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Project Summary

Test Procedure for Gamma Emitters in Drinking Water: Interlaboratory Collaborative Study

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This interlaboratory collaborative study was conducted for the test procedure, Gamma Emitting Radionuclides in Drinking Water (Method 901.1 in Prescribed Test Procedures for Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032, August 1980). The purpose of the study was to determine the estimated precision and accuracy of multilab test results when this test procedure is used for analyzing drinking water type samples containing variously concentrated mixtures of four gamma emitting radionuclides. Drinking water samples would not be expected to contain large numbers of radionuclides.

Four reference water samples containing three or all four of the gamma emitters, cobalt-60, ruthenium-106, cesium-134 and cesium-137, at concentrations ranging from 6 to 400 pCi/l, were prepared for the study. The concentrations were selected to correspond to 0.1 to 2 times the Maximum Contaminant Level (MCL) indicated in the National Interim Primary Drinking Water Regulations (NIPDWR). Test results from 32 participating laboratories were evaluated. The extent of reporting test results for the various sample radionuclides ranged from as few as six participants to all participants. For the most part, the average of the concentration values reported by the participating laboratories agreed quite well with the known values for all four samples. The only striking exceptions were the test results for ruthenium-106 at the three lower concentrations. Those results indicate that for ruthenium-106 the method is not sufficiently sensitive to meet the requirements of the NIPDWR.

A statistical analysis of the test results for cobalt-60 gave coefficients of variation for repeatability (within-laboratory precision) of 12.2, 3.5, and 4.9 percent respectively for concentration levels of 9.81, 98.8, and 201.9 picocuries per liter (pCi/l), for an average repeatability precision of 6.9 percent. The corresponding coefficients of variation for reproducibility (combined within and between laboratory) were 23, 6.6, and 5.7 percent for an average reproducibility precision of 11.8 percent. For ruthenium-106 at the 60.5 pCi/l concentration (2 MCL), the coefficient of variation for repeatability was 23 percent and the coefficient of variation for reproducibility was 32 percent. For cesium-134 at concentration levels of 7.9, 79.6, and 161 pCi/l, the coefficients of variation for repeatability were 30, 5.0, and 7.1 percent respectively, for an average repeatability precision of 14.0 percent. The corresponding coefficients of variation for reproducibility were 30, 18.5, and 8.7 for an average reproducibility precision of 19.1 percent. For cesium-137 at concentrations of 19.9, 99.5, 202.8, and 393.5 pCi/l, the coefficients of variation for repeatability were 10.2, 4.5, 4.0, and 2.0 percent respectively for an average repeatability precision of 5.2 percent. The corresponding coefficients of variation for reproducibility were 14.4, 7.2, 6.6, and

5.6 for an average reproducibility precision of 8.4 percent.

The average accuracy indexes for cobalt-60, cesium-134 and cesium-137 were 107, 94.9, and 101.6 percent respectively. For ruthenium-106 at the 60.5 pCi/l concentration, the accuracy index was 100.7 percent.

This interlaboratory collaborative study was conducted by the Mound Facility of the Monsanto Research Corporation under an Interagency Agreement, EPA-IAG-AD-89-F-1-395-0, for the Quality Assurance Division of EMSL-Las Vegas. The Mound Facility of Monsanto Research Corporation operates under DOE Contract Number DE-AC04-76-DP00053. The work covered the period from November 1, 1980 to November 1, 1981.

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

Many man-made radionuclides decay by gamma photon emission. Because gamma photons are discrete in energy, they can be resolved and quantitated by gamma spectrometry. The NIPDWR list the MCL for all significant man-made radionuclides. The required detection limits of the test procedure used to measure those radionuclides are 0.1 MCL, unless otherwise stated in Table B of Section 141.25 of the Regulations. The test procedure in this study uses a gamma spectrometric analysis of unprocessed (no chemical separations) portions of drinking water samples. The purpose of the study was to estimate the precision and accuracy of the test procedure from multilaboratory test results of prepared samples that contain radionuclide concentrations ranging from 0.1 MCL to 2 MCL. The radionuclides tested in this study were cobalt-60, ruthenium-106, cesium-134, and cesium-137.

The test procedure did not stipulate which of the two commonly used detectors to use. The two commonly used gamma detectors are the thallium activated sodium iodide, NaI(Tl), detector and the lithium drifted germanium, Ge(Li), detector. The sodium iodide detectors generally have higher counting efficiencies than the germanium detectors, but the germanium detectors have considerably better resolution than the sodium iodide detectors. Also, a specific data reduction method was not stipulated in the test procedure. Therefore, participants were at liberty to use the counting systems and data reduction methods available to them.

Procedures

Analytical Test Procedure

The analytical test procedure used in this collaborative study was Method 901.1, "Gamma Emitting Radionuclides in Drinking Water," which was published in EPA-600/4-80-032, August 1980, "Prescribed Procedures for Measurement of Radioactivity in Drinking Water." Method 901.1 is also contained in Appendix B of the Project Report.

Collaborative Test Procedure

Four reference samples, a copy of the EPA Method 901.1, "Gamma Emitting Radionuclides in Drinking Water," standard solutions of the gamma emitters to be measured, and a set of the collaborative study instructions were sent to 38 laboratories. The four reference samples contained different concentrations of the four gamma emitters used in the study. Test results from 32 laboratories were received and evaluated.

Data Processing Procedures

A statistical evaluation of the test results was conducted with the use of procedures described in E-691, E-177, and E-178 of the ASTM Standard Part 41, 1980, to determine the repeatability precision (within-laboratory variation), the reproducibility precision (combined within- and between-laboratory variation), and the accuracy of the test procedure. The standard deviations and equations for their calculations are listed below.

Standard deviation of replicate test results within Lab i, for sample j, (S_{ij})

$$S_{ij} = \left[\sum_{h=1}^{n_{ij}} (X_{ijh} - \overline{X_{ij}})^2/(n_{ij} - 1) \right]^{1/2} \quad \text{Eq. 1}$$

where: X_{ijh} = the result reported for the h replicate of the j sample material by Lab i

$\overline{X_{ij}}$ = the mean of the individual results of sample j for Lab i

n_{ij} = the number of replicates of sample j reported by Lab i.

Repeatability (within-laboratory) standard deviation for sample j, (S_{r_j})

$$S_{r_j} = \left(\frac{(n_{1j} - 1)S_{ij}^2 + (n_{2j} - 1)S_{2j}^2 + \cdots (n_{pj} - 1)S_{pj}^2}{(n_{ij} + n_{2j} + \cdots n_{pj}) - P} \right)^{1/2} \quad \text{Eq. 2}$$

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

Standard deviation of individual laboratory average from grand average for the j sample material, ($S_{\overline{x}_j}$)

$$S_{\overline{x}_j} \left[\sum_{i=1}^{P} (\overline{X_{ij}} - \overline{X_j})^2/(P - 1) \right]^{1/2} \quad \text{Eq. 3}$$

where: $\overline{X_{ij}}$ = the average of the test results for sample material j by Lab i

$\overline{X_j}$ = the grand average for sample material j.

Standard deviation of between-laboratories for the j sample material, (S_{L_j})

$$S_{L_j} = \left(S_{\overline{x}_j}^2 - S_{r_j}^2/n \right)^{1/2} \quad \text{Eq. 4}$$

Reproducibility (combined within- and between-laboratory) standard deviation for the j sample material, S_{R_j}

$$S_{R_j} = \left(S_{r_j}^2 + S_{L_j}^2 \right)^{1/2} \quad \text{Eq. 5}$$

The percent coefficient of variation for repeatability (within-laboratory precision) (also called repeatability index) for sample j, ($V_{r_j}\%$)

$$V_{r_j}\% = 100\, S_{r_j}/\overline{X_j} \quad \text{Eq. 6}$$

The percent coefficient of variation for between-laboratory precision for sample j, ($V_{L_j}\%$)

$$V_{L_j}\% = 100\, S_{L_j}/\overline{X_j} \quad \text{Eq. 7}$$

The percent coefficient of variation for reproducibility (combined within- and

between-laboratory precision) (also called reproducibility index) for sample j, (V_{R_j}%)

$$V_{R_j}\% = 100\, S_{R_j} / \overline{X_j} \qquad \text{Eq. 8}$$

Accuracy index, a percent relationship of the grand average to the known value for the j sample material, (A_j%)

$$A_j\% = 100 \frac{\overline{X_j}}{Y_j} \qquad \text{Eq. 9}$$

where: Y_j = the known value for the j sample material (pCi/l).

t-test to determine significant differences or systematic error for sample j, (t_j)

$$t_j = \frac{\overline{X_j} - Y_j}{S_{\bar{x}_j} / (P)^{1/2}},$$

(P-1) degrees of freedom Eq. 10

where: P = number of participants
Y_j = known value of the sample j concentration
t_c = critical values shown in Tables 1 through 4, values for t_j greater than t_c are significantly different and show a systematic error.

Results and Discussion

A summary of the statistical evaluation of the test results for the four radionuclides is given in Tables 1 through 4. Table 5 shows the radionuclide concentrations for the four samples.

Measurement parameters varied greatly for the study (see Table 11 of the full report). Three sodium iodide and 31 germanium detectors were used in the study. All germanium detectors were of the lithium drifted type. One laboratory used only 50 ml sample portions, whereas all other laboratories used 400 ml or greater sample portions (average volume used was 1,850 ml). Counting times varied from 50 minutes to over 4,000 minutes (average counting time being about 1,240 minutes). Spectral stripping was achieved by computer calculation for 22 sets of results, by hand calculation for eight sets of results, and by a combination of computer and hand calculation for four sets of results.

Although the test results obtained with sodium iodide detectors were less than 10 percent of the total, a brief study of these results indicates that they did not contribute to the limitations or biases of the test procedure to a significantly greater degree than the germanium detector test results.

Table 1 shows the t_j value to be greater than the critical value (t_c) for the lowest concentration of cobalt-60 (0.1 MCL). The grand average of the test results, then, was significantly different from the known value and therefore was biased on the high side. Test results for the other two concentrations (MCL and 2 MCL) were in good agreement with the known values (accuracy indexes of 102.2 and 99.9 percent). The table shows an average repeatability precision of 6.9 percent and an average reproducibility precision of 11.8 percent.

Table 2 shows a general failure of the participating laboratories to determine the lowest concentration (0.2 MCL). The table also shows significant high biases for the next two concentrations (0.5 MCL and MCL). The grand average of the test results for the highest concentration (2 MCL) was in good agreement with the known value (accuracy index of 100.7 percent). The table shows an average repeatability precision of 23 percent and an average reproducibility precision of 36 percent.

Table 3 shows significantly low biases for the two highest concentrations (MCL and 2 MCL). The lowest concentration grand average (0.1 MCL) was in good agreement with the known value (accuracy index of 98.7 percent). The average repeatability precision was 14.0 percent and the average reproducibility precision was 19.1 percent.

Table 4 shows a high bias for the lowest concentration (0.1 MCL) and good agreement between the test results of the three higher concentrations (0.5 MCL, MCL, and 2 MCL) and the known values (respective accuracy indexes of 100.0, 99.7, and

Table 1. *Cobalt-60 (Co-60) in Water, Precision and Accuracy Summary*

Parameter[a]	Co-60 (0.1 MCL)	Co-60 (MCL)	Co-60 (2 MCL)	Average
Y_j (pCi/l)	9.81	98.8	201.9	
$\overline{X_j}$ (pCi/l)	11.7	101.0	201.6	
$S_{\bar{x}_j}$ (pCi/l)	2.5	6.1	9.1	
S_{r_j} (pCi/l)	1.43	3.5	9.9	
S_{L_j} (pCi/l)	2.3	5.6	5.8	
S_{R_j} (pCi/l)	2.7	6.6	11.5	
V_{r_j} (%)	12.2	3.5	4.9	6.9
V_{L_j} (%)	20	5.6	2.9	9.5
V_{R_j} (%)	23	6.6	5.7	11.8
A_j (%)	119.3	102.2	99.9	107.
t_j	3.63	2.07	-0.19	
t_c (P)[b]	2.62 (23)	2.79 (33)	2.80 (34)	

[a] *Terms defined in text.*
[b] *Number of laboratories that reported data.*

Table 2. *Ruthenium-106 (Ru-106) in Water, Precision and Accuracy Summary*

Parameter[a]	Ru-106 (0.2 MCL)	Ru-106 (0.5 MCL)	Ru-106 (MCL)	Ru-106 (2 MCL)	Average
Y_j (pCi/l)	5.9	15.4	29.9	60.5	
$\overline{X_j}$ (pCi/l)	<47	28.0	38.3	60.9	
$S_{\bar{x}_j}$ (pCi/l)	-	12.8	9.6	16.6	
S_{r_j} (pCi/l)	-	7.5	7.2	13.7	
S_{L_j} (pCi/l)	-	11.6	8.1	13.5	
S_{R_j} (pCi/l)	-	13.8	10.8	19.2	
V_{r_j} (%)	-	27	19	23	23
V_{L_j} (%)	-	41	21	22	28
V_{R_j} (%)	-	49	28	32	36
A_j (%)	-	181.8	128.1	100.7	137
t_j	-	2.41	3.03	0.09	
t_c (P)[b]	-	1.82 (6)	2.29 (12)	2.41 (15)	

[a] *Terms defined in text.*
[b] *Number of laboratories that reported data.*

Table 3. *Cesium-134 (Cs-134) in Water, Precision and Accuracy Summary*

Parameter[a]	Cs-134 (0.1 MCL)	Cs-134 (MCL)	Cs-134 (2 MCL)	Average
Y_j (pCi/l)	7.9	79.6	161.0	
$\bar{X}_j$ (pCi/l)	7.8	73.3	151.2	
$S_{\bar{X}_j}$ (pCi/l)	1.0	9.6	10.6	
S_{r_j} (pCi/l)	2.3	3.7	10.8	
S_{L_j} (pCi/l)	0[c]	9.2	7.4	
S_{R_j} (pCi/l)	2.3	9.9	13.1	
V_{r_j} (%)	30	5.0	7.1	14.0
V_{L_j} (%)	0[c]	12.6	4.9	8.7
V_{R_j} (%)	30	18.5	8.7	19.1
A_j (%)	98.7	92.1	93.9	94.9
t_j	–0.40	–3.83	–5.39	
t_c (P)[b]	2.44 (16)	2.80 (34)	2.80 (34)	

[a] *Terms defined in text.*

[b] *Number of laboratories that reported data.*

[c] *Following the ASTM E691 procedures, the value is set = 0.*

Table 4. *Cesium-137 (Cs-137) in Water, Precision and Accuracy Summary*

Parameter[a]	Cs-137 (0.1 MCL)	Cs-137 (0.5 MCL)	Cs-137 (MCL)	Cs-137 (2 MCL)	Average
Y_j (pCi/l)	19.9	99.5	202.8	393.5	
$\bar{X}_j$ (pCi/l)	21.5	99.5	202.2	389.3	
$S_{\bar{X}_j}$ (pCi/l)	2.7	6.4	12.1	20.9	
S_{r_j} (pCi/l)	2.2	4.5	8.0	7.8	
S_{L_j} (pCi/l)	2.2	5.6	10.7	20.2	
S_{R_j} (pCi/l)	3.1	7.2	13.4	21.7	
V_{r_j} (%)	10.2	4.5	4.0	2.0	5.2
V_{L_j} (%)	10.2	5.6	5.3	5.2	6.6
V_{R_j} (%)	14.4	7.2	6.6	5.6	8.4
A_j (%)	108.0	100.0	99.7	98.9	101.6
t_j	3.25	0.0	–0.29	–1.17	
t_c (P)[b]	2.75 (30)	2.77 (32)	2.80 (34)	2.80 (34)	

[a] *Terms defined in text.*

[b] *Number of laboratories that reported data.*

Table 5. *Reference Sample Radionuclide Concentrations*

Sample	Radionuclide Concentrations, pCi/l			
	cobalt-60	ruthenium-106	cesium-134	cesium-137
1	201.9	60.5	161.0	202.8
2	98.8	15.4	7.9	393.5
3	9.81	5.9	-	19.9
4	-	29.9	79.6	99.5

98.9 percent). The average repeatability precision was 5.2 percent and the average reproducibility precision was 8.4 percent.

Conclusions

Although many variations existed in the measurement parameters in the study, there was generally good agreement between the test result grand averages and the known values for all concentrations (0.1 MCL to 2 MCL) for cobalt-60, cesium-134, cesium-137, and for the highest concentration (2 MCL) of ruthenium-106. This study demonstrates that the test procedure used can produce acceptable results over a rather wide range of variation in the measurement parameters. It is essential to the success of the procedure that the counting system be calibrated at the same sample-to-detector geometry that will be used for counting samples.

The high biases shown for the lowest concentration (0.1 MCL) for cobalt-60 (Table 1) and cesium-137 (Table 4) are not serious.

The low bias for the cesium-134 measurements is likely due to summing effects which can cause lower counting efficiencies. However, the bias is not serious, since it is only an average of 5.1 percent for the concentration range of 0.1 MCL to 2 MCL.

The study shows that the test procedure is not sufficiently sensitive for the measurement of ruthenium-106 with the sample volumes and counting times used in the study. The NIPDWR require a measurement sensitivity of 0.1 MCL (ruthenium-106 MCL is 30 pCi/l). The test procedure has adequate sensitivity for cobalt-60, cesium-134, and cesium-137.

Recommendations

The test procedure in this study should be used to analyze drinking water samples for gamma emitting radionuclides for compliance under the Safe Drinking Water Act. An applicability test should be included in the procedure to determine whether the test procedure for a given set of conditions of counting time, counting efficiency, and sample volume can be used to analyze drinking water samples for a selected radionuclide.

Section 1.4 of the "Scope and Application" should be changed to read:

> The method is applicable for analyzing water samples that contain radionuclides emitting gamma photons with energies ranging from about 60 to 200 keV. The required sensitivity of measurement for the more hazardous gamma emitters is listed in the National Interim Drinking Water Regulations (NIPDWR), Section 141.25. For a method to be in compliance, the detection limits for photon emitters must be 1/10 of the applicable limit (MCL).

Section 1.5 of the "Scope and Applications" should be amended to read:

> The criterion for the application of this test procedure to analyze drinking water samples for a selected radionuclide to comply with the NIPDWR is derived from Equation 4 of Appendix C, using the factor 2 for the 95%

confidence factor instead of 1.96 and is given by the following expression.

$$\frac{4 + (16 + 32tB)^{1/2}}{2t \times E \times b \times 2.22 \times V} \leq 0.1 \text{ MCL (pCi/l)}$$

where:
- t = counting time in minutes for the sample and the background
- B = background in cpm of photon energy peak in question
- E = photon counting efficiency, cpm/dpm
- b = abundance of photon question, γdpm/dpm
- 2.22 = conversion constant, dpm/pCi
- V = volume of sample analyzed, liters (l)

Analysts using this test procedure for the measurement of gamma emitters in drinking water should determine counting efficiencies for each radionuclide to be measured, with standard solutions at exactly the same geometry (sample-to-detector geometry) as that at which samples are to be counted. This will provide accurate counting efficiencies and cancel summing effects. If counting efficiency is read from a general efficiency curve, then care should be taken to make a separate correction for summing effects when that is known to occur with particular radionuclides analyzed.

The present study showed that ruthenium-106 at the 2 MCL concentration can be measured by the test procedure, and the average lower limit of detection was estimated to be 44 pCi/l (1.5 MCL). Therefore, an increased sensitivity by a factor of 15 to 20 is needed to meet the required sensitivity (lower detection limit of 3 pCi/l, required by NIPDWR). The low gamma abundance per decay and the relatively low MCL are largely the causes for the inadequate sensitivity of the test procedure for ruthenium-106. However, ruthenium-106 also decays with beta particle emission at a decay abundance of 100 percent. The high beta abundance combined with the considerably higher beta counting efficiency (than for gamma-ray) would provide adequate sensitivity for ruthenium-106. Therefore, a method that provides for the separation of ruthenium-106 from water samples followed by a beta count is recommended.

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The complete report, entitled "Test Procedure for Gamma Emitters in Drinking Water: Interlaboratory Collaborative Study," (Order No. PB 83-207 381; Cost: $10.00, subject to change) will be available only from:

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