



Standard Test Method for Tritium in Drinking Water¹

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^{ε1} NOTE—Sections 1.4, 10.1.1, 10.1.2, and 12.3.1 were editorially updated in July 2002.

1. Scope

1.1 This test method covers the determination of tritium in drinking water (as T₂O or HTO) by liquid scintillation counting of the tritium beta particle activity.

1.2 This test method is used successfully with drinking water. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.3 The tritium concentrations, which can be measured by this test method utilizing currently available liquid scintillation instruments, range from less than 0.037 Bq/mL (1 pCi/mL) to 555 Bq/mL (15 000 pCi/mL) for a 10-mL sample aliquot. Higher tritium concentrations can be measured by diluting or using smaller sample aliquots, or both.

1.4 The maximum contaminant level for tritium in drinking water as given by the National Interim Primary Drinking Water Regulations (NIPDWR) is 0.740 Bq/mL (20 pCi/mL). The NIPDWR lists a required detection limit for tritium in drinking water of 0.037 Bq/mL (1 pCi/mL), meaning that drinking water supplies, where required, should be monitored for tritium at a sensitivity of 0.037 Bq/mL (1 pCi/mL). In Appendix X1, Eq X1.3 is given for determining the necessary counting time to meet the required sensitivity for drinking water monitoring.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

D 1129 Terminology Relating to Water²

D 1193 Specification for Reagent Water²

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D19 on Water²

D 3370 Practices for Sampling Water from Closed Conduits²

¹ This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.04 on Methods of Radiochemical Analysis.

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² *Annual Book of ASTM Standards*, Vol 11.01.

D 3648 Practices for the Measurement of Radioactivity³

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129. For terms not defined in this test method or in Terminology D 1129, reference may be made to other published glossaries.⁴

4. Summary of Test Method

4.1 In this test method, a 100-mL drinking water sample aliquot is treated with a small amount of sodium hydroxide and potassium permanganate, distilled, and a specified fraction of the distillate is collected for tritium analysis. The alkaline treatment is to prevent other radionuclides, such as radioiodine and radiocarbon from distilling over with the tritium. Some drinking water supplies will contain trace quantities of organic compounds, especially surface water sources that contain fish and other life. The permanganate treatment is to oxidize trace organics in the sample aliquots which could distill over and cause quenching interferences. A middle fraction of the distillate is collected for tritium analysis because the early and late fractions are more apt to contain interfering materials for the liquid scintillation counting process.

4.2 As the sample distills, there is a gradient in the tritium concentration in the accumulating distillate; therefore, it is important to collect the same fraction of the distillate for all samples and standards for tritium analysis.

4.3 The collected distillate fraction is thoroughly mixed and a portion (up to 10 mL) is mixed with liquid scintillator solution, and after dark adapting, is counted in the liquid scintillation counting system for tritium beta particle activity.

5. Significance and Use

5.1 This test method was developed for measuring tritium in water to determine if the concentration exceeds the regulatory statutes of drinking water. This test method also is applicable for the determination of tritium concentration in water as required by technical specifications governing the operations of

³ *Annual Book of ASTM Standards*, Vol 11.02.

⁴ *American National Glossary of Terms in Nuclear Science and Technology*, available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036..

nuclear power facilities. With suitable counting technique, sample size, and counting time a detection limit of less than 37 Bq/L (1000 pCi/L) is attainable by liquid scintillation.

6. Interferences

6.1 A reduced counting efficiency may result from quenching in the sample scintillator mixture. Quenching is caused by impurities in the sample, which can inhibit the transfer of energy, or by colored materials, which may absorb some of the emitted light. Corrections for quenching can be made by the use of internal standards⁴ or by the ratio method.⁵ The approach described in this test method, distillation after alkaline permanganate treatment, eliminates quenching substances, as well as radionuclides which might be present in a volatile chemical form such as radioiodine and radiocarbon. A boiling chip must be used with each distillation to avoid bumping, which can amount to a carry over excursion.

6.2 Scintillator stock solution or samples exposed to daylight must be dark-adapted. Also, toluene or xylene base scintillators exposed to fluorescent lighting should be dark-adapted for a minimum of 6 h and dioxane base scintillators exposed to fluorescent lighting for 24 h. All fluors should be checked for excitation under lighting conditions being used, and if possible, they should be exposed only to red light.

7. Apparatus

7.1 *Liquid Scintillation Spectrometer*, coincidence-type.

7.2 *Liquid Scintillation Vials*, of low-potassium glass are recommended. Polyethylene vials may be used when dioxane scintillator solution is used.

7.3 *Distillation Apparatus*—For aqueous distillation, 250-mL and 1000-mL round bottom borosilicate flasks, connecting side arm adapter,⁶ condenser, graduated cylinder, boiling chips, and heating mantle.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁷ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.1.1 All chemicals should be of reagent-grade or equivalent whenever they are commercially available.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type III.

8.3 *Reagents of Distillation Treatment:*

8.3.1 *Sodium Hydroxide Pellets.*

8.3.2 *Potassium Permanganate.*

8.4 *Background Water*, with tritium activity below the minimum detectable activity (most deep well waters are low in tritium content).

8.5 *Scintillator Solutions:*

8.5.1 *Dioxane Liquid Scintillator Solution*—Dissolve 4 g of scintillation-grade PPO (2,5-diphenyloxazole), 0.05 g of scintillation-grade POPOP [1,4-bis (5-phenyloxazolyl-2-yl)-benzene], and 120 g of naphthalene in 1 L of spectroquality, 1,4-dioxane. Store the solution in a dark (amber) bottle. This solution can be used with glass or polyethylene vials.

8.5.2 *Solution G Scintillator Solution*—Dissolve 18 g of scintillation-grade PPO (2,5-diphenyloxazole) and 3.6 g of scintillation-grade BIS-MSB [p-bis (o-methylstyryl) benzene] in 2 L of spectroquality p-xylene. Add 1 L of Triton N-101⁸ detergent to the p-xylene scintillator solution. Dissolve 50 g of SXS (sodium xylene sulfonate) in 100 mL of water and add this solution to the p-xylene scintillator-Triton solution. Mix thoroughly. Store the solution in a dark (amber) bottle. This solution should be used with glass vials since the p-xylene solvent evaporates slowly through the wall of the polyethylene vials.

8.5.3 Other commercially available scintillators can be used, such as the environmentally safe di-isopropyl naphthalene based scintillators. It is the responsibility of the user to verify the acceptability of a substitute scintillator.

9. Sampling

9.1 Collect the sample in accordance with Practices D 3370.

9.2 Since tritium in drinking water is likely to be in the form of T₂O or HTO, there is no need for special handling or preservation.

10. Calibration

10.1 *Determination of Recovery and Counting Efficiency Factors:*

10.1.1 Prepare in a 1-L volumetric flask, a tritium standard solution containing approximately 17 disintegrations/(dps)/mL using low level tritium background raw water (undistilled) and standard tritium activity. Label this solution as *raw water tritium standard solution*. Distill approximately 600 mL of water obtained from the same raw water source (RWS) as above (without tritium activity added).

10.1.1.1 Use this distillate for background tritium determinations. Using the distillate and standard tritium activity, prepare a tritium standard solution in a 500-mL volumetric flask to contain the same specific activity as the raw water tritium standard solution. Label this solution as distilled water tritium standard solution.

10.1.2 *Aqueous Alkaline Permanganate Distillation*—Place a 100-mL aliquot of the raw water tritium standard solution in a 250-mL distillation flask. Add 0.5 g of sodium hydroxide, 0.1 g of potassium permanganate, and a boiling chip. Proceed with the distillate according to the procedure described in 11.1,

⁵ Bush, E.T., "General Applicability of the Channels Radio Method of Measuring Liquid Scintillation Counting Efficiencies," *Analytical Chemistry*, 35:1024, 1963.

⁶ Corning part no. 9060 has been found satisfactory for this purpose.

⁷ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

⁸ Triton products are available from Rohm and Haas Company, Independence Mall West, Philadelphia, PA 19105.

discard 10 mL, and collect 50 mL of distillate for analysis. Mix the 50-mL distillate fraction. Repeat the distillation with two more 100-mL aliquots for triplicate analyses.

10.1.3 Prepare for counting three aliquots of the raw water tritium standard solution distillate (from 10.1.2), three aliquots of the distilled water tritium standard solution, and three aliquots of the distilled raw water (for background). Mix 4 mL of water with 16 mL of the dioxane scintillator solution, or 10 mL of water with 12 mL of Solution G scintillator solution in a liquid scintillator vial (glass vials should be used for detergent-type scintillator solutions). Shake well, dark-adapt the vials overnight, and count in a liquid scintillation counter. Count each vial long enough to meet the required detection (0.037 Bq/mL) or longer (see Appendix X1 for calculating required counting time).

11. Procedure

11.1 Add 0.5 g of sodium hydroxide and 0.1 g of potassium permanganate to a 100-mL aliquot of the sample in a 250-mL distillation flask. Add a boiling chip to the flask. Connect a side-arm adapter and a condenser to the outlet of the flask. Place a graduated cylinder at the outlet of the condenser. Heat the sample to boiling to distill, collect the first 10 mL of distillate as a separate fraction and discard it.

NOTE 1—It is important that only the first 10-mL fraction be discarded or the same fraction for samples and standards alike since there is a gradient in the tritium concentration of the distillate. Collect the next 50 mL of distillate for tritium analysis. Thoroughly mix the 50-mL distillate fraction.

11.2 Thoroughly mix 4 mL of the distillate with 16 mL of the dioxane scintillator or 10 mL of distillate with 12 mL of Solution G scintillator in a liquid scintillation vial. Three aliquots of each sample distillate should be analyzed for tritium.

11.3 Prepare background standard tritium-water solutions for counting, using the same amount of water and the same scintillator as used in the preparation of samples. Use low tritium background distilled water for these preparations (distillate of most deep well water sources is acceptable, but each source should be checked for tritium activity before using).

11.4 Dark-adapt all samples, backgrounds, and standards. Count the samples, backgrounds, and standards at least long enough to meet the required detection limit (0.037 Bq/mL) for the sample (see Appendix X1 for calculating counting time for required detection limit). The RWS distillate should be counted for sufficient time to accumulate at least 50 000 net counts.

12. Calculation

12.1 *Counting Efficiency, ε:*

$$\epsilon = \frac{DWS, cps - B}{DWS, dps} \quad (1)$$

where:

DWS = distilled water standard, and

B = background aliquot count rate, cps.

12.2 *Recovery Correction Factor, F:*

$$F = \frac{RWS \text{ distillate, cps} - B}{\epsilon \times RWS, dps \text{ (before distillation)}} \quad (2)$$

where:

RWS = raw water standard.

12.3 *Sample Tritium Activity, A:*

$$A(Bq/mL) = \frac{R - B}{\epsilon \times V \times F} \quad (3)$$

where:

R = sample aliquot gross count rate, cps,

B = background aliquot count rate, cps,

ε = counting efficiency, as determined in Eq 1,

V = volume of the sample aliquot, mL, and

F = recovery factor, as determined in Eq 2.

12.3.1 Error associated with the results of the analysis should be reported.

12.4 The total propagated uncertainty associated with the measured concentration, *A*, can be calculated as follows:

$$\sigma_A(Bq/mL) = A(Bq/mL) * \sqrt{\left(\frac{\delta_N}{N}\right)^2 + \left(\frac{\delta_\epsilon}{\epsilon}\right)^2 + \left(\frac{\delta_V}{V}\right)^2 + \left(\frac{\delta_F}{F}\right)^2} \quad (4)$$

where:

A = tritium concentration in Bq/mL,

N = net count rate in cps = *R* - *B*,

t_B = counting time for background in s,

t_R = counting time for sample in s,

σ_N = 1 σ uncertainty of the net count rate in cps = $\sqrt{R/t_R + B/t_B}$,

σ_V = 1 σ uncertainty in volume measurement,

σ_ε = 1 σ uncertainty in counting efficiency, and

σ_F = 1 σ uncertainty in recovery factor.

13. Quality Control

13.1 Before this test method is utilized for the analysis of samples, a counter quality control or tolerance chart shall be established to ensure the counting system is operating within prescribed limits. The quality control or tolerance chart shall be established at the time the counting system is calibrated.

13.2 Prepare a quality control or tolerance chart as recommended in Practices D 3648. The counting system shall be checked by analyzing a QC source daily or prior to used. The result of the QC analysis shall be tabulated or plotted on the control or tolerance chart and evaluated according to Practices D 3648.

13.3 Evaluate the counting system's background periodically. The background data shall be maintained in a logbook or plotted on a trend chart.

13.4 Precision and bias can be assessed in the following manner. The precision of an individual measurement can be approximated by the total propagated uncertainty and bias can be assessed by the analysis of NIST-traceable spiked samples with known quantities of radioactivity.

14. Precision and Bias ⁹

14.1 The collaborative test conducted on this test method included fifteen laboratories each with one operator. Three

⁹ Supporting data are available from ASTM Headquarters. Request RR:D-19-1146.

activity levels between 0.26 and 11.10 Bq/mL were tested with three replicates per level. The determination of the precision and bias statements were made in accordance with Practice D 2777.

14.2 These collaborative test data were obtained using reagent grade water. For other matrices, these data may not apply.

14.3 *Precision*—The overall and single operator precision have been found to vary with level as presented in Table 1.

14.4 *Bias*—The bias of this test method, based upon the collaborative test data, was found to vary with level as presented in Table 1.

TABLE 1 Observed Tritium Precision and Bias Data

Added, Bq/mL	Measured, Bq/mL	Absolute Bias, Bq/mL	Percent	Precision	
				S_o	S_r
0.26	0.25	0.01	-3.8	0.015	0.035
1.01	0.95	0.06	-5.9	0.020	0.120
11.4	10.5	0.9	-7.9	0.170	1.370

15. Keywords

15.1 drinking water; H-3; liquid scintillation; negative radioactivity; radioisotope; tritium

APPENDIX

(Nonmandatory Information)

X1. DETERMINATION OF THE NECESSARY COUNTING TIME FOR A REQUIRED DETECTION LIMIT (SENSITIVITY)

X1.1 Section 141.25 (C) of the National Interim Primary Drinking Water Regulations (NIPDWR) defines detection limit as follows:

For the purpose of monitoring radioactivity concentrations in drinking water, the required sensitivity of the radioanalysis is defined in terms of a detection limit. The detection limit shall be that concentration which can be counted with a precision of $\pm 100\%$ at the 95% confidence level ($1.96 \sigma_N$ where σ_N is the standard deviation of the net counting rate of the sample).

X1.1.1 In this definition, the following equation is implied.

$$\sigma_N = \frac{N}{1.96} \tag{X1.1}$$

where:

cps = $1.96 \sigma_N$, and
 N = net cps = $R - B$.

X1.1.2 Also, from Appendix X2, the standard deviation of the counting rate can be calculated from the equation:

$$\sigma_N = \sqrt{\frac{R}{t_R} + \frac{B}{t_B}} \tag{X1.2}$$

where:

R = gross count rate, cps,
 B = background count rate, cps,
 t_R = counting time for the gross count, s, and
 t_B = counting time for the background, s.

X1.1.2.1 Let $t_R = t_B = t$. Then

$$\sigma_N = \sqrt{\left(\frac{R+B}{t}\right)} \tag{X1.3}$$

and

$$\sigma_N^2 = \left(\frac{R+B}{t}\right)$$

X1.1.3 Since the gross count rate, R , is equal to the net count rate, N , plus the background count rate, B , $R = N + B$; then:

$$\sigma_N^2 = \left(\frac{N+2B}{t}\right) \tag{X1.4}$$

X1.1.3.1 Now, combine Eqs :

$$\frac{\sigma_N^2}{3.84N + 7.68} = \frac{\left(\frac{N+2B}{t}\right)}{tN^2} = \left(\frac{N}{1.96}\right)^2 \tag{X1.5}$$

X1.2 *Example*—The required detection limit for tritium in drinking water is 0.037 Bq/mL. Determine the counting time that is required to meet that detection limit when a 10-mL sample aliquot is counted at a counting efficiency of 15% and a background count rate of 0.27 cps.

X1.2.1 *Calculation:*

$0.037 \text{ Bq/mL} \times 10 \text{ mL} = 0.37 \text{ Bq}$
 $0.37 \text{ Bq} \times 1.0 \text{ dps/Bq} = 0.37 \text{ dps}$
 $0.37 \text{ dps} \times 0.15 \text{ cps/dps} = 0.0555 \text{ cps} = N$.

X1.2.2 Then, substitute $N = 0.0555$ and $B = 0.27$ in Eq X1.3. The required counting time would be as follows:

$$t = \frac{3.84(0.0555) + 7.68(0.27)}{(0.0555)^2} \tag{X1.6}$$

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