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Project Summary

Test Procedure for Iodine-131 in Drinking Water: Interlaboratory Collaborative Study

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An interlaboratory collaborative study was conducted on a test procedure for measuring the iodine-131 concentration in drinking water. The purpose of the study was to determine the estimated precision and accuracy of test results from participating laboratories using this test procedure and analyzing drinking water samples.

***Drinking water samples containing* iodine-131 at concentrations on the designated collection date of 7.8, 25.9, and 78.3 picocuries per liter were analyzed in triplicate by 11 collaborators (10 laboratories) using the test procedure.**

A statistical analysis of the test results showed coefficients of variation for repeatability (within-laboratory precision) of 8.7, 10.5, and 7.7 percent respectively for the three samples for an average repeatability precision of 9.0 percent. The analysis also gave coefficients of variation for reproducibility (combined within-and between-laboratory precision) of 17.4, 15.5, and 15.7 percent for the respective samples for an average reproducibility precision of 16.2 percent.

The average carrier iodine recoveries were 76.4, 79.3, and 79.8 percent respectively for the three samples, giving an overall average of 78.5 percent. A comparison of the grand average test results for the three samples with the known values for those samples shows accuracy indexes of 97.4, 97.3, and 84.8 percent respectively, for an average accuracy for the test method of 93.2 percent.

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 report is submitted as partial fulfillment of an Interagency Agreement, EPA-IAG-79-D-X0736, between the Environmental Protection Agency and the Department of Energy (DOE). Work was done at the Mound Facility of the Monsanto Research Corporation under DOE Contract Number DE-AC04-76-DP00053. The work covered the period of September 1, 1979 to June 15, 1980.

The National Interim Primary Drinking Water Regulations (NIPDWR) require the use of approved test procedures for analyzing public drinking water supplies for contaminants. The NIPDWR contains provisions for the use of alternate test procedures with precision and accuracy equivalent to or better than the approved test procedure. This report describes a multilaboratory test of a method selected for the analysis of drinking water samples for iodine-131 concentrations. The purpose of the study was to determine what precision and accuracy could be expected in the test results from laboratories using the method for analyzing drinking water supplies for iodine-131 contamination.

The NIPDWR requires a sensitivity (lower detection limit) of 1 picocurie per liter (pCi/l) for measuring iodine-131 concentrations in drinking water supplies. Iodine-131 decays by emitting a beta particle and a gamma photon. Gamma spectroscopy has good specificity for gamma emitters, but its sensitivity will meet the required sensitivity (1 pCi/l) only if the iodine-131

is first separated from multiliter size samples. The method tested, and described here, requires separating the iodine-131, using carrier iodine, from one or more liters of sample and then counting the beta activity produced by the separated iodine, in a low beta background counting system.

Procedures

1. Analytical Test Procedure

The analytical procedure used in this study consists of detailed steps in which the iodine-131 with added iodate carrier is separated from the sample as palladium iodide. The iodine-131 (plus carrier) is reduced to the iodide state with sodium sulfite, precipitated as silver iodide, and purified with zinc powder and by two precipitations as palladium iodide. The final palladium iodide is collected on a filter and then counted for beta activity. The recovery of the added carrier is determined for each sample by weighing the palladium iodide precipitate. The counting efficiency is determined using the same amount of iodate carrier as is used in the procedure and standard iodine-131 activity, precipitated as palladium iodide, and beta counted.

2. Collaborative Test Procedure

A copy of the test procedure was sent to potential participant laboratories; those laboratories stating their willingness to participate were used in this study.

Three reference sample solutions were prepared using tap water, sodium thiosulfate and sodium carbonate preservatives, known quantities of iodine-131 activity, and lithium nitrate (for batch homogeneity testing). The three reference solutions contained iodine-131 concentrations of 7.8, 25.9, and 78.3 pCi/l respectively (activity calculated for the collection date to which analytical results were to be normalized). The first, middle, and last 3.5-liter fractions of each sample batch were used for homogeneity tests.

Each participant was sent an instruction sheet, a data report sheet, and iodine-131 standard solution for calibrations, and a 3.5-liter portion of each of the three sample solutions.

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}

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

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}

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

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

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

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

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

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}

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

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

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

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

$$V_{r_j}\% = 100\, S_{r_j}/\overline{X}_j \quad (6)$$

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

$$V_{L_j}\% = 100\, S_{L_j}/\overline{X}_j \quad (7)$$

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

$$V_{R_j}\% = 100\, S_{R_j}/\overline{X}_j \quad (8)$$

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

$$A_j\% = 100 \frac{\overline{X}_j}{Y_j} \quad (9)$$

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

$$t_j = \frac{\overline{X}_j - Y_j}{S_{\overline{x}_j}/(P)^{1/2}}, \text{ (P-1) degrees of freedom} \quad (10)$$

where: P = number of participants

Y_j = known value of the sample j iodine-131 concentration

t_c = 2.23, critical value for 11 participants, values for t greater than 2.23 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, which lists the following statistical parameters and values for the three iodine-131 concentrations:

1. The known value, Y_j, for each of the iodine-131 concentrations in pCi/l.
2. The grand average value, $\overline{X}_j$, for each iodine-131 concentration (from 11 participants) in pCi/l.

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

Parameter [a]	Iodine-131 (pCi/l) 1	2	3	Average
Y_j (pCi/l)	7.8	25.9	78.3	
$\bar{X}_j$ (pCi/l)	7.6	25.2	66.4	
A_j%	97.4	97.3	84.8	93.2
$S_{\bar{x}_j}$ (pCi/l)	1.19	3.25	9.54	
S_{r_j} (pCi/l)	0.66	2.64	5.14	
S_{L_j} (pCi/l)	1.14	2.87	9.07	
S_{R_j} (pCi/l)	1.32	3.90	10.43	
V_{r_j}%	8.7	10.5	7.7	9.0
V_{L_j}%	15.0	11.4	13.7	13.4
V_{R_j}%	17.4	15.5	15.7	16.2

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

3. The accuracy index, A_j% (from 11 participants) for each iodine-131 concentration, and the average accuracy index over the concentration range of 7.8 to 78.3 pCi/l.
4. The standard deviation of the grand average values for the three iodine-131 concentrations, $S_{\bar{x}_j}$.
5. The repeatability (within-laboratory) standard deviation, S_{r_j}, for each iodine-131 concentration.
6. The between-laboratories standard deviation, S_{L_j}, for each iodine-131 concentration.
7. The reproducibility (combined within- and between-laboratory) standard deviation, S_{R_j}, for each iodine-131 concentration.
8. The coefficients of variation for repeatability, V_{r_j}%; for between-laboratory precision, V_{L_j}%; and for reproducibility, V_{R_j}%, for each iodine-131 concentration and the averages of each for the concentration range of 7.8 to 78.3 pCi/l.

The 66.4 pCi/l grand average compared to the 78.3 pCi/l known value showed a significant difference or systematic error. A t-test gave a t_j value of 4.13 compared to the critical value (t_c) of 2.23 for 11 participants. Therefore, 66.4 pCi/l is significantly different than 78.3 pCi/l and shows a low bias for the method for that level of iodine-131 concentration.

Conclusions

The repeatability precision (within-laboratory precision), reproducibility precision (the combined within- and between-laboratory precision), and accuracy have been determined by a multilaboratory test of the method. Criteria by which to evaluate an alternate test procedure for equivalency have been established.

Accuracy indexes of 97.4, 97.3, and 84.8 percent for the 7.8, 25.9, and 78.3 pCi/l iodine-131 concentration samples respectively, and an average accuracy index of 93.2 percent were obtained with this test procedure. The study did not reveal an explanation for the lower 84.8 percent accuracy for the sample with the highest iodine-131 concentration.

The estimated repeatability (within-laboratory), single-operator, single-machine, same-day, relative precision of the test procedure for the determination of iodine-131 concentrations in drinking water at the 7.8 pCi/l level (averaged over the 11 participants) is ±1.3 pCi/l (17.4 percent, 2S percent); at the 25.9 pCi/l level (averaged over the 11 participants) is ±5.3 pCi/l (20.9 percent, 2S percent); and at the 78.3 pCi/l level (averaged over the 11 participants) is ±10.3 pCi/l (15.5 percent, 2S percent), for an average 2S percent of 18.0 percent for the range of iodine-131 concentrations of 7.8 to 78.3 pCi/l.

The estimated reproducibility (combined within- and between-laboratory), multioperator (multilaboratory), single-machine, same-day, relative precision of the test procedure in the determination of iodine-131 concentrations at the 7.8 pCi/l level (averaged over the 11 participants) is ±2.7 pCi/l (35.8 percent, 2S percent); at the 25.9 pCi/l level (averaged over the 11 participants) is ±8.2 pCi/l (32.6 percent, 2S percent); and at the 78.3 pCi/l level (averaged over the 11 participants) is ±21.5 pCi/l (32.3 percent, 2S percent), for an average 2S percent of 33.6 percent for the range of iodine-131 concentrations of 7.8 to 78.3 pCi/l.

The variations observed in the iodine carrier recoveries by the 11 participants for the three samples showed a dependence on analyst technique for the method. Also, the similar average iodine carrier recoveries for the three samples (76.4, 79.3, and 79.8 percent respectively) does not offer any possible explanation for the low bias observed for the sample with the 78.3 pCi/l iodine-131 concentration.

The sensitivity of the test procedure is not limited as much by the chemistry of the procedure (iodine recovery) as it is by the background and the counting efficiency of the counting system used. With a beta background of <5 cpm and a counting efficiency of >20 percent, the sensitivity of measurement (lower detection limit) required in the NIPDWR (1 pCi/l) can easily be met. All participants whose test results were used in the precision and accuracy analysis of this study used counting instruments with beta backgrounds <5 cpm and counting efficiencies >20 percent.

Recommendations

It is recommended that the method tested in this study be investigated for procedure steps that result in analyst technique dependence (as demonstrated by the variations in the iodine carrier recoveries ranging from 48 to 100 percent). One possible weakness in the procedure is in the instructions for the reaction of solid zinc powder with solid silver iodide in an aqueous system.

The procedure should be modified to include a more detailed procedure for the preparation of a palladium iodide-131 counting standard and for the determination of the counting efficiency. A revision of section 6.5, the standardization of potassium iodate, is recommended.

The method should be re-tested to determine if the low bias is real for the 78.3 pCi/l iodine-131 concentration and higher levels.

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The complete report, entitled "Test Procedure for Iodine-131 in Drinking Water: Interlaboratory Collaborative Study," (Order No. PB 83-207 589; Cost: $10.00, subject to change) will be available only from:
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