

Tritium

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TRITIUM IN WATER - ACID ELECTROLYSIS
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TRITIUM IN WATER - LIQUID SCINTILLATION COUNTING

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APPLICATION

The procedure is used for the rapid determination of tritium by liquid scintillation (LS) spectrometry. It applies to all clear liquid samples and it can be completed in a short period (1 to 2 h) once efficiency curves have been established. The procedure is designed for a Tri-Carb 2250CA LS counter using Insta-Gel XF cocktail and it requires distillation of the samples so that they are free of salts and other interfering radionuclides.

The ³H spectral range or window setting is first defined. The counting efficiencies are then determined by using efficiency curves (quench curves). The efficiency curve is a plot of the counting efficiency as a function of the quench index parameter (QIP). The QIP is also known as the automatic external standardization (AES) number or the transformed spectral index of the external standard (tSIE). A sample aliquot is prepared with a measured volume of a scintillation cocktail that is then placed in a programmed LS counter for spectrum analysis.

SPECIAL APPARATUS

1. Packard Tri-Carb 2250-CA LS spectrometer
2. Low ⁴⁰K borosilicate glass scintillation vials
3. Glass distillation apparatus
4. Refrigerator
5. Tritium source - sealed 20-mL scintillation vial with cocktail.

6. Carbon-14 source - sealed 20-mL scintillation vial with cocktail.
7. Background source - sealed 20-mL scintillation vial with cocktail.
8. Glass containers - where ³H is of concern to minimize evaporative loss of water.

SPECIAL REAGENTS

1. Standardized solutions of ³H water
2. Insta-gel-XF or equivalent scintillation cocktail
3. 30% H₂O₂
4. Ethanol (95%)
5. Quenching agent - e.g., chloroform, nitromethane, carbon tetrachloride, nitric acid, etc. (**Note:** Some of the quenching agents listed are **highly** toxic and/or are carcinogens, e.g., carbon tetrachloride, and the safety of handling and disposal is the responsibility of the user.)

INTERFERENCES

1. Perform a ³H distillation if information more accurate than gross tritium is needed.
2. Reanalyze samples with excessively high count rates (e.g., > 1,000,000 counts min⁻¹) using less sample material. (**Note:** When using this procedure, the calculated ³H concentration may be higher than the actual concentration because of possible interferences from other low-energy beta emitters and the beta continuum of high-energy beta particles.)
3. Add several drops of 30% H₂O₂ to the vial to bleach the sample if quenching causes the efficiency to drop to one fourth of the highest efficiency. (**Note:** Deep color in the samples may cause severe quenching that will lower the counting efficiency.)

DETERMINATION

A. Window settings. (see **Note 1**)

1. Prepare unquenched ³H standards in the same geometry as the analytical samples. Set the energy regions for ³H (Region A) using the guidance found in the applicable LS counter manual.
2. Optimize the energy regions using the guidance found in the operating manual (the figure of merit is a common way to optimize the regions of interest). Follow Step 3 as an alternate.
3. Perform a spectrum analysis using the ³H standard, and visually adjust the energy range of Region A (0 to 19 keV, ³H) to maximize the count rate and minimize the energy range. A balance between the count rate and the energy range should be obtained (see **Note 2**).

Notes:

1. Determine the ³H window settings before counting the samples and backgrounds.
2. If the sample is not distilled there may be interference from low energy beta particles with the same energy as ³H, as well as from the beta continuum from high energy beta particles.

B. Efficiency as a function of quenching. (see **Note**)

1. Use a small volume (10-50 μ L) of ³H tracer solution that has sufficient activity to give a counting error of < 1%. Prepare approximately 6-8 standards.
2. Record the tracer information (including volume, activity concentration, reference date, etc.). In order to obtain a range of quenching from high to low efficiency, pipette various volumes of the quenching agent (i.e., nitromethane) into vials, separately labeled. The following quenching agent volumes are presented as an example: 0, 0.01, 0.02, 0.03, 0.05, and 0.08 mL. (**Note: Do not** use deionized water to dilute the aqueous standard to a volume consistent with the sample set preparation.)

3. Dispense enough scintillation cocktail into each glass vial to make up the final volumes consistent with the sample set to be analyzed (e.g., 15 mL).
4. Cap and shake vigorously the scintillation vials for 10 to 20 sec. Wipe the vials clean with 95% ethanol and a paper towel. Refrigerate the vials for at least 10 min.
5. Check the stability and operational order of the LS counter before running the standards and the samples. This can be done by: counting the background, the ³H standard, and the ¹⁴C standard provided by the instrument manufacturer; using an appropriate spreadsheet program; and then comparing the count rate of these standards with previously determined standard data according to criteria currently in use.
6. Count a background sample (prepared similarly to the standards) and the ³H standards for 30 min (or until 1% counting statistics are obtained) in the regions selected on the LS counter. Record the corresponding energy regions given by the instrument.
7. Calculate the net count rate for each vial by subtracting the prepared background count rates in Region A from the measured gross count rates in Region A.
8. Determine the beta efficiency (Eff_{β}) for each vial in units of count per min/ disintegrations per min by dividing the net activity measured in counts min⁻¹ by the calculated activity added in dpm. Also, estimate the uncertainty in the β -efficiency, $\epsilon-(Eff)$ for each vial.
9. Generate the β -efficiency curve by plotting $\ln(Eff_{\beta})$ versus the QIP. (**Note:** Many LS counting systems are equipped with programs to generate efficiency curves. To use these applications, the operating manual should be referenced.)
10. Perform a least squares fit on the plot. Record the coefficients (a) and (b) for the equation $Eff = a \exp(b \cdot QIP)$ and the fitting coefficient, R. Obtain the QIP from the intercept [$\ln a$] and the slope [b].

Note: Establish efficiency curves (efficiency vs. QIP) by using artificially quenched standards. Check the efficiency curves annually and regenerate them if any major component of the instrumentation is replaced.

SAMPLE PREPARATION

1. Mark the sample identification on the appropriate scintillation vials with ink that is not removable using ethanol.
2. Pipette a known amount (e.g., 2.0 - 5.0 mL) of each sample into the appropriate scintillation vials.
3. Dispense an appropriate amount (e.g., 15 mL) of scintillation cocktail into each scintillation vial.
4. Secure the cap onto each of the scintillation vials, then shake the vials vigorously for 10 to 20 sec. Wipe each vial on the outside with a paper towel wet with ethanol to remove any fingerprints.
5. Refrigerate the samples for at least 10 min before counting. (**Note:** The samples may also need to be “dark adapted” to minimize the potential for delayed scintillations. This can be accomplished by postponing the start of counting for 10-15 min.)
6. Prepare a background sample in the same manner as the samples. A prepared background sample is one that is developed using stable compounds (e.g., dead water), and has a matrix as similar as possible to that of the samples being analyzed.
7. Count the sample for an appropriate time (e.g., 10 min) in the energy regions specified in **Determination**, Step 7. Record the QIPs given by the instrument. Return the samples to a well-ventilated area and store until disposal when the sample counts are completed.

CALCULATIONS

Perform the calculations internally with the LS software when using the DPM mode, or refer to EPA-600 4-80-032, Method 906.0 (Krieger and Whittaker, 1980).

REFERENCE

Krieger, H. L. and E. L. Whittaker

“Prescribed Procedures for Measurements of Radioactivity in Drinking Water”

U. S. Environmental Protection Agency EPA-600 4-80-032, Method 906.0, August
(1980)