

SECTION 10
TRITIUM IN DRINKING WATER
METHOD 906.0

1. Scope and Application

- 1.1 This method covers the measurement of tritium (as T₂O or HTO) in a sample of drinking water by liquid scintillation spectrometry. This technique assures the identification of tritium in drinking water at a concentration fifty-fold lower than promulgated in the Safe Drinking Water Act, PL 93-523.
- 1.2 The maximum contaminant level for tritium in drinking water as given in the National Interim Primary Drinking Water Regulations (NIPDWR) is 20,000 pCi/l. The NIPDWR list a required detection limit for tritium in drinking water of 1000 pCi/l or 1 pCi/ml, meaning that drinking water supplies, where required, should be monitored for tritium at a sensitivity of 1 pCi/ml. In Appendix C, the use of equation (3) will determine the necessary counting time required to meet the sensitivity for drinking water monitoring.
- 1.3 By counting standard tritium and background samples at the same time as the prepared drinking water samples, the results and the behavior of the liquid scintillation spectrometer can be routinely monitored.

2. Summary of Method

- 2.1 A 100 ml aliquot of a drinking water sample is treated with a small amount of sodium hydroxide and potassium permanganate, then is 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 (especially surface water sources that contain fish and other life). The permanganate treatment oxidizes trace organics in the sample aliquot 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.
- 2.2 The collected distillate fraction is thoroughly mixed and a portion is mixed with liquid scintillator solution, and after dark adapting, is counted in the liquid scintillation counting system for tritium beta particle activity.
- 2.3 The scintillator solution, mixed with the radioactive sample, is excited by beta particles and emits light pulses by a molecular de-excitation process. The number of pulses per unit time is proportional to the quantity of activity present. Multiple solutes are used in the scintillator to provide the best combination of wavelength and pulse height for this application. The pulses are detected by two photomultiplier tubes connected in coincidence and converted to electric signals.

The amplified pulses are recorded and the count rate is measured. The efficiency of the system can be determined by use of prepared tritiated water standards having the same density and color as the sample.

3. Sample Handling and Preservation

3.1 The drinking water sample should be collected in its natural state, and should not be acidified. Since tritium in drinking water is very much apt to be in the form of T_2O or HTO there is no need for special handling or preservation.

4. Interferences

4.1 Tritium in background water is an interference. Slightly elevated levels are present in surface waters so deep well sources for background water should be used.

4.2 All fluors should be checked for excitation under lighting conditions being used and if necessary they should be exposed only to red light. Dioxane-base scintillators exposed to fluorescent lighting should be dark-adapted for 24 hours. Toluene-or xylene-base scintillators exposed to fluorescent lighting should be dark-adapted for a minimum of 1 hour.

4.3 The use of plastic vials may cause build-up of static charge and give erratic results.

5. Apparatus - See Appendix D for details and specifications.

5.1 Coincidence-type liquid scintillation spectrometer.

5.2 Liquid scintillation vials: Low-potassium glass is recommended. Polyethylene vials may be used when dioxane liquid scintillator solution is used.

5.3 Distillation apparatus: For aqueous distillation: 250-ml and 1000-ml round bottom pyrex flasks, connecting side arm adapter (such as Corning part #9060), condenser, graduated cylinder, boiling chips, and heating mantle.

6. Reagents

6.1 Reagents for distillation treatment: sodium hydroxide pellets and potassium permanganate. (ACS - reagent grade)

6.2 Background water with tritium activity below the minimum detectable activity (most deep well waters are low in tritium content).

6.3 Scintillator solutions:

6.3.1 Solution G liquid scintillator solution: Dissolve 18g scintillation-grade PPO (2,5-diphenyloxazole) and 3.6g scintillation-grade BIS-MSB p-bis (o-

methylstyryl) benzene in 2 liters of spectroquality p-xylene. Add 1 liter Triton N-101 detergent (Rohm & Haas) to the p-xylene scintillator solution. Dissolve 50g SXS (sodium xylene sulfonate) in 100 ml distilled water and add this solution to the p-xylene scintillator-Triton solution. Mix thoroughly. Store the solution in a dark (amber) bottle. The organic solvent evaporates slowly through the wall of the polyethylene vials. For this reason counting samples should be completed within 3 days after preparation.

- 6.3.2 Detergent-type liquid scintillator solutions are available as commercial preparations. They are also prepared with aromatic hydrocarbon solvents and should therefore, when used with plastic vials, be counted within 3 days for the reason stated above. (See Representative Sources of Laboratory Supplies, Appendix E)
- 6.3.3 Dioxane liquid scintillator solution: Dissolve 4g scintillation-grade PPO (2,5-diphenyloxazole), 0.05g scintillation-grade POPOP 1,4-bis (5-phenyloxazolyl-2-yl) benzene, and 120g naphthalene in 1 liter of spectroquality 1,4-dioxane. Store the solution in a dark (amber) bottle. This solution can be used with glass or polyethylene vials.

7. Calibrations

- 7.1 Determination of Recovery and Counting Efficiency Factors - (See calculations, Section 9.2 and 9.3)
 - 7.1.1 Into a 1-liter volumetric flask, pipette a tritium standard solution containing approximately 1000 disintegrations per minute (dpm) per ml and dilute to volume using low level tritium background raw water (undistilled) and standard tritium activity. Label this solution "Raw Water Tritium Standard Solution." For tritium background determinations, distill approximately 600 ml of water, obtained from the same raw water source as above (without tritium activity added). Using the distillate and standard tritium activity, prepare a tritium standard solution in a 500-ml volumetric flask containing the same specific activity as the "Raw Water Tritium Standard Solution." Label this solution "Distilled Water Tritium Standard Solution."
 - 7.1.2 Aqueous permanganate distillation:
To a 100-ml aliquot of the "Raw Water Tritium Standard Solution" in a 250-ml distillation flask, add 0.5g sodium hydroxide, 0.1g potassium permanganate, and a boiling chip. Proceed according to the procedure described in section 8.1. Discard the first 10 ml and collect 50 ml of the distillate for analysis. Mix well. Repeat the distillation with two more 100-ml aliquots for triplicate analyses.

- 7.1.3 For liquid scintillation counting:
Prepare 3 aliquots of the “Raw Water Tritium Standard Solution” distillate (from step 7.1.2), 3 aliquots of the “Distilled Water Tritium Standard Solution;” and 3 aliquots of the distilled raw water (for background). Mix 4 ml water with 16 ml of the dioxane scintillator solution or 8 ml water with 12 ml of a detergent-type scintillator solution in a liquid scintillator vial (glass vials should be used for detergent-type scintillator solutions). Shake well and dark-adapt the vials overnight. Count each vial in a liquid scintillation counter long enough to meet the required detection limit (1 pCi/ml) or longer (see Appendix C for calculating required counting time).

8. Procedure

- 8.1 Add 0.5g sodium hydroxide and 0.1g 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, and insert a graduated cylinder at the outlet of the condenser (Fig. 5). Heat the sample to boiling to distill, and discard the first 10 ml of distillate as a separate fraction. (It is important that the first 10-ml fraction for samples and standards alike be discarded, since there is a gradient in the tritium concentration of the distillate). Collect the next 50-ml of distillate for tritium analysis and mix thoroughly.
- 8.2 Mix 4 ml of the distillate with 16 ml of the dioxane liquid scintillator or 8 ml of the distillate with 12-ml of a detergent-type scintillator solution in a liquid scintillation vial.
- 8.3 Prepare background and 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).
- 8.4 Dark-adapt all samples, backgrounds, and standards. Count the samples, backgrounds, and standards at least long enough to meet the required detection limit (1 pCi/ml) for the sample (see Appendix C for calculating required time).

Note: In normal counting operation, tritium is counted with a window setting where the figure of merit is at maximum.

$$\text{Figure of Merit} \quad \frac{E^2}{B} = \frac{(\text{Efficiency})^2}{(\text{Background})}$$

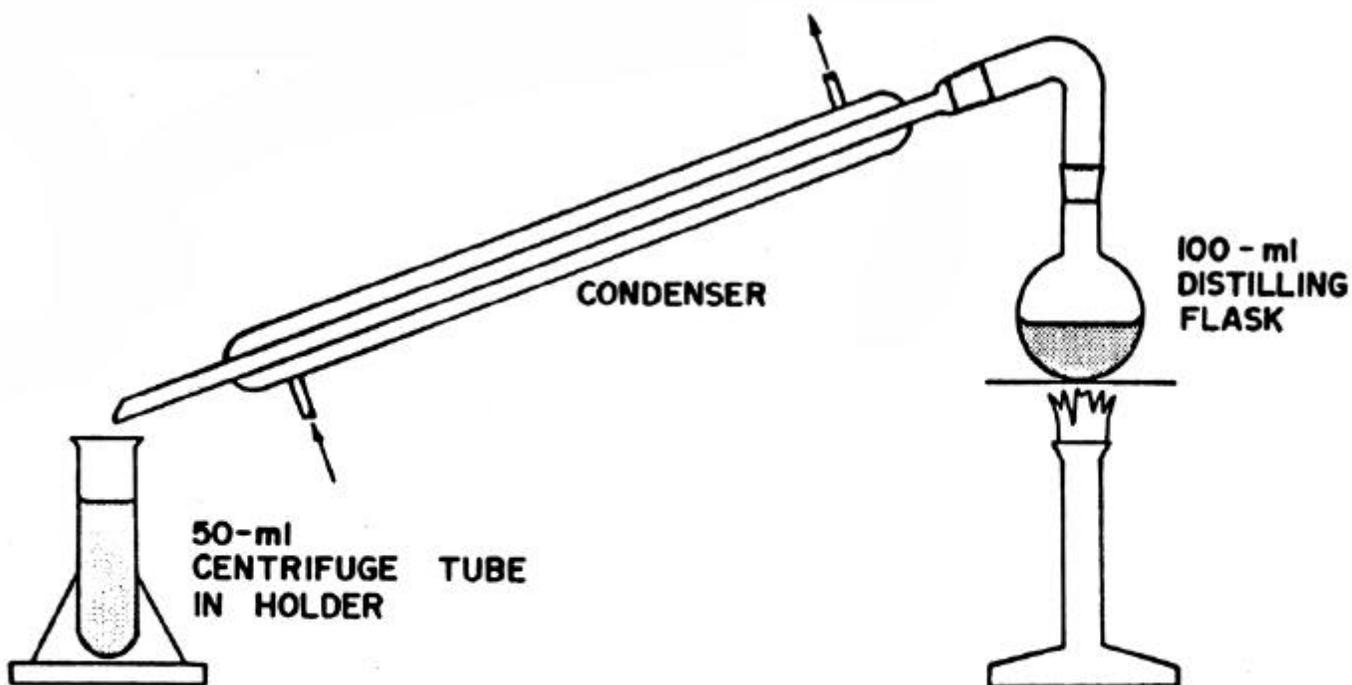


Figure 5. Distillation apparatus for tritium analysis

9. Calculations

9.1 Calculate the tritium concentration, A, in picocuries per liter as follows:

$$A = \frac{(C - B) \times 1000}{2.22 \times E \times V \times F}$$

where:

- C = sample count rate, cpm,
- B = background count rate, cpm,
- E = counting efficiency, as determined in Section 9.2,
- V = volume of the sample aliquot in ml,
- F = recovery factor, as determined in Section 9.3
- 2.22 = conversion factor for dpm/pCi.

9.2 Determine the counting efficiency, E, as follows:

$$E = \frac{D - B}{G}$$

where:

$$\begin{aligned} D &= \text{distilled water standard count rate, cpm,} \\ B &= \text{background count rate, cpm, and} \\ G &= \text{activity of distilled water standard (dpm)} \end{aligned}$$

9.3 Calculate the recovery correction factor, F, as follows:

$$F = \frac{L - B}{E \times M}$$

where:

$$\begin{aligned} L &= \text{raw water standard distillate count rate, cpm,} \\ B &= \text{background count rate, cpm,} \\ E &= \text{counting efficiency, as determined in Section 9.2, and} \\ M &= \text{activity of raw water standard (before distillation), dpm.} \end{aligned}$$

10. Precision and Accuracy

- 10.1 In an interlaboratory collaborative test of the method three water samples were analyzed for tritium by 25 laboratories. The three water samples were prepared by spiking tap water with measured amounts of tritiated water of known concentrations.
- 10.2 The data from three laboratories for the three water samples were rejected from the statistical analysis because their scores in the ranked results of the laboratory averages were outside the acceptable range for 25 laboratories and 3 samples.
- 10.3 The coefficients of variation for the combined within-laboratory precision for the three samples ranged from 2.1 to 5.2 percent.
- 10.4 The coefficients of variation for the precision of the method between laboratories for the three samples ranged from 21.0 to 28.8 percent.
- 10.5 The coefficients of variation for the total error between laboratories based on a single analysis for the three samples ranged from 21.3 to 29.2 percent.
- 10.6 In the statistical test to detect method bias, the method showed no bias for tritium concentrations at the 7 pCi/ml level to a small bias on the low side for concentrations at the 300 pCi/ml level (average analytical value about 9 percent lower than the known value).

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