



Designation: D4107 – 20

Standard Test Method for Tritium in Drinking Water¹

This standard is issued under the fixed designation D4107; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of tritium in drinking water 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 untested water 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 United States Environmental Protection Agency (U.S. EPA) National Primary Drinking Water Regulations (NPDWR) is 0.740 Bq/mL (20 pCi/mL). The NPDWR 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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recom-*

mendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

2. Referenced Documents

2.1 ASTM Standards:²

- D1129 Terminology Relating to Water
- D1193 Specification for Reagent Water
- D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
- D3370 Practices for Sampling Water from Flowing Process Streams
- D3648 Practices for the Measurement of Radioactivity
- D7902 Terminology for Radiochemical Analyses

2.2 Other Documents:

- ANSI N42.22 Traceability of Radioactive Sources to the National Institute of Standards and Technology (NIST) and Associated Instrument Quality Control³
- BIPM-5 Decay Data Evaluation Project (DDEP)⁴
- NUDAT⁵

3. Terminology

3.1 Definitions:

- 3.1.1 For definitions of terms used in this standard, refer to Terminology **D1129**.
- 3.1.2 For definitions of terms used in this standard relating to radiochemical analysis, refer to Terminology **D7902**.

4. Summary of Test Method

4.1 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 prevents other radionuclides, such as radioiodine and radiocarbon from distilling over with the tritium. Some drinking water supplies will contain trace quantities of organic compounds,

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 For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ Available from Institute of Electrical and Electronics Engineers, Inc. (IEEE), 445 Hoes Ln., Piscataway, NJ 08854-4141, <http://www.ieee.org>.

⁴ Available from BIPM, Sèvres Cedex, France, <https://www.bipm.org>.

⁵ Available from National Nuclear Data Center at Brookhaven National Laboratory, W Princeton Ave, Yaphank, NY 11980, <http://www.nndc.bnl.gov>.

especially surface water sources that contain fish and other life. The permanganate treatment oxidizes 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 due to isotope effects; 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 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 Reduced detection 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 standard additions or by the ratio method.⁶ 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 other than 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,⁷ 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.⁸ 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. Some reagents, even those of high purity, may contain naturally-occurring radioactivity, such as isotopes of uranium, radium, actinium, thorium, rare earths, potassium compounds, or artificially produced radionuclides, or combinations thereof. Consequently, when such reagents are used in the analysis of low-radioactivity samples, the activity of the reagents should be determined under analytical conditions that are as close as practicable to those used for the test sample. The activity contributed by the reagents should be accounted for and applied as a correction when calculating the test sample result.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193, 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-101⁹ detergent to the p-xylene scintillator solution. Dissolve 50 g of SXS (sodium xylene sulfonate) in 100 mL of water and add

⁷ Corning Part No. 9060 has been found satisfactory for this purpose.

⁸ *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

⁹ The sole source of supply of the apparatus known to the committee at this time is Rohm and Haas Company, Independence Mall West, Philadelphia, PA 19105. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

⁶ Bush, E. T., "General Applicability of the Channels Ratio Method of Measuring Liquid Scintillation Counting Efficiencies," *Analytical Chemistry*, Vol 35, No. 1024, 1963.

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.

8.6 Tritium standard solution as tritiated water traceable to the SI through a national metrology institute (NMI) such as NIST, or an ANSI N42.22 reference material provider with a concentration of approximately 17 kBq/mL.

9. Sampling

9.1 Collect the sample in accordance with Practices **D3370**.

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 Detection Efficiency Factors:*

10.1.1 Prepare in a 1-L volumetric flask, a tritium standard solution containing approximately 17 Bq/mL using low level tritium background raw water, RWS (undistilled), and standard tritium activity. Label this solution as *raw water tritium standard solution, RWTS*.

10.1.1.1 Distill approximately 600 mL of water obtained from the same raw water source (RWS) as above (without tritium activity added). 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, DWTS*.

10.1.2 *Aqueous Alkaline Permanganate Distillation*—Place a 100-mL aliquot of the RWTS 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**, 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. This is the distilled raw water tritium standard (DRWTS).

10.1.3 Prepare for counting three aliquots of the DRWTS distillate tritium standard solution (from **10.1.2**), three aliquots of the DWTS, 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.

11.2 Collect the next 50 mL of distillate for tritium analysis. Thoroughly mix the 50-mL distillate fraction.

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.

11.3 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.

11.4 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).

11.5 Dark-adapt all sample test sources (STS), backgrounds, and standards. Count the STS, background subtraction counts, 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 DRWS distillate STS should be counted for sufficient time to accumulate at least 50 000 net counts.

12. Calculation

12.1 Calculate the *detection efficiency*, ϵ , and its *associated uncertainty*, $u(\epsilon)$, as follows:

$$\epsilon = \frac{R_{\text{DWTS}} - R_{\text{b}}}{A_{\text{DWTS}}} \quad (1)$$

$$u(\epsilon) = \sqrt{\frac{\left(\frac{R_{\text{DWTS}} + R_{\text{b}}}{t_{\text{DWTS}} + t_{\text{b}}}\right)}{A_{\text{DWTS}}^2} + \epsilon^2 \left(\frac{u(A_{\text{DWTS}})}{A_{\text{DWTS}}}\right)^2} \quad (2)$$

where:

- A_{DWTS} = activity of distilled water tritium standard, in becquerels (Bq),
- R_{b} = background subtraction count count rate, in counts per second (s⁻¹),
- R_{DWTS} = distilled water tritium standard count rate (s⁻¹),
- $u(A_{\text{DWTS}})$ = standard uncertainty of the activity A_{DWTS} (Bq),
- t_{DWTS} = count time for the distilled water tritium standard (seconds), and
- t_{b} = count time for the background sample (seconds).

12.2 *Recovery Correction Factor, F:*

$$F = \frac{R_{\text{DWTS}} - R_{\text{b}}}{\epsilon \times A_{\text{RWTS}}} \quad (3)$$

where:

R_{DRWTS} = count rate of distilled raw water standard (s^{-1}),
and
 A_{RWTS} = activity of (undistilled) raw water tritium standard
Bq.

12.3 Sample Tritium Activity, AC , for Each Aliquot:

$$AC = \frac{R_a - R_b}{\varepsilon \times F \times V \times e^{-\lambda t}} \quad (4)$$

where:

R_a = STS gross count rate (s^{-1}),
 ε = detection efficiency, as determined in Eq 1,
 V = volume of the distillate added to STS (mL),
 F = recovery factor, as determined in Eq 3,
 λ = decay constant for tritium, $(\ln 2) / t_{1/2}$,
 $t_{1/2}$ = half-life of tritium, 4497 days,^{10,11} and
 t = elapsed time between sampling and counting, in days.

12.4 The result of the measurement has an uncertainty due to counting statistics (counting uncertainty). The component of the combined standard uncertainty of the tritium concentration in the sample due to counting statistics, $u_{\text{cC}}(AC)$, is given by:

$$u_{\text{cC}}(AC) = \frac{\sqrt{\frac{R_a}{t_a} + \frac{R_b}{t_b}}}{\varepsilon \times F \times V \times e^{-\lambda t}} \quad (5)$$

where:

t_b = count time of the background sample, in seconds.

12.5 The combined standard uncertainty, $u_{\text{c}}(AC)$, of the measured concentration can be calculated as follows:

$$u_{\text{c}}(AC) = \sqrt{u_{\text{cC}}^2(AC) + AC^2 \left[\left(\frac{u(F)}{F} \right)^2 + \left(\frac{u(V)}{V} \right)^2 + \left(\frac{u(\varepsilon)}{\varepsilon} \right)^2 \right]} \quad (6)$$

where:

AC = measured tritium concentration (Bq/mL), from Eq 4,
 $u_{\text{cC}}(AC)$ = standard counting uncertainty of AC , from Eq 5,
 $u(V)$ = standard uncertainty of the volume, V ,
 $u(\varepsilon)$ = standard uncertainty of the detection efficiency, ε , from Eq 2, and
 $u(F)$ = standard uncertainty of the recovery factor. The standard uncertainty of F could be determined by repeated measurements; however, since F will generally be close to 1, the uncertainty may be assumed to be 0.

12.6 For each sample measurement, calculate the critical activity concentration, L_C , in becquerels per milliliter (Bq/mL), as follows:

$$L_C = \frac{1.65 \sqrt{R_b \times t_a \times \left(1 + \frac{t_a}{t_b} \right)}}{\varepsilon \times t_a \times F \times V \times e^{-\lambda t}} \quad (7)$$

NOTE 2—The k factor of 1.645 assumes a Type I error rate of 5%. Factors corresponding to other error rates may be applied as appropriate depending of the data/measurement quality objectives.

12.7 When the detection criterion of 12.6 is used, calculate the *a priori* minimum detectable activity concentration (MDC) as follows:

$$MDC = \frac{2.71 + 3.29 \sqrt{R_b \times t_a \times \left(1 + \frac{t_a}{t_b} \right)}}{\varepsilon \times t_a \times F \times V \times e^{-\lambda t}} \quad (8)$$

NOTE 3—Eq 8 is only valid for Type I and Type II error rates of 5%. The formulation will need to be modified if data/measurement quality objectives specify different tolerable decision error rates.

13. Quality Control

13.1 In order to provide reasonable assurance that the analytical results obtained using this test method are valid and accurate within the confidence limits of this test method, quality control (QC) samples are analyzed with each batch of samples undergoing analysis. Each batch should include not more than 20 samples, including those used for QC purposes. Laboratory or project quality assurance plans may contain more restrictive process QC requirements. The following minimum QC procedures must be followed when running the test method:

13.2 Initial Demonstration of Laboratory/Instrument Quality:

13.2.1 If a laboratory or analyst has not performed this test before or there has been a major change in the measurement system, a precision and bias study must be performed to demonstrate laboratory/instrument capability. A significant change is defined as any change, repair, or alteration of any component in the system which maybe expected to affect the response of the measurement system. See Practices D3648 for recommended practices.

13.2.2 Analyze seven replicates of a standard solution prepared from an independent reference material (IRM) containing at ^3H concentrations sufficient to reduce the relative standard counting uncertainty to 1% or less. The matrix used for the demonstration should represent a water sample typical for which the procedure will be used, for example, drinking water.

13.2.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of precision and mean bias of 10% and $\pm 10\%$, respectively, based on a review of the collaborative study data. Practice D2777 should be consulted on the manner by which precision and mean bias are determined from the initial demonstration study. The study should be repeated until the precision and bias are within the given limits.

13.2.4 Analyze three replicates of a blank solution matrix. The matrix used for the demonstration should represent a water sample typical for which this test method will be used, for example, drinking water. The total dissolved solids (TDS) of the matrix should approximate that which may be encountered in normal use.

¹⁰ "Table of Radionuclides," *BIPM Monographie 5*, Vol 3, pp. 1–4, available from www.bipm.org/utis/common/pdf/monographieRI/Monographie_BIPM-5_Tables_Vol3.pdf, accessed July 22, 2019.

¹¹ Two online references for expertly evaluated nuclear data, including radionuclide half-lives and their uncertainties, are recommended: BIPM-5 and NUDAT2. Other sources of nuclear data may be used at the user's discretion. In all cases, the source should be clearly documented.