United States
Environmental Protection
Agency

Environmental Monitoring Systems
Laboratory
Las Vegas NV 89114

Research and Development

EPA-600/S4-83-038 Nov. 1983

EPA

Project Summary

Test Procedure for Uranium in Drinking Water: Interlaboratory Collaborative Study

C. A. Phillips, C. T. Bishop, and E. L. Whittaker

An interlaboratory collaborative study was conducted for a test procedure to measure the concentration of uranium in drinking water. The purpose of the study was to estimate the precision and accuracy for the test procedure that can be expected when the procedure is used by any competent laboratory. The test procedure was published in the EPA Manual, "Prescribed Procedures for Measurement of Radioactivity in Drinking Water" [EPA-600/4-80-032, August 1980].

Drinking water samples containing uranium alpha concentrations of 8.1, 17.4, and 75.3 pCi/l were analyzed (in triplicate by most participants) by 19 collaborating laboratories using the test procedure. Statistical analysis of the test results, using procedures recommended by the ASTM [E-691, E-177, E-178, ASTM Standard Part 41, 1980] showed coefficients of variation for repeatability (within-laboratory precision) of 14.6, 8.1, and 8.3 percent respectively for the three uranium concentrations for an average repeatability precision of 10.3 percent. The analysis also showed coefficients of variation for reproducibility (combined within- and between-laboratory precision) of 15.3, 14.9, and 9.1 percent for the respective sample uranium concentrations for an average reproducibility precision of 13.1 percent.

A comparison of the grand average test results with the known values for the three samples demonstrated accuracy indexes of 98.0, 102.6, and 101.9 percent respectively, for an accuracy index of 100.8 percent in the range of uranium alpha concentrations between 8 pCi/l and 75 pCi/l.

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) state, in Section 141.15, that the maximum containment level for gross alpha particle activity "... (including radium-226 but excluding radon and uranium) ..." is 15 pCi/l. This statement implies that whenever a gross alpha measurement of a drinking water sample exceeds 15 picocuries per liter (pCi/l), an analysis for uranium should be done to determine the uranium alpha contribution to the gross alpha concentration. The method listed in the NIPDWR for the measurement of uranium in drinking water is a fluorometric method which determines uranium in mass units. It is now known (subsequent to the promulgation of the NIPDWR) that the ratio of uranium alpha activity to uranium mass concentration in ground waters can vary significantly from that which is common to natural

uranium ore deposits. Therefore, a test procedure that will better relate total uranium alpha activity to gross alpha activity in drinking water samples is needed to either complement or replace the approved method.

The method of analysis used in this study is a simplified version of a method that measures the uranium isotopic concentrations in the sample by alpha spectrometry. This method measures total uranium alpha activity, the measurement needed for a gross alpha assessment of a drinking water sample.

Conclusions

The estimated repeatability precision (within-laboratory precision), reproducibility precision (the combined within- and between-laboratory precision), and the accuracy have been determined for the test procedure by a multilaboratory test in this study and they are hereby set up as criteria by which to evaluate an alternate test procedure for equivalency.

The study showed accuracy indexes of 98.0, 102.6, and 101.9 percent for an average of 100.8 percent for the test procedure over the uranium alpha concentration range of 8 to 75 pCi/l, indicating that accurate test results can be obtained with the test procedure used in this study.

The estimated coefficients of variation for repeatability (repeatability index) for the three uranium concentration levels were calculated to be 14.6, 8.1, and 8.3 percent (respectively, for 8.1, 17.4 and 75.3 pCi/l) for an average repeatability index of 10.3 percent.

The estimated coefficients of variation for reproducibility (reproducibility index) for the three uranium concentration levels were calculated to be 15.3, 14.9, and 9.1 (for 8.1, 17.4, and 75.3 pCi/l, respectively) for an average reproducibility index of 13.1 percent.

Although there was no stable isotope carrier to determine the uranium chemical recovery for each sample, separate samples spiked with known uranium radioactivity and analyzed by the test procedure, along with the test samples, showed good recoveries. The recoveries for the 18 laboratories averaged 91 ± 15 percent.

The test procedure did not contain significant systematic errors for the method for uranium alpha concentrations up to 75 pCi/l in drinking water samples.

Recommendations

The test procedure in this study (described in detail in Appendix B) of the Project Report should be used to monitor drinking water samples for uranium alpha contribution to the gross alpha activity when the gross alpha activity exceeds 15 pCi/l as specified in the NIPDWR.

A change should be made in the preparation of the separated uranium fraction for counting the alpha activity. It is also recommended that the change be verified experimentally to demonstrate the benefit to Method 908.0 [EPA-600/4-80-032] before it is incorporated into the test procedure. To make that change in the preparation of the separated uranium fraction for alpha counting, the following changes and additions to the Test Procedure (Method 908.0) are proposed. Replace existing steps 8.2.5 through 8.2.9 with the following 8.2.5 through 8.2.10 steps.

8.2.5 Elute the uranium with six column volumes of 0.1N HCl, collecting the eluate in a 150-ml beaker.

8.2.6 Evaporate the eluate to near dryness, then add 1 ml 12N HCl (conc.), 10 ml of water, 0.2 ml 20% $TiCl_3$, and 1 ml of lanthanum carrier solution, stir.

8.2.7 Add 0.5 ml HF (conc.), stir well and allow to stand for 30 minutes.

8.2.8 Filter through 47 mm, 0.2 µm pore membrane filter, collecting the coprecipitated U/LaF_3.

8.2.9 Wash the U/LaF_3 with 10 ml of water followed by 10 ml of ethanol.

8.2.10 Air dry the filter for at least 1 hour before counting for alpha activity.

Add the following item to the "Apparatus" section of the procedure.

5.7 0.2 µm pore, 47 mm diameter membrane filter that withstands the acid treatment in the Test Procedure and will lay flat after drying (such as Gelman AN-200).

And add the following items to the "Reagents" section of the procedure.

6.15 Lanthanum nitrate, (1.0 mg La^{+3}/ml). Dissolve 3.11 g $La(NO_3)_3 \cdot 6H_2O$ in one liter of 0.1N HNO_3.

6.16 Hydrofluoric acid, 25N : HF (conc.) sp. gr. 1.18, 49%.

6.17 Titanium trichloride $TiCl_3$: 20%.

The term "column volume" in the test procedure should be clarified. This can be done by simply giving the milliliters of the resin bed volume specified in the procedure. A resin bed 1.3 cm in diameter by 8.0 cm high will have a volume of 10.6 ml. Then in Section 8.2.3 of the procedure, after the expression "-- with 6 column volumes", put in parentheses (6 x 10.6 ml = 63.6 ml, or 65. ml, rounded to the nearest 5 ml).

Since no carrier or tracer is used in the procedure to determine chemical recovery, it is recommended that with each set of samples to be analyzed by this test procedure, a spiked sample (to determine recovery) and a sample duplicate (to verify precision) be analyzed. This recommendation should be incorporated into the procedure.

Procedures

1. Analytical Test Procedure

The test procedure used in this study is described in detail in Appendix B of the Project Report. The water sample is acidified by adding HCl and the sample boiled to eliminate carbonate and bicarbonate ions. Uranium is coprecipitated with ferric hydroxide and separated from the sample. The uranium is then separated from other radionuclides which were carried down with the ferric hydroxide by dissolving the hydroxide precipitate in 8 N HCl, putting the solution through an anion exchange column, washing the column with 8 N HCl, and finally eluting the uranium with 0.1 N HCl. The eluate (containing the uranium from the sample) is evaporated and the uranium chemical form is converted to nitrate. The nitrate residue is transferred to a stainless steel planchet, dried, flamed, and counted for alpha particle activity.

2. Collaborative Test Procedure

A total of 25 laboratories agreed to participate in the collaborative study and 19 laboratories submitted test results. Test results from 18 laboratories (results from 1 laboratory were rejected) were used for statistical analyses for estimates of precision and accuracy.

Approximately 5 ml of an NBS standard uranium solution was sent to each participating laboratory to determine uranium recovery and uranium alpha counter efficiency.

Three stock solutions, each containing different concentration of uranium were prepared from an NBS standard. A 20-ml portion of each of these solutions was provided to each participating labora

tory. The laboratories were requested to prepare working solutions by diluting 5 ml aliquots of each solution to 1000 ml (1 liter) with drinking water. The resulting concentrations of these working solutions were 8.1 ± .4 pCi/l, 17.4 ± .9 pCi/l, and 75.3 ± 3.9 pCi/l. Each laboratory was requested to perform triplicate analyses of the three whole volume working solution samples; to analyze a 1-l sample of their drinking water to determine a blank value; and to submit completed data sheets.

3. Data Processing Procedures

A statistical evaluation of the test results was done by the 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})

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

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

$\bar{X}_{ij}$ = 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_{rj}).

Since the number of replicates is the same (3) for all participants for all three samples, the equation can be given as follows

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

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

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

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

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

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

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

$$S_{Lj} = \left(S_{\bar{x}j}^2 - S_{rj}^2/n \right)^{1/2} \quad \text{Eq. 4}$$

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

$$S_{Rj} = \left(S_{rj}^2 + S_{Lj}^2 \right)^{1/2} \quad \text{Eq. 5}$$

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

$$V_{rj}\% = 100\, S_{rj}/\bar{X}_j \quad \text{Eq. 6}$$

The coefficient of variation for between-laboratory precision for sample j, (V_{Lj}%)

$$V_{Lj}\% = 100\, S_{Lj}/\bar{X}_j \quad \text{Eq. 7}$$

The coefficient of variation for reproducibility (combined within- and between-laboratory precision) (also called reproducibility index) for sample j, (V_{Rj}%)

$$V_{Rj}\% = 100\, S_{Rj}/\bar{X}_j \quad \text{Eq. 8}$$

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

$$A_j\% = 100\frac{\bar{X}_j}{Y_j} \quad \text{Eq. 9}$$

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)

$$t_j = \frac{\bar{X}_j - Y_j}{S_{\bar{x}j}/(P)^{1/2}} \quad \text{Eq. 10}$$

(P-1) degrees of freedom

where: P = number of participants

Y_j = known value of the sample j uranium concentration

t_c = 2.10, critical value from 18 participants, values for t greater than 2.10 are significantly different and show a systematic error.

Results and Discussion

A summary of the statistical evaluation of the test results for the three samples is given in Table 1. It lists the following statistical parameters and values for the three sample uranium concentrations.

1. The known value, (Y_j), for each sample uranium concentration in pCi/l
2. The grand average value, (X_j), for each sample uranium concentration (from 18 participants) in pCi/l
3. The accuracy index, (A_j%), (from 18 participants) for each sample uranium concentration, and the average accuracy index over the concentration range of 8 to 75 pCi/l.
4. The standard deviation of the grand average values for the three sample uranium concentrations, ($S_{\bar{x}j}$)
5. The repeatability (within-laboratory) standard deviation, (S_{rj}), for each sample uranium concentration
6. The between-laboratories standard deviation, (S_{Lj}), for each sample uranium concentration
7. The reproducibility (combined within- and between-laboratory) standard deviation, (S_{Rj}), for each sample uranium concentration
8. The coefficients of variation for repeatability, (V_{rj}%); for between-laboratory precision, (V_{Lj}%); and for reproducibility, (V_{Rj}%), for each sample uranium concentration and the averages of each for the concentration range of 8 to 75 pCi/l

The test procedure showed no bias for the uranium in drinking water concentration range of 8 to 75 pCi/l.

The report is submitted as partial fulfillment of an Interagency Agreement, EPA-IAG-79-D-X0736, between the U.S. Environmental Protection Agency and the U.S. Department of Energy. Work was done by the Mound Facility of the Monsanto Research Corporation under Contract Number DE-AC04-76-DP00053. The work covered the period of April 1, 1980 to September 1, 1980.

Table 1. *Summary of Collaborative Study Results - Precision and Accuracy*

	Uranium in Drinking Water Sample			
Parameter [a]	1	2	3	Average
Y_j (pCi/l)	8.1 ± .4	17.4 ± .9	75.3 ± 3.9	
$\bar{X}_j$ (pCi/l)	7.9	17.9	76.8	
A_j%	98.0	102.6	101.9	100.8
$S_{\bar{x}_j}$ (pCi/l)	0.76	2.39	4.65	
S_{r_j} (pCi/l)	1.15	1.44	6.39	
S_{L_j} (pCi/l)	0.37	2.24	2.83	
S_{R_j} (pCi/l)	1.21	2.66	6.98	
V_{r_j}%	14.6	8.1	8.3	10.3
V_{L_j}%	4.7	12.5	3.7	7.0
V_{R_j}%	15.3	14.9	9.1	13.1

[a] *Terms are defined in the text.*

C. A. Phillips and C. T. Bishop are with Monsanto Research Corporation, Miamisburg, OH 45342; the EPA author ***Earl L. Whittaker*** *(also the EPA Project Officer, see below) is with the Environmental Monitoring Systems Laboratory, Las Vegas, NV 89114.*

The complete report, entitled "Test Procedure for Uranium in Drinking Water: Interlaboratory Collaborative Study," (Order No. PB 83-247 239; Cost: $8.50, 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
P.O. Box 15027
Las Vegas, NV 89114

☆U S GOVERNMENT PRINTING OFFICE 1983—659-017/7230

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Official Business
Penalty for Private Use $300