



Project Summary

Test Procedure for Gross Alpha Particle Activity in Drinking Water: Interlaboratory Collaborative Study

E. L. Whittaker

A new test procedure for measuring the concentration of gross alpha particle activity in drinking water samples was multi-laboratory tested with 18 laboratories in a collaborative study. Gross alpha activity values were calculated with four different alpha emitting radionuclide standard counting efficiencies to see which standard was best for gross alpha activity determinations. Thorium-230, a pure alpha emitter, appeared to be the best standard for gross alpha counting efficiency.

Water samples A, B, C, and D contained gross alpha concentrations of 74.0 pCi/L, 52.6 pCi/L, 4.8 pCi/L, and 10.0 pCi/L, respectively, at three hours after separation of the alpha emitting radionuclides from the water by coprecipitation with iron hydroxide and barium sulfate. A statistical analysis of the test results from the 18 laboratories, using the Th-230 counting efficiency, showed coefficients of variation for repeatability (within-laboratory precision) of 7.9 percent, 7.8 percent, 8.7 percent, and 8.8 percent, respectively, for an average of 8.3 percent. The analysis also showed coefficients of variation for reproducibility (combined within- and between-laboratory precision) of 20.4 percent, 16.8 percent, 18.7 percent, and 18.5 percent, respectively, for an average of 18.6 percent.

A comparison of the 18 laboratory grand average results (calculated with the Th-230 counting efficiency) with the known gross alpha particle concentrations showed accuracy indexes of 91.9 percent, 99.4 percent, 122 percent, and 94.5 percent, respectively, for an average accuracy

index of 102 percent. The t-test to show significant difference applied to the data showed a significant bias (+) for sample C but no significant bias for the other three samples.

A secondary purpose in this study was to see how well the Ra-226 concentration of a drinking water sample could be estimated from an early gross alpha count (three hours after separation) subtracted from a late gross alpha count (seven days after separation) and calculated from the equation provided in the test procedure.

Water samples A, B, C, and D contained Ra-226 concentrations of 47.2 pCi/L, 20.5 pCi/L, 3.0 pCi/L, and 0.0 pCi/L, respectively. A statistical analysis of the test results from the 18 laboratories (17 laboratories for sample C) showed coefficients of variation for repeatability (within-laboratory precision) of 8.2 percent, 9.5 percent, and 14.8 percent for samples A, B, and C, respectively, for an average of 10.8 percent. The analysis also showed coefficients of variation for reproducibility (combined within- and between-laboratory precision) of 20.5 percent, 25.8 percent, and 23.8 percent, respectively, for an average of 23.4 percent.

A comparison of the 18 laboratory (17 laboratories for sample C) grand average results with the known Ra-226 concentrations showed accuracy indexes of 98.3 percent, 102 percent, and 96.7 percent, respectively for samples A, B, and C, for an average of 99.0 percent. The t-test to show significant differences applied to the data showed no significant bias in the method.

This method for gross alpha particle concentration measurement eliminates the dissolved solids interference problem (which is a significant problem for the EPA approved method) and provides for greater sensitivity by allowing for the use of much larger samples in the analysis. It is recommended that the method be accepted as a validated method for gross alpha activity in drinking water. It is further recommended that the method be accepted as a valid method for the estimation of Ra-226 concentrations in drinking water.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The National Interim Primary Drinking Water Regulations (NIPDWR) require a gross alpha activity measurement of all public drinking water supplies as a screening determination of the presence of alpha emitting radionuclides. The need for specific radionuclide analysis of water supplies is therefore dictated by the gross alpha activity test results of those supplies.

Alpha emitting radionuclides are not separated from the dissolved solids of the sample in the Environmental Protection Agency (EPA) approved test procedures for gross alpha activity. An aliquot of the sample is simply evaporated to dryness, and the residue is counted for alpha activity. Drinking water supplies vary widely in dissolved solids concentrations (from less than 100 to over 5,000 mg per liter). The recommended maximum evaporated dissolved solids residue in a 2-inch diameter counting dish is 100 mg (5 mg per square centimeter) because of the sample residue self-absorption of the alpha particles. For drinking water supplies with dissolved solids greater than 500 mg per liter, the approved test procedure for gross alpha activity measurement is limited because of the small aliquots that can be analyzed and because of the very long counting times that are necessary to meet the required sensitivity of measurement (3 pCi/liter).

A new test procedure for gross alpha activity was reported by Robert Lieberman of the EPA Eastern Environmental Research Facility (EERF) at the 1982 Health Physics Meeting in Las Vegas, Nevada. The new procedure (see Appendix B of the Project Report) coprecipitates all alpha

emitting actinides with barium sulfate and iron hydroxide carriers, and thereby separates the alpha emitting actinides from other sample dissolved solids. Larger sample aliquots can be analyzed so that the alpha measurement sensitivity is improved, and the necessary counting time is minimized.

This new procedure, "Test Procedure for Gross Alpha Particle Activity in Drinking Water by Coprecipitation," has been tested by 18 laboratories in a collaborative study, and the results are described in this report.

A major purpose for gross alpha activity measurements of all public water supplies has been to screen those supplies for a potential Radium-226 health hazard to the public. A secondary purpose in this study was to determine how well an estimate of the Radium-226 content of a water sample could be made by an early and by a late count of the gross alpha activity after separation from the water sample.

Precision, accuracy, and bias statements are made in this report for both gross alpha activity measurements and for the estimated Radium-226 content of each sample.

The study was conducted by the author while employed at the EPA Environmental Monitoring Systems Laboratory at Las Vegas, Nevada, and this reporting of that study was done as an employee of Lockheed Engineering and Management Co., Inc. (LEMSCO), for the EPA under Contract No. 68-03-3249, Task 70.12

Procedures

Analytical Test Procedure

The analytical test procedure (method) used in this study is described in detail in Appendix B of the Project Report. The method provides for quantifying drinking water gross alpha particle concentrations from liter size samples and for estimating the Ra-226 concentrations in those samples. The method provides for coprecipitating all non-gaseous alpha emitting radionuclides in drinking water samples with barium sulfate and iron hydroxide which is followed by counting the alpha particle emissions from the coprecipitate. Two alpha counts of the coprecipitate, one early (three hours) and one late (seven days) after coprecipitate separation, are used to estimate the Ra-226 concentration of the sample.

Collaborative Test Procedure

Twenty-eight laboratories responded to an invitation to participate in the test of the method. Eighteen laboratories submit-

ted test results. Participants were provided with standard solutions (four standards) for determining standard counting efficiencies. They were also provided with four sample concentrates which were to be diluted with their tap water according to the detailed instructions (provided in Appendix C of the Project Report).

Data Processing Procedures

The data from the 18 laboratories were tested for outliers by the ASTM recommended criterion for rejection (ASTM 1980), Equation 1.

$$T_1 = (X_1 - \bar{X})/S \quad (1)$$

where: T_1 = test criterion
 X_1 = a test result for a given sample
 \bar{X} = arithmetic average of all μ values
 S = the estimate of the population standard deviation based on the sample data

Critical values for T for a five percent, two-sided level of significance were used for the rejection criterion.

A statistical evaluation of the test results was carried out by the procedures described in E-691, E-177, and E-178 of the ASTM Standard Part 41, 1980. The standard deviations, other statistical parameters, and equations for their calculations are listed below. The standard deviation of individual participant (or laboratory) test results, S_{ij} , was determined by Equation 2.

$$S_{ij} = \left[\frac{\sum_{h=1}^{n_{ij}} (X_{ijh} - \bar{X}_{ij})^2 / (n_{ij} - 1)}{n_{ij}} \right]^{1/2} \quad (2)$$

where: X_{ijh} = the result reported for the h replicate of the j sample material by lab i
 \bar{X}_{ij} = the mean of the individual results for sample j for lab i
 n_{ij} = the number of replicates reported for sample j by lab i

The repeatability (within-laboratory standard deviation, S_{rj} , for each sample was determined by Equation 3 since the number of replicates was the same (three) for all participants.

$$S_{rj} = \left(\frac{P}{1/P \sum_{i=1}^P S_{ij}^2} \right)^{1/2} \quad (3)$$

where: P = the number of participants in the study.

The standard deviation of the grand average for each sample $S_{\bar{X}_j}$, was determined by Equation 4.

$$S_{\bar{X}_j} = \left[\frac{\sum_{i=1}^P (\bar{X}_{ij} - \bar{X}_j)^2 / (P-1)}{P} \right]^{1/2} \quad (4)$$

where: \bar{X}_{ij} = the average of the test results for sample material ji by Lab i

\bar{X}_j = the grand average for sample material j

The standard deviation of between-laboratory precision for each sample material, S_{L_j} , was determined by Equation 5.

$$S_{L_j} = \left(S_{r_j}^2 - \frac{S_{r_j}^2}{n} \right)^{1/2} \quad (5)$$

The reproducibility (combined within- and between-laboratory) standard deviation for each sample, S_{R_j} , was determined by Equation 6.

$$S_{R_j} = \left(S_{r_j}^2 + S_{L_j}^2 \right)^{1/2} \quad (6)$$

The percent coefficient of variation for repeatability (within-laboratory precision [also called repeatability index]) for sample j, $V_{r_j}\%$ was determined by Equation 7.

$$V_{r_j}\% = 100 S_{r_j} / \bar{X}_j \quad (7)$$

The percent coefficient of variation for between-laboratory precision for sample j, $V_{L_j}\%$ was determined by Equation 8.

$$V_{L_j}\% = 100 S_{L_j} / \bar{X}_j \quad (8)$$

The percent coefficient of variation for reproducibility (combined within- the between-laboratory precision [also called reproducibility index]) for sample j, $V_{R_j}\%$ was determined by Equation 9.

$$V_{R_j}\% = 100 S_{R_j} / \bar{X}_j \quad (9)$$

The accuracy index, a percent relationship of the grand average to the known value for the j sample, $A_j\%$, was determined by Equation 10.

$$A_j\% = 100 \frac{\bar{X}_j}{Y_j} \quad (10)$$

where

Y_j = the known value for the j sample material (pCi/L)

Percent Bias was determined by Equation 11.

$$\% \text{ Bias} = \frac{Y - \bar{X}_j}{Y} \times 100 \quad (11)$$

where

Y = The known value.

The t-test to determine significant differences or systematic error for sample j, t_j was performed using Equation 12.

$$t_j = \frac{\bar{X}_j - Y_j}{S_{\bar{X}_j} / P^{1/2}}, (P-1) \text{ degrees of freedom} \quad (12)$$

where

P = number of participants

Y_j = known value of the sample j contaminant concentration

t_c = critical value for the number of participants, values for t_j greater than t_c are significantly different and show a systematic error.

Results and Discussion

Summaries of the statistical evaluation of the gross alpha concentration test results for the four samples, as calculated with the four standard counting efficiencies, are given in Tables 1 through 4 of this report. The multilaboratory data tables from which these evaluations were made are given in the Project Report.

Water samples A, B, C, and D contained gross alpha concentrations of 74.0 pCi/L, 52.6 pCi/L, 4.8 pCi/L, and 10.0 pCi/L, respectively, at three hours after separation from the water samples by coprecipitation. A statistical analysis of the test results from the 18 laboratories, using the Th-230 counting efficiency, showed coefficients of variation for repeatability (within-laboratory precision) of 7.9 percent, 7.8 percent, 8.7 percent, and 8.8

percent, respectively, for an average of 8.3 percent. The analysis also showed coefficients of variation for reproducibility (combined within- and between-laboratory precision) of 20.4 percent, 16.8 percent, 18.7 percent, and 18.5 percent, for an average of 18.6 percent.

A comparison of the 18 laboratory grand average results (calculated with the Th-230 counting efficiency) with the known gross alpha particle concentrations showed accuracy indexes of 91.9 percent, 99.4 percent, 122 percent, and 94.5 percent, respectively, for an average accuracy index of 102 percent. The t-test to show significant difference, when applied to the data, showed significant bias (+) for sample C but no significant bias for the other three samples.

A secondary purpose of this study was to see how well the drinking water sample Ra-226 concentration could be estimated from an early gross alpha count (three hours after separation) subtracted from a late gross alpha count (seven days after separation) and calculated from the equation provided in the test procedure. A summary of the statistical analyses of the estimated Ra-226 concentrations of the samples is given in Table 5 of this report. The multilaboratory data table from which these evaluations were made is given in the Project Report.

Water samples A, B, C, and D contained Ra-226 concentrations of 47.2 pCi/L, 20.5 pCi/L, 3.0 pCi/L, and 0.0 pCi/L, respectively. A statistical analysis of the test results showed coefficients of variation for

Table 1. Gross Alpha Particle Activity in Water Sample A Precision, Accuracy and Bias Summary

Parameter ^a	Sample A, pCi/L using various standard efficiency factors			
	Am-241	Ra-226	Th-230	Uranium
Y_j (pCi/L)	74.0 ± 3.7	74.0 ± 3.7	74.0 ± 3.7	74.0 ± 3.7
\bar{X}_j (pCi/L)	49.5	62.7	68.0	73.7
A_j (%)	66.9	84.7	91.9	99.6
Bias (%) ^b	-33.1	-15.3	-8.1	-0.40
$S_{\bar{X}_j}$ (pCi/L)	11.7	11.7	13.2	12.0
S_{r_j} (pCi/L)	3.5	5.0	5.4	6.7
S_{L_j} (pCi/L)	11.5	11.3	12.8	11.3
S_{R_j} (pCi/L)	12.0	12.3	13.9	13.1
V_{r_j} (%)	7.1	8.0	7.9	9.1
V_{L_j} (%)	23.2	18.0	18.8	15.3
V_{R_j} (%)	24.2	19.6	20.4	17.8
T_j^c	8.88	4.09	1.93	0.10

^aParameters are described in text.

^bThe sign before the number indicates the direction of bias.

^cThe critical value (t_c) for significant difference for 18 participating labs is 2.11 at the 5 percent significance level.

Table 2. Gross Alpha Particle Activity in Water Sample B Precision, Accuracy and Bias Summary

Parameter ^a	Sample B, pCi/L using various standard efficiency factors			
	Am-241	Ra-226	Th-230	Uranium
Y_j (pCi/L)	52.6 ± 2.6	52.6 ± 2.6	52.6 ± 2.6	52.6 ± 2.6
\bar{X}_j (pCi/L)	38.0	48.4	52.3	58.9
A_j (%)	72.2	92.0	99.4	112.0
Bias (%) ^b	-27.7	-8.0	-0.6	+12.0
$S_{\bar{X}_j}$ (pCi/L)	7.1	8.6	8.2	10.5
$S_{\bar{Y}_j}$ (pCi/L)	2.8	3.7	4.1	5.0
S_{L_j} (pCi/L)	6.9	8.3	7.8	10.1
S_{R_j} (pCi/L)	7.4	9.1	8.8	11.3
$V_{\bar{Y}_j}$ (%)	7.4	7.6	7.8	8.5
V_{L_j} (%)	18.1	17.1	14.9	17.1
V_{R_j} (%)	19.5	18.8	16.8	19.2
T_j^c	8.74	2.07	0.15	2.54

^aParameters are described in text.

^bThe sign before the number indicates the direction of bias.

^cThe critical value (t_c) for significant difference for 18 participating labs is 2.11 at the 5 percent significance level.

Table 3. Gross Alpha Particle Activity in Water Sample C Precision, Accuracy and Bias Summary

Parameter ^a	Sample C, pCi/L using various standard efficiency factors			
	Am-241	Ra-226	Th-230	Uranium
Y_j (pCi/L)	4.8 ± 0.24	4.8 ± 0.24	4.8 ± 0.24	4.8 ± 0.24
\bar{X}_j (pCi/L)	4.29	5.38	5.87	6.53
A_j (%)	89.4	112.0	122.0	136.0
Bias (%) ^b	-10.6	+12.1	+22.3	+36.0
$S_{\bar{X}_j}$ (pCi/L)	0.83	1.01	1.02	1.18
$S_{\bar{Y}_j}$ (pCi/L)	0.37	0.53	0.51	0.57
S_{L_j} (pCi/L)	0.81	0.96	0.98	1.13
S_{R_j} (pCi/L)	0.89	1.10	1.10	1.26
$V_{\bar{Y}_j}$ (%)	8.6	9.8	8.7	8.7
V_{L_j} (%)	18.9	17.8	16.7	17.3
V_{R_j} (%)	20.7	20.4	18.7	19.3
T_j^c	2.55	2.42	4.32	6.04

^aParameters are described in text.

^bThe sign before the number indicates the direction of bias.

^cThe critical value (t_c) for significant difference for 18 participating labs is 2.11 at the 5 percent significance level.

repeatability (within-laboratory precision) of 8.2 percent, 9.5 percent, and 14.8 percent for samples A, B, and C, respectively, for an average of 10.8 percent. The analysis also showed coefficients of variation for reproducibility (combined within- and between-laboratory precision) of 20.5 percent, 25.8 percent, and 23.8 percent, respectively, for an average of 23.4 percent.

A comparison of the 18 laboratory (17 laboratories for sample C) grand average

results with the known Ra-226 concentrations showed accuracy indexes of 98.3 percent, 102 percent, and 96.7 percent for an average accuracy index of 99.0 percent for the method. The t-test to show significant difference, when applied to the data, showed no significant bias in the method.

Radium-224 with its parent thorium-228 is a possible interference in the estimation of Ra-226 from a two-count gross alpha measurement. At equal concentrations of Ra-226 and Ra-224, and

with the Ra-224 being supported by its parent Th-228, the estimation of the Ra-226 concentration will be biased high by about 40 percent. While Ra-224 is a possible interference, it is not a likely interference because the geochemistry of thorium tends to make Th-228 more sedimentary than soluble. Appendix D of the Project Report gives Ra-224 interference calculations which are based upon theoretical calculations and not upon analytical tests.

Conclusions

The problem of high dissolved solids in gross alpha activity measurements of drinking water samples is eliminated by this test procedure. This test procedure also provides for increased sensitivity over the approved method by allowing for the use of larger sample aliquots in gross alpha measurements.

The physical instability of iron hydroxide precipitate when dried on a filter (especially a membrane filter) without the aid of a holding agent can result in loss of precipitate, contamination of the alpha counting system, and poor reproducibility of the test procedure. After a single-laboratory test of the method and before this multi-laboratory study, the method was modified to include the addition of 5 mg of paper pulp fiber to the sample aliquot during the coprecipitation of the barium sulfate and iron hydroxide carriers. This change stabilized the coprecipitate on the filter and eliminated the associated problems.

The average accuracy indexes for gross alpha particle concentrations for the four water samples, as calculated with Am-241, Ra-226, Th-230, and uranium counting efficiencies, were 74.5 percent, 94.2 percent, 102 percent, and 113 percent, respectively. Thorium-230 appears to be the best standard for gross alpha particle concentration determinations of drinking water samples.

The difference in gross alpha activity between a late alpha count (seven days after separation) and an early alpha count (three hours after separation) can be used to estimate the Ra-226 concentration of a drinking water sample with good accuracy in the absence of Th-228, Ra-224 interference. The presence of uranium and polonium-210 in some of the samples did not bias the Ra-226 estimates. Table 6 in this report lists the known alpha emitting radionuclide concentrations of the four samples.

The combining of the coprecipitate recovery factor with the counting efficiency

Table 4. Gross Alpha Particle Activity in Water Sample D Precision, Accuracy and Bias Summary

Parameter ^a	Sample D, pCi/L using various standard efficiency factors			
	Am-241	Ra-226	Th-230	Uranium
Y_j (pCi/L)	10.0 ± 0.5	10.0 ± 0.5	10.0 ± 0.5	10.0 ± 0.5
\bar{X}_j (pCi/L)	6.95	8.83	9.45	10.59
A_j (%)	69.54	88.3	94.5	106.0
Bias (%) ^b	-30.5	-11.7	-5.5	+6.0
$S_{\bar{X}_j}$ (pCi/L)	1.60	2.12	1.61	1.46
S_{η_j} (pCi/L)	0.57	0.77	0.83	0.90
S_{L_j} (pCi/L)	1.56	2.07	1.54	1.36
S_{R_j} (pCi/L)	1.66	2.21	1.75	1.63
V_{η_j} (%)	8.2	8.7	8.8	8.5
V_{L_j} (%)	22.4	23.4	16.3	12.8
V_{R_j} (%)	23.9	25.0	18.5	15.4
T_j^c	8.03	2.34	1.45	1.73

^aParameters are described in text.

^bThe sign before the number indicates the direction of bias.

^cThe critical value (t_c) for significant difference for 18 participating labs is 2.11 at the 5 percent significance level.

Table 5. Estimated Radium-226 in Water Samples Precision, Accuracy and Bias Summary

Parameter ^a	Water Samples ^b			
	A	B	C	D
Y_j (pCi/L)	47.2 ± 2.4	20.5 ± 1.0	3.0 ± 0.1	0.0
\bar{X}_j (pCi/L)	46.4	20.9	2.9	0.0
A_j (%)	98.3	102.	96.7	
Bias (%) ^b	-1.7	+1.9	-3.3	
$S_{\bar{X}_j}$ (pCi/L)	8.8	5.1	0.6	
S_{η_j} (pCi/L)	3.8	2.0	0.43	
S_{L_j} (pCi/L)	8.7	5.0	0.55	
S_{R_j} (pCi/L)	9.5	5.4	0.69	
V_{η_j} (%)	8.2	9.5	14.8	
V_{L_j} (%)	18.7	23.9	19.0	
V_{R_j} (%)	20.5	25.8	23.8	
T_j^d	0.39	0.33	0.71	

^aParameters are described in text.

^bSee the text for water sample radionuclide content.

^cThe sign before the number indicates the direction of bias.

^dThe critical value (t_c) for significant difference for 18 participating labs is 2.11 at the 5 percent significance level. The t_c for 17 labs (sample C) is 2.12.

coprecipitated by the method be used for gross alpha particle determinations of drinking water samples.

It is recommended that this test procedure be considered a valid method for estimation of Ra-226 concentrations in drinking water.

factor into a single factor (referred to as the counting efficiency factor in this report) appears to be acceptable when standards are carried through the same analytical process as the samples. Coprecipitate weights reported by the laboratories for the standard samples and water samples (listed in the Project Report) showed good precision within laboratories.

Recommendations

It is recommended that the method tested in this study be considered a valid alternate test procedure for the determination of gross alpha particle concentrations in drinking water.

It is recommended that the Th-230 counting efficiency of standard samples

Table 6. Sample Spike Concentrations and Gross Alpha Test Results

	Sample Spike Concentrations		Gross Alpha pCi/L ^a		
		Am-241	Ra-226	Th-230	Uranium
Sample A					
Ra-226	47.2 pCi/L	49.5 ± 11.7	62.7 ± 11.7	68.0 ± 13.2	73.7 ± 12.0
Po-210	24.1 pCi/L				
^b Gross Alpha	74.0 pCi/L				
Sample B					
Ra-226	20.5 pCi/L	38.0 ± 7.1	48.4 ± 8.6	52.3 ± 8.2	58.9 ± 10.5
Po-210	10.4 pCi/L				
Uranium	20.5 pCi/L				
^b Gross Alpha	52.6 pCi/L				
Sample C					
Ra-226	3.0 pCi/L	4.29 ± .83	5.38 ± 1.01	5.87 ± 1.02	6.53 ± 1.18
Po-210	1.5 pCi/L				
^b Gross Alpha	4.8 pCi/L				
Sample D					
Uranium	10.0 pCi/L	6.95 ± 1.60	8.83 ± 2.12	9.45 ± 1.61	10.59 ± 1.46
^b Gross Alpha	10.0 pCi/L				

^aGross alpha activity values for each sample as determined with the four standard counting efficiencies.

^bGross alpha activity at three hours after separation.

E. L. Whittaker is with Lockheed Engineering and Management Services Company, Incorporated, Las Vegas, NV 89114.

A. N. Jarvis is the EPA Project Officer (see below).

The complete report, entitled "Test Procedure for Gross Alpha Particle Activity in Drinking Water: Interlaboratory Collaborative Study," (Order No. PB 86-236 957/AS; Cost: \$11.95, subject to change) will be available only from:

National Technical Information Service
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