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Tritium Monitoring in Natural Waters -
Interlaboratory Comparison Program Results for Round Two

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ABSTRACT:

A round-robin interlaboratory comparison program to monitor tritium in natural waters has been established. Currently, five independent laboratories are participating in this round-robin program. Tritium standards are prepared by one of the laboratory participants and analyzed by the other participants in each round of the round-robin. This report encompasses the results of the set of standards prepared by the Radiation Analytical Sciences Section of the Lawrence Livermore National Laboratory (LLNL) for the second round of this enriched tritium intercomparison program.

Two aqueous tritium standard solutions, A and B, were prepared by sequential dilution of a National Institute of Standards and Technology ^3H standard. The concentrations of the standards solutions, A and B, were 147 ± 16 pCi/L ^3H and 444 ± 31 pCi/L ^3H , respectively (2σ uncertainty). One blank solution was also prepared. The standards and blank were prepared using water collected from the Nevada Test Site Potable Water Well 4. This well is known to contain only trace amounts of tritium. The participating laboratories measured the ^3H in standards A and B and blanks by liquid scintillation counting after distillation and electrolytic enrichment or directly

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via ^3He mass spectrometry. The results reported for standards A and B are within the 2σ uncertainties of the known values. These excellent results reflect the quality of the techniques employed.

I. INTRODUCTION:

In light of quality assurance (QA) and quality control (QC) expectations, which weigh heavily upon analytical laboratories, intercomparison programs are a means of method validation and performance verification. Good performance in such a program may be used as an indicator of overall performance. We chose to initiate an interlaboratory comparison program to study tritium in natural waters to provide continuous validation of our analytical methods and additional performance verification beyond our own internal QC. This report provides the necessary QA of our efforts. To our knowledge, this is the first interlaboratory comparison program pertaining to the study of tritium in natural waters. A total of five laboratories are participating in this program. The participants, as well as their host organizations, are listed in Table I.

The methods in use by the laboratory participants consist of either the distillation-electrolytic enrichment with liquid scintillation counting or ^3He mass spectrometry. Only one of the laboratories is using the latter, but the data from this method provide results which validate those obtained from distillation-electrolytic enrichment. Table II identifies the analytical techniques in use by the participating laboratories.

II. ANALYTICAL METHODS:

The distillation-electrolytic enrichment techniques [1-9] are commonly employed to concentrate tritium in aqueous media. Theoretical reviews of the process exist [2, 4-6, 8] and the theoretical arguments will not be repeated here. In the electrolytic enrichment step, water is broken down into its constituent H_2 and O_2 gases by electrolysis. This technique utilizes the inherently slower reaction rate of tritium, 3H (because of its larger atomic mass versus normal hydrogen, 1H , and deuterium, 2H), to preferentially concentrate tritium in the remaining solution. Choice of electrode systems and other factors significantly effect the concentration factor achieved [8].

The majority of electrolytic enrichment systems use an Fe or stainless steel cathode and a Ni anode and operate under either conditions of constant current or constant voltage. The electrolytic enrichment system employed at LLNL is the type described in Refs. 5, 6, 10. The 3He mass spectrometric method is described in Ref. 11 and is a well-established technique [12] to measure environmental levels of tritium.

III. PREPARATION AND DISTRIBUTION OF THE STANDARD AND BLANK SAMPLES:

A. Stock solution container preparation:

Four high-density polyethylene carboys (5 gallon volume) were leached with dilute HNO_3 (≈ 0.15 M, prepared from SeaStar ultra pure nitric acid and Milli-Q water[†]). Our Milli-Q water is prepared at a resistivity of $18\text{ M}\Omega$ and is routinely shown to contain less than $\approx 2 - 6\text{ pCi/L } ^3H$ on average. The carboys

were leached for approximately two days and the nitric acid solution discarded. All components of the carboys were rinsed three times with Milli-Q water. The carboys were air dried, labeled (A, B, C, and D), and weighed prior to transport to the Nevada Test Site (NTS). The weights of the empty carboys are shown in Table III.

B. Collection of "dead water" for preparation of stock standards:

Nevada Test Site Potable Water Well 4 was chosen as the "dead water" source because it is known to contain only trace amounts of tritium. Well 4 was activated by one of the technicians at NTS at about 08:00 on 11/03/94. The carboys were transported to Well 4 on 11/03/93 and arrived at about 11:00. The well was at equilibrium because it had run for nearly three hours. The carboys were rinsed two times with Well 4 water and filled with Well 4 water. The carboys were capped and transported back to Mercury for shipment via Aviation Methods Incorporated to Lawrence Livermore National Laboratory (LLNL). Because of "head-space" constraints imposed by the Department of Transportation, the carboys were uncapped for a very short time to drain some of the dead water. The carboys were hand-carried to building 151 at LLNL. The carboys were weighed, and the external areas wiped clean prior to placement in an N₂ atmosphere glove box. The N₂ atmosphere box was evacuated to -10 inches Hg and refilled with dry N₂ six times. The weights of the filled carboys are given in Table III.

C. Preparation of intercomparison stock standards:

A National Institute of Standards and Technology (NIST) ³H standard (SRM 4926D, 2.897×10^3 Bq/g ³H, assayed on July 25, 1989) was used to make a primary dilution standard. To a 200 mL volumetric flask (class A, glass),

18.435 g of the NIST standard was added and diluted to 200 mL with Milli-Q water. The resulting primary dilution standard was calculated to be 208.5 Bq/g ^3H , after application of a decay correction to 01-January-1994. A copy of the NIST certificate is provided as attachment 1.

To prepare the interlaboratory comparison stock standards, carboys A and B were spiked with the primary dilution standard. An appropriate aliquot of the primary dilution standard was weighted in a plastic weighing boat, passed into the N_2 atmosphere box, and added to carboy A to produce a ^3H concentration in the intercomparison ^3H stock standard A of approximately 150 pCi/L. The weighing boat was washed with approximately 2 mL of Milli-Q water and the washings added to the carboy to ensure a quantitative transfer. The procedure was repeated with carboy B with an appropriate amount of primary dilution standard to produce an intercomparison ^3H stock standard B of about 450 pCi/L. Each resulting solution was mixed with a clean plastic propeller stirrer inside the N_2 atmosphere glove box. The carboys were capped immediately after stirring. The relevant data are presented in Table IV. The calculated ^3H concentrations in carboys A and B are 147 ± 16 pCi/L and 444 ± 31 pCi/L, respectively. The reported uncertainty is 2σ and includes contributions of error from the weights, volumes, evaporation loss during the glove box transfer, and NIST standard. The factors included in the estimation of the uncertainty are listed in Table V.

D. Preparation and distribution of the intercomparison ^3H standards:

Eighteen glass safety bottles (1 liter, externally coated with polyethylene) were leached with dilute HNO_3 (≈ 0.15 M, prepared from SeaStar ultra pure nitric acid and Milli-Q water) for approximately 2 weeks.

The nitric acid solution was discarded and all components of the bottles were rinsed three times with Milli-Q water. The bottles were air dried, and labeled. Of the eighteen bottles, six were filled with standard A, six with standard B and six with blank water from carboy C. The participants were not expected to report the results from measurement of the matrix blank. The labeling system for the standards consisted of a nine character sample identifier which denoted the year of preparation (93), the name of the preparing laboratory (LLNL), a batch number (ranging from 01 - 06), and a designator for the carboy source (A or B), e.g. 93LLNL01A. The blanks were labeled in the same manner except the word BLANK was substituted for the batch number and carboy source designator, e.g. 93LLNLBLANK. The standards were distributed in blind fashion to the participating laboratories for analysis. The laboratories were only informed of the possible concentration range, 100 - 500 pCi/L ^3H .

IV. RESULTS AND STATISTICAL ANALYSIS:

Each of the participating laboratories performed analyses of each standard three times and reported the results of each analysis to LLNL in pCi/L. The errors reported were 2σ and were to be reported in pCi/L. Some of the laboratories, however, reported the uncertainties as percentages. Tables VI, VII and VIII list the results, as reported to LLNL, for the samples designated as 93LLNL0(1-6)A, 93LLNL0(1-6)B and 93LLNLBLANK, respectively. The LLNL results are included in the tables and figures for completeness, but are not to be used in an overall statistical analysis because LLNL prepared the standards.

Figure 1 is a plot of the individual values reported by each participant for standard A (93LLNL01A - 93LLNL06A). Figure 2 is a plot of the 2σ standard deviation of the averages of the reported values for standard A. Based on these results, a low bias in standard A is evident. Figure 3 is a plot of the individual values reported by each participant for standard B (93LLNL01B - 93LLNL06B). Figure 4 is a plot of the 2σ standard deviation of the averages of the reported values for standard B. A low bias is evident in standard B, though not as pronounced as that observed in standard A.

Overall, the data reported for both standards is somewhat lower than the known values. All the data reported for standard A and B (see Figs. 1 - 4) is within 2σ of the known concentrations. All of the averages of the reported values fall below the known value which indicates an overall low bias in standards A and B. This may be the result evaporation of the standard aliquot during transfer into the N_2 atmosphere box. This should influence standard A more than standard B because the 0.025 g estimated uncertainty due to evaporation loss is a larger fraction of the 0.544 g aliquot than the 1.614 g aliquot.

Figure 5 shows the range of reported values from each participant normalized to the known concentration of the standard. Again, all values fall within the 2σ uncertainty of the known concentrations, but a low bias is evident.

IV. CONCLUSION:

In the case of both standard A and B, the averages of the reported values fall within the uncertainty of the known concentrations. This

provides evidence for the quality of the methods employed by the participating laboratories.

A low bias in the concentration of the standards is evident. More careful attention to the preparation of the standards to reduce losses by evaporation is required. In addition, the blank water appears to have ^3H at the level of about 5 pCi/L. This may be the result of contamination which occurred during the brief time the water was exposed to the air at NTS (see collection of dead water section). More careful attention which reduces the possibility of contamination from atmospheric ^3H is required.

IV. ACKNOWLEDGMENTS:

The analytical laboratory participants wish to thank Richard H. Pearl, Manager of the Hydrological Resources Management Program of the Department of Energy, for providing the initial request for analytical assessment which resulted in the formation of this enriched tritium intercomparison subcommittee.

This work was supported by the U. S. Department of Energy under Contracts W-7405-ENG-48 (LLNL), DE-AC08-90-NV10845 (DRI), ~~DE-A108-86-NV1052 (EPA)~~, and DE-AC08-94NV11432 (REEC_o).

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[†]Milli-Q Reagent Water System by Continental Water Systems.

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Table I. Participants, and host organizations, of the enriched tritium interlaboratory comparison program. HRMPDOE = Hydrological Resources Management Program of the Department of Energy, Las Vegas, Nevada; DRI = Desert Research Institute, Reno, Nevada; EPA = Environmental Protection Agency, Las Vegas, Nevada; LLNL = Lawrence Livermore National Laboratory, Livermore, California; REEC Co = Reynolds Electrical and Engineering Company, Inc., Las Vegas, Nevada.

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Richard H. Pearl	HRMPDOE
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Yvonne Booker	REECo
Kevin R. Krenzien	REECo

Table II. Analytical techniques in use by the participating laboratories to study tritium in natural waters. Two LLNL laboratories are participating.

DRI	Electrolytic Enrichment and Liquid Scintillation
EPA	Electrolytic Enrichment and Liquid Scintillation
LLNL	Electrolytic Enrichment and Liquid Scintillation
LLNL	^3He Mass Spectrometry
REEC	Electrolytic Enrichment and Liquid Scintillation

Table III. Tare weights and filled weights of the carboys. The carboys were weighed with their respective lids.

Carboy	A	B	C	D
Gross Wt. (g)	22610	22277	22630	22862
Tare Wt. (g)	1781	1780	1784	1776
Net Wt. H ₂ O (g)	20829	20497	20846	21086

Table IV. Weights of the primary dilution standard used to prepare the enriched tritium intercomparison standards. Bq is equivalent to 1 disintegration/second.

Carboy	A	B
Tritium conc. in primary dilution standard (Bq/g)	208.5	208.5
Amount of primary dilution standard used (g)	0.544	1.614
Total water in the carboy + standard (g)	20830	20499
Enrichment stock standard concentration (Bq/g)	0.00545	0.0164
Enrichment stock standard concentration (pCi/L)	147	444

Table V. Errors associated with preparation of the intercomparison ^3H standards A and B used to calculate the overall uncertainty in the concentrations. All errors are 1σ .

^3H Concentration Error	
Reported error of the NIST Standard	0.86%
Volume error of the primary dilution standard	3%
Total concentration error	3.12%
Error in the weights	
Error in the weight of standard used including evaporation loss during passage into the glove box (g)	0.025
Error in the weight of water in the carboys (g)	25
Total error of weights in standard A	4.6%
Total error of weights in standard B	1.6%
Overall uncertainty in the intercomparison standards	
Overall uncertainty in standard A	5.6%
Overall uncertainty in standard B	3.5%

Table VI. Results reported for standard A. All results are in pCi/L ^3H , unless otherwise indicated. N.R. = not reported.

Institution	Standard	Result(s)	Error (2σ)
DRI	93LLNL01A	144	21.8
		127	13.2
		N.R.	N.R.
REEC _o	93LLNL02A	sample replaced	sample replaced
EPA	93LLNL03A	138	5
		134	5
		158	6
LLNL	93LLNL04A	145.1	14.5
		142.4	14.2
		147.3	14.7
LLNL	93LLNL05A	136	5.3%
		132	5.8%
		140	4.6%
REEC _o	93LLNL06A	121	10.2%
		143	9.0%
		148	8.8%

Table VII. Results reported for standard B. All results are in pCi/L ^3H , unless otherwise indicated. N.R. = not reported.

Institution	Standard	Result(s)	Error (2 σ)
DRI	93LLNL01B	419 416 N.R.	22.8 26.5 N.R.
REEC _o	93LLNL02B	sample replaced	sample replaced
EPA	93LLNL03B	416 442 473	8 8 8
LLNL	93LLNL04B	436.7 443.3 N.R.	43.7 44.3 N.R.
LLNL	93LLNL05B	447 440 429	3% 3% 3.1%
REEC _o	93LLNL06B	410 413 442	4.5% 4.4% 4.2%

Table VIII. Results reported for the blank solutions. All results are in pCi/L ^3H , unless otherwise indicated. The participants were not expected to report their results for the blank. N.R. = not reported.

Institution	Standard	Result(s)	Error (2σ)
DRI	93LLNL01B	N.R. N.R. N.R.	N.R. N.R. N.R.
REEC _o	93LLNL02B	sample replaced	sample replaced
EPA	93LLNL03B	-2.3 1.2 -2.5	3 3 3
LLNL	93LLNL04B	4.6 7.4 3.2	2.5 2.5 2.5
LLNL	93LLNL05B	3.0 16 1.2	100% 100% 100%
REEC _o	93LLNL06B	8.15 4.94 4.30	112% 185% 212%

FIG. 1. Plot of all reported data for standard A. The error bars represent the 2σ error of each point. Data for standard number 93LLNL02A was not reported. The actual concentration of tritium in the standard is represented by the thick black line. The 1σ , 2σ and 3σ errors of the standard are indicated.

FIG. 2. Averages of the reported values for standard A with their respective 2σ uncertainties. The actual concentration of tritium in the standard is represented by the thick black line. The 1σ , 2σ and 3σ errors of the standard are indicated.

FIG. 3. Plot of all reported data for standard B. The error bars represent the 2σ error of each point. Data for standard number 93LLNL02B was not reported. The actual concentration of tritium in the standard is represented by the thick black line. The 1σ , 2σ and 3σ errors of the standard are indicated.

FIG. 4. Averages of the reported values for standard B with their respective 2σ uncertainties. The actual concentration of tritium in the standard is represented by the thick black line. The 1σ , 2σ and 3σ errors of the standard are indicated.

FIG. 5. Range of the averaged reported values for standards A and B normalized to the actual concentration of the standard. The black regions represents the range for standard A and the dotted regions represent the range for standard B. The higher value of the black and dotted regions, for a given sample set, is the 2σ upper limit of the averaged reported values for that set. The lower value of the black and dotted regions, for a given sample set, is the 2σ lower limit of the averaged reported values for that set. A low bias is evident.

Attachment 1: The NIST ^3H Standard Certification. **National Institute of Standards & Technology****Certificate****Standard Reference Material 4926D
Radioactivity Standard**

Radionuclide	Hydrogen-3
Source identification	SRM 4926-D
Source description	^3H -water flame-sealed in glass ampoule ⁽¹⁾
Volume	18 mL
Radioactivity concentration	$2.897 \times 10^3 \text{ Bq g}^{-1}$ ⁽²⁾
Reference time	1200 EST July 25, 1989
Overall uncertainty	0.86 percent ⁽³⁾
Measuring instrument	$4\pi\beta$ liquid-scintillation counter calibrated by internal gas counting
Half life	$12.43 \pm 0.05 \text{ years}$ ⁽⁴⁾

This Standard Reference Material was prepared in the Center for Radiation Research, Ionizing Radiation Division, Radioactivity Group, Dale D. Hoppes, Group Leader.

Gaithersburg, MD 20899
August, 1989

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

*Notes on back

Attachment 1: The NIST ^3H Standard Certification.NOTES

- (1) Ampoule contains approximately 18 milliliters of solution. The ampoule is a modified 20 milliliter low-potassium borosilicate-glass ampoule. The neck has been replaced with a 10/30 ground glass fitting. A 10/30 outer joint cap is enclosed for use with the ampoule.
- (2) Aliquots of this master solution and of the 1978 tritiated water standard SRM 4926C were made up gravimetrically with liquid scintillator into 30 and 15 vials, respectively, and intercompared by liquid-scintillation counting.
- (3) The overall uncertainty was formed by taking three times the quadratic combination of standard deviations of the mean, or approximations thereof, for the following:
a) 50 liquid-scintillation measurements	0.06 percent
b) $n = 6$ gas counting measurements	0.05 percent
c) gram-mole measurements	0.08 percent
d) extrapolation and length-compensation in gas counting	0.05 percent
e) liquid-scintillation intercomparison of 1961 and 1978 standards	0.10 percent
f) half-life correction for $\Delta t = 11$ years	0.24 percent
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For further information, please contact J.M. Calhoun, (301) 975-5538.

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