-purity silica to give 200 pounds each of three diluted standards containing 50.2, 15.5, and 5.15 pCi/g of radium-226 with a relative standard deviation of each calculated from the dilution of 0.25 percent. Each diluted standard was then analyzed 27 times to obtain a statistically valid evaluation of the homogeneity of such large batches of material. The means, experimental standard deviations of the individual results about the means, and the theoretical standard deviations of the individual measurements were 50.2 ± 0.8 (± 0.3), 15.12 ± 0.23 (± 0.10), and 5.12 ± 0.10 (± 0.03) pCi/g, respectively. On 89 analyses covering a 178-fold range in concentrations and a 48-fold range in sample sizes, the relative standard deviation of each group was always less than 2 percent, part of which must have been caused by sample inhomogeneity. Not a single chemical yield dropped below 94 percent, and 40 percent of the results gave yields above 96 percent.