United States
Environmental Protection
Agency

Environmental Monitoring
Systems Laboratory
Las Vegas, NV 89193-3478

Research and Development

EPA/600/S2-87/082 July 1988

EPA

Project Summary

Two Test Procedures for Radon in Drinking Water: Interlaboratory Collaborative Study

E.L. Whittaker, J.D. Akridge and J. Giovino

Two analytical methods for the determination of radon concentrations in water were tested in a multilaboratory study with twenty-eight participating laboratories. Eighteen laboratories analyzed prepared samples by the liquid scintillation (LS) method, and twelve laboratories analyzed the same samples by the Lucas Cell (LC) method. Several laboratories analyzed the samples by both methods.

Because of the short half life of radon-222 (3.82 days), special standard and samples were prepared in which each standard and each sample contained its own sealed radium-226 source that emanated radon-222 into the standard and sample water containment. There was a radon hold-back loss factor associated with the standards and samples that were provided to the participant laboratories. However, because the standards and samples were prepared identically, the radon hold-back loss was common to standards and samples alike and did not bias the test results.

A comparison of the grand averages for the three samples with the known values for those samples showed good accuracy for both methods. The accuracy index was not less than 94 percent for any of the three samples when analyzed by either method. The average accuracy for the LS method for the three samples was 95.2 ± 2.0 percent, and for the LC method it was 100.7 ± 4.6 percent at the 95 percent confidence level.

Test results for the LS method showed better precision than test results for the LC method. The average repeatability (within-laboratory precision) for the LS method was 3.6 ± 3.0 percent at 95 percent confidence, and for the LC method it was 6.4 ± 3.8 percent at 95 percent confidence. The average reproducibility (combined within- and between-laboratory precision) for the LS method was 10.2 ± 4.2 percent at 95 percent confidence, and for the LC method it was 17.6 ± 4.2 percent at 95 percent confidence.

The importance of the sampling technique to the analytical accuracy is discussed in the project report.

The authors and the Project Officer recommend that the two analytical methods be considered as validated and equivalent methods.

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

This is a summary report of a multilaboratory test of two analytical

methods for the purpose of validating those methods. In one method, liquid scintillation (LS) counting of 10 mL portions of water samples for the alpha and beta particle emissions from the radon and its short lived decay progeny is used to determine radon/water concentrations. In the second method, the radon gas is emanated from measured portions of water samples into pre-evacuated Lucas Cells (LC) in which only the alpha particle emissions from the radon and its short lived decay progeny are counted to determine radon/water concentrations. Twenty-eight laboratories participated in the multilaboratory study, eighteen laboratories in the LS method and twelve laboratories in the LC method.

Standards and samples that contained their own radium-free-radon/water generating sources were prepared and used in the study.

This study was conducted by the principal author as an employee of Lockheed Engineering and Management Services Company, Inc., for the EPA under Contract No. 68-03-3249.

Procedures

1. Analytical Test Procedures

The two analytical methods that were tested in this study are described in detail in Appendix B and Appendix D of the project report. The Appendix B method is the EPA liquid scintillation method. The Appendix D method is the Lucas Cell detector method detailed for water grab samples.

2. Collaborative Test Procedure

Forty laboratories responded to an invitation to participate in the two-method multilaboratory validation study. Standards, samples and instructions were sent to the participating laboratories. Twenty-eight laboratories submitted test result data, eighteen laboratories for the LS method and twelve laboratories for the LC method.

Precision, accuracy and bias values were calculated for the three samples that were analyzed by each of the two methods. The radon/water concentration levels in Samples A, B and C were 1600 pCi/L, 16,000 pCi/L and 66,000 pCi/L, respectively.

Results and Discussion

Table 1 lists the test result averages, individual laboratory standard deviations from replicate analyses, the number of replicates averaged, and the factor (cpm/pCi) for converting counts per minute to picocuries of radon-222, for the liquid scintillation (LS) method. Only two laboratory average outliers were found in those test results (both for Sample B). Laboratory 21 analyzed the samples two times by the LS method, once using the mineral oil liquid scintillator cocktail and once using a detergent-type liquid scintillator cocktail (data included in Table 1).

Table 2 is a statistical summary of the accuracy, bias and precision of the Table 1 test results, as calculated by the equations given in the Data Processing Procedures. The 95.2 percent accuracy index corresponds to a negative bias of 4.8 ± 2.0 percent (95 percent confidence). The 4.8 ± 2.0 percent negative

Table 1. *Liquid Scintillation Method*

Laboratory	Factor cpm/pCi ± S	Radon-222 pCi/1000 g ± S			Replicates (n)
		Sample A	Sample B	Sample C	
1	8.88 ± 0.00	1,571 ± 31	16,308 ± 46	67,076 ± 30	2
2	8.25 ± 0.23	1,570 ± 31	16,065 ± 235	65,797 ± 1160	6
3	7.26 ± 0.19	1,599 ± 75	15,404 ± 293	58,934 ± 750	4
4	8.45 ± 9.05	1,568 ± 8	16,270 ± 33	51,916 ± 130	2
6	8.13 ± 0.34	1,283 ± 82	16,966 ± 419	67,666 ± 1014	3
7	7.50 ± 0.23	1,656 ± 62	16,734 ± 237	68,432 ± 1416	5
10	8.59 ± 0.06	1,501 ± 11	14,943 ± 1112	61,020 ± 660	2
11	7.51 ± 0.45	1,358 ± 78	(10,387 ± 646)[b]	68,366 ± 309	3
13	6.75 ± 0.08	1,671 ± 33	16,916 ± 174	55,733 ± 1878	3
15[a]	7.70 ± 0.17	1,604 ± 152	16,548 ± 487	48,940 ± 2543	6
17	8.30 ± 0.49	1,280 ± 20	17,060 ± 110	52,050 ± 1140	2
18	8.40 ± 0.08	1,629 ± 18	15,158 ± 166	65,862 ± 295	3
18	8.12 ± 0.37	1,568 ± 97	14,722 ± 581	63,341 ± 3220	6
20	8.08 ± 0.10	1,828 ± 33	12,968 ± 362	76,640 ± 132	3
21	8.19 ± 0.05	1,614 ± 22	16,660 ± 157	69,427 ± 250	3
21[a]	9.12 ± 0.09	1,567 ± 28	15,300 ± 229	60,920 ± 627	3
23	6.82 ± 0.003	1,556 ± 30	15,281 ± 256	65,375 ± 1039	2
26	9.00 ± 0.09	1,553 ± 31	15,920 ± 360	66,560 ± 625	3
27	3.64	1,290	14,200	60,700	1
27	3.34 ± 0.47	1,117 ± 309	(9,804 ± 5,665)[b]	66,141 ± 1380	2
$\bar{X} \pm S_{\bar{X}}$		1,520 ± 169	15,700 ± 1100	62,900 ± 6600	
Known Value (Y)		1,620 ± 49	16,300 ± 501	66,200 ± 2030	

[a]Detergent liquid scintillator was used instead of mineral oil liquid scintillator.
[b]Outlier not used in the grand average.

Table 2. *Liquid Scintillation Method (Accuracy, Bias, and Precision Summary)*

Parameter[a]	Sample A	Sample B	Sample C	Average % Values ± S
Y_j (pCi/L)	1620 ± 49	16,300 ± 501	66,200 ± 2030	
$\bar{X}_j$ (pCi/L)	1520	15,700	62,900	
A_j (%)	94.0	96.5	95.0	95.2 ± 1.0
Bias (%)[b]	-6.0	-3.5	-5.0	-4.8 ± 1.0
$S_{\bar{X}j}$ (pCi/L)	169	1,097	6,653	
S_{rj} (pCi/L)	87	385	1,628	
S_{Lj} (pCi/L)	168	1,090	6,640	
S_{Rj} (pCi/L)	189	1,160	6,840	
V_{rj} (%)	5.7	2.5	2.6	3.6 ± 1.5
V_{Lj} (%)	11.1	6.9	10.6	9.5 ± 1.9
V_{Rj} (%)	12.4	7.4	10.9	10.2 ± 2.1
T_j-1[c]	2.56	2.22	2.22	
T_j-3	1.44	0.35	2.01	

[a] *Parameters are described in the test.*
[b] *The sign before the number indicates the direction of bias.*
[c] *The critical value (t_c) for significant difference at the 5 percent significance level for 18 labs (Sample B) is 2.105 and for 20 labs (Samples A and C) is 2.090.*
T_j-1 values are calculated from Table 1 test results.
T_j-3 values are calculated from Table 3 test results.

bias is a significant (real) bias as indicated by the T values for the samples being greater than the critical values for T. However, that bias is not a serious bias and is likely due to a loss of radon activity in the transfer of successive aliquots from the same sample bottle water for replicate analyses.

Table 2 shows that the estimated average repeatability (within-laboratory precision) of the liquid scintillation method over the radon/water concentration of 1,600 to 66,000 pCi/L is 3.6 ± 3.0 percent at 95 percent confidence.

Table 2 shows that the estimated average reproducibility (combined within- and between-laboratory precision) of the liquid scintillation method over the radon/water concentration range of 1,600 to 66,000 pCi/L is 10.2 ± 4.2 percent at 95 percent confidence.

Tables 3, 4 and 4a are not listed in this summary report but are included in the Project Report.

Table 5 lists the laboratory test result averages, their standard deviations from replicate analyses, the number of replicates averaged, and the factor (cpm/pCi) for converting counts per minute to picocuries of radon-222, for the Lucas Cell (LC) method. No outliers were found in the Table 5 test result averages.

Table 6 is a statistical summary of the accuracy, bias, and precision of the Table 5 test results, as calculated by the equations given in the Data Processing Procedures. A comparison of the known values for Samples A, B, and C with the respective grand averages of the Table 5 test results shows an average accuracy index of 100.7 ± 4.6 percent at 95 percent confidence. The bias values of +1.9 percent, +2.7 percent and -2.6 percent for Samples A, B and C, respectively, are within the 95 percent confidence limits of the average accuracy index. The t-test to show significant difference applied to known values and grand averages for the samples shows that there are no significant differences (T values for the samples are less than the critical value).

Table 6 shows that the estimated average repeatability (within-laboratory precision) of the Lucas Cell method over the radon/water concentration range of 1,600 to 66,000 pCi/L is 6.4 ± 3.8 percent at 95 percent confidence.

Table 6 shows that the estimated average reproducibility (combined within- and between-laboratory precision) over the radon/water concentration range of 1,600 to 66,000 pCi/L is 17.6 ± 4.2 at 95 percent confidence.

Conclusions

A satisfactory multilaboratory test of the two analytical methods was demonstrated by the low number of outlier test results (2 out of 60 laboratory averages for the liquid scintillation method and none for the Lucas Cell method).

Equivalency of the two methods was demonstrated by the high accuracy of the test results obtained by both methods (accuracy index was not less than 94 percent for any of the three samples when analyzed by either method), and the lack of a serious bias by either method.

A comparison of Table 2 and Table 6 shows the liquid scintillation (LS) method had better precision than the Lucas Cell (LC) method. The average repeatability (within-laboratory precision) for the LS method was 3.6 ± 3.0 percent at 95 percent confidence, and for the LC method it was 6.4 ± 3.8 percent at 95 percent confidence. The average reproducibility (combined within- and between-laboratory precision) for the LS method was 10.2 ± 4.2 percent at 95 percent confidence, and for the LC method it was 17.6 ± 4.2 percent at 95 percent confidence.

There was a combined hold-back/transfer radon loss (HB/TL) associated with the type of standards and samples that were provided to the participants. However, since standards and samples were prepared identically, the hold-back/transfer radon loss was common to standards and samples alike and did not bias the test results.

The variations in the cpm/pCi factors in Table 1 are not reflected by corresponding differences in the sample radon-222 concentration test results. This shows that the differences in the sample aliquot transfer technique used by the laboratories did not significantly affect the test results because standards

Table 5. *Lucas Cell Method*

Laboratory	Factor cpm/pCi ± S	Radon-222 pCi/1000 g ± S			Replicates (n)
		Sample A	Sample B	Sample C	
5	3.79 ± .08	1,838 ± 96	17,450 ± 815	72,280 ± 12,418	5
8	4.24 ± .04	1,608 ± 26	14,514 ± 72	45,730 ± 392	2
12		1,552	17,550	60,780	1
14	2.50 ± .04	1,702 ± 93	16,493 ± 1452	73,921 ± 2604	3
16	4.78 ± .13	1,510 ± 84	16,746 ± 935	65,854 ± 2510	6
17	4.89 ± .04	1,495 ± 265	16,950 ± 300	49,200 ± 520	2
19	4.67 ± .21	1,636 ± 60	16,680 ± 827	67,756 ± 2459	6
21	4.66 ± .15	1,586 ± 68	16,466 ± 277	66,197 ± 1445	3
22	±		13,537 ± 379		5
24	4.57 ± .24	2,059 ± 81	19,600 ± 580	79,670 ± 5752	5
25	1.53 ± .13	1,550 ± 85	19,257 ± 792	77,900 ± 2339	2
28	0.1053	2,100 ± 200	21,000 ± 2000	70,000 ± 7000	-
$\bar{X}$		1650	16,770	64,520	
$S_{\bar{X}}$		261	2480	12,020	
Known Value (Y)		1620 ± 49	16,300 ± 501	66,200 ± 2030	

and samples were transferred by the same technique within each laboratory.

A comparison of the cost per analysis between the two methods favors the LS method significantly when LS counting capability is available to the analyst.

Recommendations

The authors recommend that the two analytical methods tested in this multi-laboratory test be considered validated and equivalent for the determination of radon/water concentrations in potable water systems.

It is recommended that sampling be considered as a critical part of the analytical procedure for analytical methods that are specified for the determination of radon/water concentrations. A positive pressure sampling or transfer technique should be used, avoiding negative pressure techniques, aeration, and turbulence whenever it is possible.

For the LS method it is recommended that samples be transferred to LS vials directly at the sampling site as described in the EPA method (Appendix B), but by a positive pressure technique similar to the one described in the NIRS Sampling Instruction-Radon (Appendix C of the Project Report), filling the LS vial only to the shoulder of the bottle. Pre-weighing the LS vials containing 10 mL of mineral oil cocktail and weighing again after water sample has been added provides for determining sample size. Poly Seal caps on the LS vials seem to retain the mineral oil cocktail better than other caps.

The emanation bubblers for the LC method are both fragile and expensive. Therefore, it is recommended that samples be collected in the field in 4-ounce or larger glass bottles fitted with Poly Seal caps and the sample bottles brought or sent to the laboratory for an early analysis by the LC method. Samples should be collected by a positive pressure sampling technique as described in the Appendix D procedure of the Project Report. An alternative positive pressure sampling technique has been described by the Sanitation and Radiation Laboratory of the California Health Department (Appendix E of the Project Report).

Table 6. *Lucas Cell Method (Accuracy, Bias, and Precision Summary)*

Parameter[a]	Sample A	Sample B	Sample C	Average % Values ± S
Y_j (pCi/L)	1620 ± 49	16,300 ± 501	66,200 ± 2,030	
$\bar{X}_j$ (pCi/L)	1650	15,770	64,500	
A_j (%)	101.9	102.7	97.4	100.7 ± 2.3
Bias (%)[b]	+1.9	+2.7	-2.6	
$S_{\bar{X}}$ (pCi/L)	261	2,480	12,020	
S_{rj} (pCi/L)	94	776	5,792	
S_{Lj} (pCi/L)	259	2,470	11,900	
S_{Rj} (pCi/L)	276	2,590	13,200	
V_{rj} (%)	5.7	4.6	9.0	6.4 ± 1.9
V_{Lj} (%)	15.7	14.8	18.4	16.3 ± 1.5
V_{Rj} (%)	16.8	15.5	20.5	17.6 ± 2.1
T_j[c]	0.411	0.624	0.498	

[a]Parameters are described in the test.
[b]The sign before the number indicates the direction of bias.
[c]The critical value (T_c) for significant difference at the 5 percent significance level for 12 labs (Sample B) is 2.18 and for 11 labs (Samples A and C) is 2.20.

E.L. Whittaker is with Lockheed Engineering and Management Services Company, Inc. Las Vegas NV 89114; ***J.D. Akridge*** *and* ***J. Giovino****, EPA authors, are with the Environmental Monitoring Systems Laboratory, Las Vegas, NV 89193-3478.*
Chung-King Liu *is the EPA Project Officer (see below).*
The complete report, entitled "Two Test Procedures for Radon in Drinking Water: Interlaboratory Collaborative Study," (Order No. PB 88-197 306/AS; Cost: $14.95, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Project Officer can be contacted at:
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Las Vegas, NV 89193-3478