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Standard Test Method for Tritium in Drinking Water¹

This standard is issued under the fixed designation D 4107; 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.

~~ε¹Note—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 T_2O 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 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~~ 1.4 The maximum contaminant level for tritium in drinking water as given by the United States Environmental Protection Agency (U.S. EPA) 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:*²

D 1129 Terminology Relating to Water

D 1193 Specification for Reagent Water

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

D 3370 Practices for Sampling Water from Closed Conduits

D 3648 Practices for the Measurement of Radioactivity

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.³

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.

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*, Vol 11.01, volume information, refer to the standard's Document Summary page on the ASTM website.

³ *Annual Book of ASTM Standards*, Vol 11.02: 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, www.ansi.org.

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 A reduced ~~counting~~ 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 internal standards³ or by the ratio method.⁴ 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 flours should ~~hebe~~ 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,⁵ 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.⁶ 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

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.

⁴ Bush, E.T., "General Applicability of the Channels Radio Method of Measuring Liquid Scintillation Counting Efficiencies," *Analytical Chemistry*, 35:1024, 1963.

⁶ Bush, E.T., "General Applicability of the Channels Radio Method of Measuring Liquid Scintillation Counting Efficiencies," *Analytical Chemistry*, 35:1024, 1963.

⁵ Corning part no. 9060 has been found satisfactory for this purpose.

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⁶ *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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

scintillation-grade BIS-MSB [p-bis (o-methylstyryl) benzene] in 2 L of spectroquality *p*-xylene. Add 1 L of Triton N-101⁷ 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.

8.6 Tritium standard solution as tritiated water traceable to a National Standards Laboratory such as NIST or NPL, approximately 17 kBq/mL.

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 Detection Efficiency Factors:*

~~10.1.1 Prepare~~ 10.1.1 Prepare in a 1-L volumetric flask, a tritium standard solution containing approximately 17 disintegrations/s (dps)/mL 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). ~~10.1.1.1 Use~~ 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 ~~raw water tritium standard 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 ~~raw water DRWTS distillate~~ tritium standard solution-distillate (from 10.1.2), three aliquots of the ~~distilled water tritium standard solution, 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. ~~Collect the next 50 mL of distillate for tritium analysis. Thoroughly mix the 50-mL distillate fraction.~~

11.23 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.

11.34 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).

11.45 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 DRWS distillate should be counted for sufficient time to accumulate at least 50 000 net counts.

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 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, which you may attend.

12. Calculation

12.1 ~~Counting Efficiency, Detection Efficiency, ϵ :~~

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

$$\epsilon = RDWTS - RbADWTS$$

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

ADWTS

where:

- ~~DWS_{ADWTS} = distilled water standard, and activity of distilled water tritium standard, in becquerels (Bq),~~
 ~~BR_b = background aliquot count rate, cps, background aliquot count rate, in counts per second (s^{-1}),~~
 ~~R_{DWTS} = distilled water tritium standard count rate (s^{-1}),~~
 ~~$u(A_{DWTS})$ = standard uncertainty of the activity ADWTS (Bq),~~
 ~~t_{DWTS} = count time for the distilled water tritium standard (seconds),~~
 ~~t_b = count time for the background sample (seconds).~~

12.2 ~~Recovery Correction Factor, F :~~

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

$$F = RDWTS - Rb\epsilon \times ARWTS$$

RDRWTS

where:

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

12.3 ~~Sample Tritium Activity, A Sample Tritium Activity, AC, for each aliquot:~~

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

$$AC = Ra - Rb\epsilon \times F \times V \times e^{-\lambda t}$$

Ra

where:

- ~~RR_a = sample aliquot gross count rate, cps, sample aliquot gross count rate (s^{-1}),~~
 ~~BR_b = background aliquot count rate, cps, background aliquot count rate (s^{-1}),~~
 ~~ϵ = counting detection efficiency, as determined in Eq 1,~~
 ~~V = volume of the sample aliquot, mL, and volume of the sample aliquot (mL),~~
 ~~F = recovery factor, as determined in Eq 2, recovery factor, as determined in Eq 2,~~
 ~~λ = decay constant for tritium, $(\ln 2) / t_{1/2}$,~~
 ~~$t_{1/2}$ = half-life of tritium, 4500 d,~~
 ~~t = elapsed time between sampling and counting, in days.~~

~~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:~~

~~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, $u_c(AC)$, is given by:~~

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

$$u_c(AC) = Ra - Rb\epsilon \times F \times V \times e^{-\lambda t}$$

t b

where:

- ~~At_b = tritium concentration in Bq/mL, count time of the background sample, in seconds.~~

~~12.5 The combined standard uncertainty, $u_c(AC)$, of the measured concentration can be calculated as follows:~~

$$u_c(AC) = \sqrt{u_{cc}(AC)^2 + AC^2 \left[\left(\frac{u(F)}{F}\right)^2 + \left(\frac{u(V)}{V}\right)^2 + \left(\frac{u(\epsilon)}{\epsilon}\right)^2 \right]} \quad (5)$$

where: