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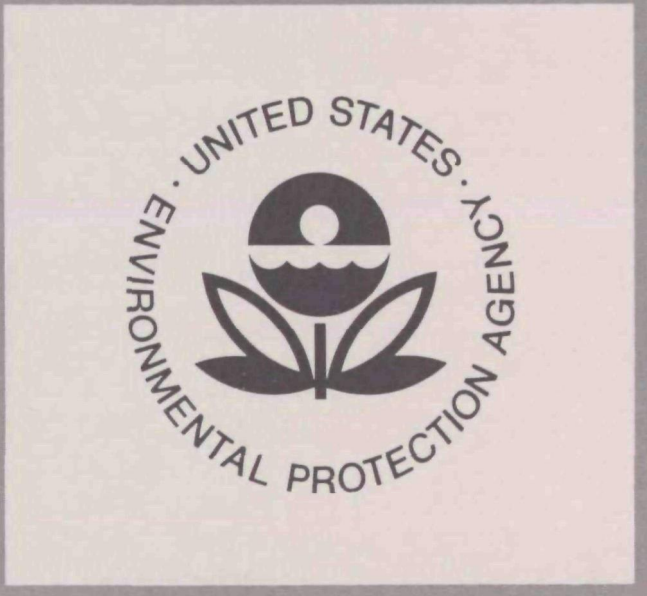
TENTATIVE REFERENCE METHOD FOR MEASUREMENT OF TRITIUM IN ENVIRONMENTAL WATERS



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by

Quality Assurance Branch
Monitoring Systems Research and Development Division
Environmental Monitoring and Support Laboratory
Las Vegas, Nevada 89114

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Effective June 29, 1975, the National Environmental Research Center-Las Vegas (NERC-LV) was designated the Environmental Monitoring and Support Laboratory-Las Vegas (EMSL-LV). This Laboratory is one of three Environmental Monitoring and Support Laboratories of the Office of Monitoring and Technical Support in the U.S. Environmental Protection Agency's Office of Research and Development.

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TENTATIVE REFERENCE METHOD FOR MEASUREMENT OF TRITIUM IN ENVIRONMENTAL WATERS

1. Principle and Applicability

The most common method used for the analysis of tritium in an aqueous solution is liquid scintillation counting. In liquid scintillation counting, the sample material is incorporated into a liquid scintillator solution and the light pulses generated by the interaction between the nuclide and the scintillator are counted by means of a single photomultiplier tube, or more commonly by two tubes operating in coincidence.

For tritium analysis a fluorescent substance dissolved in a suitable solvent is used (called a liquid scintillator). The sample is dissolved or suspended directly in the liquid scintillator. Beta particles, emitted as the tritium decays, interact with the liquid scintillator to produce very small light pulses. The number of pulses per unit time is proportional to the quantity of activity present. In most liquid scintillation counting instruments light pulses are detected and converted to electrical signals by two photomultiplier tubes operated in coincidence. These electrical signals are amplified, recorded, and the count rate determined. The pulse height is proportional to the energy of the beta particle which excited the scintillator molecule. Therefore, radionuclides which have significantly different beta energies can be selectively counted from the same sample with instruments that have pulse height discrimination capability. The spectrometer is calibrated with standard solutions of tritiated water. Background, standards, and unknown samples are counted alternately to nullify errors which could result from instrument drift or from aging of the scintillator solutions.

In the method described here, samples of potable water sources are treated by an alkaline permanganate distillation (1) and samples of nonpotable water sources are treated by an azeotropic-benzene, alkaline permanganate distillation (2). For both types of samples (also standards), 100 milliliters (ml) of sample (or standard) is used, the first 10 ml of water distillate is discarded, and the next 50 ml of water distillate is collected for analysis.

This method is applicable to the measurement of tritium activities in potable and nonpotable water sources, and the aqueous fractions of other types of samples such as biological and soil samples.

2. Range and Sensitivity

The minimum concentration of tritium in water to which this method is applicable will depend on sample size, counting efficiency, and counting time. The decay of radioactivity is random in nature rather than uniform. Therefore, the emissions of radioactive decay (in this case, beta particles) must be counted sufficiently long to obtain the desired statistical reliability. It is recommended that samples be counted long enough so that samples with tritium activity as low as the detection limit of the method and counting instrument used will have a counting error at the 95 percent confidence level of no more than the sample net count rate (when counting error counts per minute (cpm) equals net cpm, the counting error is 100 percent). For instance, when a 10-ml sample distillate aliquot is mixed with 10 ml of liquid scintillator solution (such as Solution G, see Section 6) in a glass counting vial and counted in a liquid scintillation counter for 20 minutes, with a gross count rate of 18.7 cpm, a background count rate of 16 cpm, and a counting efficiency of 15 percent, tne sample will have a net count rate of 2.7 cpm and a counting error of plus or minus (±) 2.6 cpm at the 95 percent confidence level. This corresponds to a detection limit of 0.8 ± 0.8 pCi/ml. Counting error can be reduced

by lower background, higher counting efficiency, longer counting time, and with more sample tritium activity. See the Appendix for error and statistical calculations.

The range of tritium concentrations which can be measured by the method, utilizing currently available liquid scintillation instruments, is from less than 1 pCi/ml to 15,000 pCi/ml for 10-ml sample aliquot size. Higher tritium concentrations can be measured by diluting and/or using smaller sample aliquots.

The method provides for the detection of tritium levels well below the maximum allowable concentrations above natural background as indicated in the Federal Register, Title 10, Part 20, Section 20.106, paragraph (e), with reference to Appendix B, Table II (1/3 of 3000 pCi/ml equals 1000 pCi/ml).

3. Interferences

3.1 Significant reduction in the absolute counting efficiency may result from quenching (attenuation of pulse heights) caused by impurities in the sample which are introduced into the scintillator solution and which will inhibit the transfer of energy, or by color in the sample which may absorb the emitted light. Correction must be made for quenching or quenching materials should be removed from the sample. Correction for quenching can be accomplished either by the use of an internal standard (3) or by the channels ratio method of quench correction (4). The approach in the method described here is to eliminate quench interference materials and such volatile radionuclides as radioiodine and radiocarbon. An alkaline permanganate distillation of aqueous samples should eliminate most quench interferences as well as radioiodine and radiocarbon. Too vigorous a distillation will carry over interfering materials with the distillate, as is easily seen with a sample treated with potassium permanganate. (The permanganate color in the distillate does not appear to quench, up to concentrations of 10 parts per million, but it is evidence of

carryover of unwanted materials.) An azeotropic-benzene distillation of aqueous samples greatly minimizes the carryover of inorganic as well as volatile organic materials. A boiling chip must be used with each distillation to avoid bumping, which can amount to a carryover excursion.

3.2 Scintillator stock solutions or samples exposed to daylight must be dark-adapted for at least 24 hours. If toluene or xylene base scintillators are exposed to fluorescent lighting they should be dark-adapted for a minimum of 6 hours. If dioxane base scintillators are exposed to fluorescent lighting, 24-hour dark-adaption is necessary. All fluors should be checked for excitation under lighting conditions being used and if possible they should be exposed only to red light.

4. Precision and Accuracy

4.1 Samples with tritium activity above 200 pCi/ml can be analyzed with a precision of less than ± 6 percent at the 95 percent confidence level and samples with as little activity as 1 pCi/ml can be analyzed with a precision of less than ± 10 percent.

4.2 Overall accuracy can be calculated from the accuracy of the standard used (data furnished by the supplier) combined with the precision and accuracy of the method. Accuracy is dependent on the influence of interferences. Interferences are minimized in this method.

5. Apparatus

Coincidence-type liquid scintillation spectrometer

Liquid scintillation vials, low-potassium glass is recommended. Polyethylene vials may be used when dioxane scintillator solution is used.

One-liter, tight-sealing, polyethylene bottles

Labels for sample identification

Distillation apparatus:

For aqueous distillation: 250-ml round bottom pyrex flask; connecting side arm adapter (such as Corning part #9060), condenser, graduated cylinder, boiling chips, and heating mantle

For azeotropic-benzene-aqueous distillations: 500-ml round bottom flask, Barrett-type distilling receiver (such as Corning part #3622), condenser, boiling chips, graduated cylinder, and heating mantle

6. Reagents. All chemicals should be of "reagent-grade" or equivalent whenever they are commercially available.*

Reagents for distillation treatment: sodium hydroxide pellets, potassium permanganate, and benzene

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

Scintillator solutions:

Dioxane liquid scintillator solution: Thoroughly mix 4 grams (g) PPO (2,5-diphenyloxazole), 0.05 g POPOP [1,4-bis(5-phemyloxazolyl-2-yl)benzene],

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* "Reagent Chemicals, American Chemical Society Specifications," American Chemical Society (ACS), Washington, DC. For reagents not listed by the ACS see "Reagent Chemicals and Standards" by Joseph Rosin, D. Van Nostrund Company, Inc., New York, NY, or the "United States Pharmacopeia" for purity tests.

and 120 g of solid napthalene in 1 liter of spectroquality 1,4-dioxane. Store the solution in a dark (amber) bottle no longer than 2 months. This solution can be used with glass or polyethylene vials.

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 liters of spectroquality p-xylene. Add 1 liter of Triton N-101 detergent (Rohm & Haas) to the p-xylene scintillator solution. Dissolve 50 g of SXS (sodium xylene sulfonate) in 100 ml of distilled 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.

"Handifluor"® scintillator solution (available from Mallinkrodt Chemical Works). This solution should be used with the glass vials for the reason stated above.

"Insta-Gel"® scintillator solution (available from Packard Instrument Company). This solution should be used with glass vials for the reason stated above.

7. Procedure

7.1 Sampling

Sampling should be accomplished as described in "Environmental Radioactivity Surveillance Guide," published by the U.S. Environmental Protection Agency as report ORP/SID 72-2.

7.2 Analysis

7.2.1 For samples of potable water sources: 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 100°-105° C to distill, discard the first 10 ml of distillate (should contain most of the ammonia from amines and amino compounds), and then collect the next 50 ml of distillate for tritium analysis. Thoroughly mix the distillate fraction.

7.2.2 For samples of nonpotable water sources: Add 0.5 g of sodium hydroxide, 0.2 g of potassium permanganate, and 200 ml of benzene to a 100-ml sample aliquot in a 500-ml distillation flask. Add a boiling chip to the flask. Attach a Barrett-type distilling receiver and condenser to the flask. Heat the flask contents to 78°-82° C to distill and discard the first 10 ml of water distillate. Do not collect more than 10 ml and then drain the bottom 10 ml because there is a gradient in the tritium concentration of the distillate and it is important that the same fractional part of samples and standards be discarded. After discarding the first 10 ml of water distillate, collect the next 50 ml of water distillate for tritium analysis. Thoroughly mix the distillate fraction.

7.2.3 Thoroughly mix 4 ml of the distillate with 16 ml of the dioxane scintillator or 10 ml of distillate with 12 ml of Insta-Gel, Handifluor, or Solution G scintillators in a liquid scintillation vial. Three aliquots of the sample distillate should be analyzed for tritium.

7.2.4 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).

7.2.5 Dark-adapt all samples, backgrounds, and standards. Count the samples, backgrounds, and standards. Count samples containing less than 200 pCi/ml for 100 minutes and samples containing more than 200 pCi/ml for 50 minutes.

8. Calibration

8.1 Determination of Recovery and Counting Efficiency Factors

8.1.1 Prepare a tritium standard solution in a 1-liter volumetric flask containing approximately 1000 disintegrations per minute (dpm) per ml. Use low level tritium background raw water (undistilled) and standard tritium activity for preparing this solution. Label this solution "Raw Water Tritium Standard Solution." Distill approximately 600 ml of water, obtained from the same source as above (without tritium activity added). Use this distillate for background tritium corrections. Using the distillate and standard tritium activity, prepare a tritium standard solution in a 500-ml volumetric flask to contain the same activity concentration as the "Raw Water Tritium Standard Solution." Label this solution "Distilled Water Tritium Standard Solution."

8.1.2 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. After discarding the first 10 ml of distillate, collect 50 ml of distillate by the procedure described in paragraph 7.2.1. Mix the distillate fraction. Repeat this distillation step with two more 100-ml aliquots for triplicate analyses.

8.1.3 Azeotropic-benzene-aqueous alkaline permanganate distillation: Place a 100-ml aliquot of the "Raw Water Tritium Standard Solution" in a 500-ml distillation flask. Add 0.5 g of sodium hydroxide, 0.2 g of potassium permanganate, 200 ml of benzene, and a boiling chip. After discarding the first 10 ml of water distillate, collect 50 ml of water distillate by the procedure described in paragraph 7.2.2. Mix the distillate fraction. Repeat the distillation step with two more 100-ml aliquots for triplicate analyses.

8.1.4 Prepare for counting three aliquots of the "Raw Water Tritium Standard Solution" distillate (from step 8.1.2 or 8.1.3), 3 aliquots of the "Distilled Water Tritium Standard Solution," and 3 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 the Instal-Gel, Handifluor, or Solution G scintillator solutions in liquid scintillator vials (glass vials should be used for the Insta-Gel, Handifluor, and Solution G scintillator solutions). Dark-adapt the vials overnight and count in a liquid scintillation counter. Count each vial for 50 minutes.

9. Calculations and Reporting

9.1 Counting Efficiency

$$e = \frac{\text{cpm of Distilled Water Standard - cpm of background}}{\text{dpm of Distilled Water Standard}}$$

9.2 Recovery Correction Factor

$$F = \frac{\text{cpm of Raw Water Standard distillate - cpm of background}}{e \times \text{dpm of Raw Water Standard (before distillation)}}$$

9.3 Sample Tritium Activity

$$A\ (pCi/ml) = \frac{C - B}{2.22 \times e \times V \times F}$$

where C = cpm for sample aliquot

B = cpm for background aliquot

e = counting efficiency, as determined above

V = volume of the sample aliquot in ml

F = recovery factor, as determined above

Error associated with the results of the analysis should also be reported. See Appendix for error and statistical calculations.

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APPENDIX. ERROR AND STATISTICAL CALCULATIONS

Because of the random nature of radioactive disintegrations there is an error associated with any measured count of these disintegrations. The variability of any measurement is indicated by the standard deviation. The standard deviation in the counting rate is determined by the following equation:

$$\sigma\ (R) = \left(\frac{R_o}{t_1} + \frac{B}{t_2}\right)^{\frac{1}{2}}$$

where R_o = gross count rate

t_1 = counting time for the gross count

B = background count rate

t_2 = counting time for the background count

The counting error for a given sample expressed in pCi/ml and at the 95% confidence level is shown by:

$$E = \frac{1.96\sigma(R)}{2.22\ eVF}$$

where 1.96 = 95% confidence factor

2.22 = dpm/pCi

e = efficiency factor, cpm/dpm

V = volume of the aliquot analyzed, in ml

F = recovery factor

The standard deviation of a number of experimental analyses or observations is determined by:

$$S_n = \left[\sum_{i=1}^{m} (n_i - \bar{n})^2/(m - 1)\right]^{\frac{1}{2}}$$

where n = activity (pCi/ml) of a given sample

$\bar{n}$ = mean activity (pCi/ml) of a series of analyses

m = the number replicate analyses

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

A tentative reference method for the measurement of tritium in potable and non-potable environmental water is described. Water samples are treated with sodium hydroxide and potassium permanganate and then a water fraction is separated from interferences by distillation. Two distillation procedures are described, a simple aqueous distillation for samples from potable water sources, and an aqueous-azeotropic-benzene distillation for nonpotable water sources.

Alliquots of a designated distillate fraction are measured for tritium activity by liquid scintillation detection. Distillation recovery and counting efficiency factors are determined with tritium standards. Results are reported in picocuries per milliliter.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
tritium distillation calibrating standards radioactivity radiochemistry quality assurance	reference method liquid scintillation	07B 14B 18B

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