Designation: D7168 – 11$^{\varepsilon 1}$

StandardTest Method for
^{99}Tc in Water by Solid Phase Extraction Disk[1]

This standard is issued under the fixed designation D7168; 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.

ε^1 NOTE—Added research report footnote to Section 16 editorially in June 2013.

1. Scope

1.1 This test method describes a solid phase extraction (SPE) procedure to separate ^{99}Tc from environmental water samples (that is, non-process and effluent waters). Technetium-99 beta activity is measured by liquid scintillation spectrometry.

1.2 This test method is designed to measure ^{99}Tc in the range of approximately 0.037 Bq/L (1.0 pCi/L) or greater for a one litre sample.

1.3 The values stated in SI units are to be regarded as standard. Values given in parentheses are provided for information purposes only.

1.4 This method has been used successfully with tap water. It is the user's responsibility to ensure the validity of this test method for samples larger than 1 L and for waters of untested matrices.

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.* For specific hazard statements, see Section 9.

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 Closed Conduits
D4448 Guide for Sampling Ground-Water Monitoring Wells
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
D6001 Guide for Direct-Push Groundwater Sampling for Environmental Site Characterization
D7282 Practice for Set-up, Calibration, and Quality Control of Instruments Used for Radioactivity Measurements

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D1129.

4. Summary of Test Method

4.1 A measured aliquant of sample is transferred to a beaker. Hydrogen peroxide is added to facilitate the formation of the extractable pertechnetate ion. The sample may be heated to oxidize organics if such are suspected to be present. The entire sample is passed through a technetium-selective SPE disk onto which the pertechnetate is adsorbed. The disk is transferred to a liquid scintillation vial, cocktail added, and the contents well mixed. The beta emission rate of the sample is determined by liquid scintillation spectrometry. Chemical yield corrections are determined by the method of standard additions.

4.2 Minor differences in processing between Extraction Chromatographic Resin Discs and PTFE Membrane Disks are addressed in Variations A and B of the method.

5. Significance and Use

5.1 This method has not been evaluated for all possible matrices. Method suitability should be determined on specific waters of interest.

6. Interferences

6.1 Suspended materials must be removed by filtration or centrifuging prior to processing the sample. Suspended particulate matter in the sample will be physically trapped in part or in whole on or in the SPE extraction material. This may lead to potential inclusion of radionuclide bearing solids or to signal quenching in the liquid scintillation measurement.

6.2 Technetium-99 activity in the sample may overwhelm the signal from the ^{99}Tc spike addition and interfere with accurate determination of chemical yield. Samples for which

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[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.

the unspiked sample count rate exceeds 50 % of the spiked sample count rate should be reprepared with an appropriately adjusted aliquant and spike addition levels to minimize contributions to uncertainty in the determination of the chemical yield.

6.3 Organic compounds present in significant quantities in the sample may degrade the extraction performance of the SPE disk or may lead to elevated levels of quench during liquid scintillation analysis. After the addition of hydrogen peroxide, the sample may be heated to destroy trace organic matter in the sample. If organic components are present in the sample which may survive the peroxide digestion, these may be removed with an appropriate organic removal resin or disk (such as Amberchrom resin or disk) prior to passing the sample through the extraction chromatographic resin disc.

6.4 The disk may retain tritium-labeled compounds. Setting the ^{99}Tc counting window above the maximum energy for the tritium beta particle will eliminate potential tritium interference.

6.5 Elevated levels of nitrates (> 10 000 ppm) will interfere with uptake of ^{99}Tc.

6.6 The higher energy region above the maximum energy for ^{99}Tc should be monitored to help identify cases of significant actinide interference.

6.7 Elevated levels of radionuclides present in anionic form such as iodate, iron (III) and antimony may interfere with measurement of technetium and lead to a positive bias in sample results. Significantly elevated levels of actinides (esp. ^{234}Th decay progeny of uranium) when present in the sample may cause a high bias in the reported ^{99}Tc activity. Manufacturer specific recommendations about interferences should be taken into consideration when determining the applicability of this method for a given matrix.

7. Apparatus

7.1 *Filtering Apparatus,* 47-mm diameter filter apparatus as recommended by the SPE manufacturer.

7.2 *Liquid Scintillation Counter,* with multiple energy region of interest (ROI) capabilities.

7.3 *Scintillation Vials,* 20-mL vials, low potassium glass or plastic, exhibiting suitable optical reproducibility so as not to cause erratic results between samples.

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. Other grades may be used, provided that the reagent is of sufficiently high purity to permit its use without increasing the background of the measurement. Some reagents, even those of high purity, may contain naturally-occurring radioactivity, such as isotopes of uranium, radium, actinium, thorium, rare earths and potassium compounds and/or artificially produced radionuclides. Consequently, when such reagents are used in the analysis of lowradioactivity samples, the activity of the reagents shall be determined under analytical conditions that are identical to those used for the sample. The activity contributed by the reagents may be considered to be a component of background and applied as a correction when calculating the test sample result. This increased background reduces the sensitivity of the measurement.

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 *Radioactive Purity*—Radioactive purity shall be such that the measured radioactivity of blank samples does not exceed the calculated probable error of the measurement.

8.4 *Technetium-Specific Solid Phase Extraction (SPE) Disks or Membranes* (Extraction Chromatographic Resin Discs[3] or PTFE Membrane Disks[3,4]).

8.5 *Hydrochloric Acid, 0.5M*—Add 42 mL concentrated HCl to 400 mL of reagent water. Dilute to 1 L with water.

8.6 *Nitric Acid,* concentrated.

8.7 *Hydrogen Peroxide,* 30 %.

8.8 *Technetium-99* as pertechnetate in water or dilute base solution, traceable to a national standards body (such as NIST in the U.S.).

8.9 *Liquid Scintillation Cocktail*—Commercially prepared LSC cocktail or equivalent.[3,5]

9. Hazards

9.1 Use extreme caution when handling all acids. They are extremely corrosive, and skin contact could result in severe burns.

9.2 When diluting concentrated acids, always use safety glasses and protective clothing, and add the acid to the water.

10. Sampling

10.1 Collect a sample in accordance with Practice D3370, D4448 or D6001.

11. Preservation

11.1 Preservation of samples being analyzed for ^{99}Tc is not required.

11.1.1 Samples may be preserved by freezing. Allow samples to come to ambient temperature prior to processing.

11.1.2 Samples may be processed if they have been previously preserved to pH less than 2 with nitric or hydrochloric acid. It is noted that high concentrations of nitric acid will

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[3] The sole source of supply of the Eichrom TEVA® Discs known to the committee at this time is Eichrom Industries, Inc., Lisle, IL. 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.

[4] 3M Empore™ Tc Rad Disks (3M, St. Paul, MN) have been found satisfactory for this purpose.

[5] Ultima Gold™ LLT (Perkin Elmer Life and Analytical Sciences, 710 Bridgeport Avenue, Shelton, CT 06484-4794) has been found satisfactory for this purpose.

adversely affect chemical yield. Although yield corrections will correct for losses, better results may be obtained by using unpreserved samples.

12. Calibration

NOTE 1—See D7282 for additional details on set-up, calibration and quality control of liquid scintillation counters.

12.1 The fractional detection efficiency ($\varepsilon_{\mathrm{Tc}}$) is determined as outlined in subsequent steps.

12.1.1 Prepare triplicate working calibration source (WCS) adding at least 20 Bq (~540 pCi) of traceable ^{99} Tc in the pertechnetate form to each of three 100 mL portions of reagent water. Each of the three samples is processed using either method variation (A or B), as appropriate.

12.1.2 Collect the effluents from the three WCS. Process the composited solution according to the method to verify that greater than 99 % of the technetium was retained by the SPE material in the calibration runs.

12.1.2.1 If analysis of the combined effluent indicates greater than 1% breakthrough of Tc, the concentration of the WCS activity should be corrected for the losses. If the breakthrough of ^{99}Tc is greater than 5%, the cause for the losses should be identified and new WCS prepared.

12.1.3 An analyte-free aliquant of 100 mL reagent water is also processed as a background subtraction count (BSC).

12.1.4 Count the three vials containing the WCS and the BSC in a liquid scintillation counter for a time sufficient to amass greater than 10 000 counts for each of the WCS.

12.1.5 Calculate the ^{99}Tc Detection Efficiency ($\varepsilon_{\mathrm{Tc}}$) for each of the three vials:

$$\varepsilon_{\mathrm{Tc}} = \frac{R_g - R_{cb}}{A_c} \tag{1}$$

where:

R_g = gross count rate of the vial in the ^{99}Tc count window in counts per second,

R_{cb} = count rate of the BSC associated with the efficiency measurement in the ^{99}Tc count window in counts per second, and

A_c = activity of standard ^{99}Tc added to each vial (Bq).

12.2 Calculate the average, $\bar{\varepsilon}_{\mathrm{Tc}}$, and the relative standard deviation, $s_r(\varepsilon_{\mathrm{Tc}})$, for the three efficiency values. The relative standard deviation of these parameters is used to estimate the relative standard uncertainty of the average efficiency, $u_r(\bar{\varepsilon}_{\mathrm{Tc}})$, as follows:

$$u_r\left(\bar{\varepsilon}_{\mathrm{Tc}}\right) = \sqrt{\frac{s_r^2\left(\varepsilon_{\mathrm{Tc}}\right)}{3} + u_r^2\left(A_c\right)} \tag{2}$$

where:

$u_r(A_c)$ = relative standard uncertainty of the activity of standard ^{99}Tc added to each vial.

12.3 A background subtraction count (BSC) vial consisting of reagent water shall be processed and analyzed with each batch of samples to determine the background count rate in counts per second (R_b) to be used for the calculation of sample results.

13. Procedure

NOTE 2—To minimize the risk of cross-contamination while ensuring reproducibility between the sample and its spiked duplicate, each aliquant-spiked aliquant pair should be run simultaneously and in parallel, using separate dedicated filtration apparatus.

NOTE 3—The sample aliquant is typically 1 L but depending on the activity present and the required detection limit for the analysis, this may vary from 0.1 to several litres.

NOTE 4—A background subtraction count (BSC) consisting of a vial, cocktail and blank disk is performed with each batch to determine the background count rate to be subtracted from each measurement (R_b in Eq 3). If the BSC is to be reused, the user should determine its stability and shelf-life.

13.1 *Method Variation A*—For use with Extraction Chromatographic Resin Discs:

13.1.1 For each sample and OC sample to be processed, transfer duplicate 1 L aliquants of sample to each of two beakers.

13.1.2 Acidify samples to pH 2 with nitric acid, if not done previously.

13.1.3 Add a known quantity (~20 Bq) of a traceable ^{99}Tc solution to the second aliquant of the sample which is labeled as the spiked sample. (See section 6.2 for comment on appropriate spiking level.)

13.1.4 Add 10 mL of 30 % H_2O_2 to each sample while stirring.

13.1.5 If the presence of organic interferences is suspected, heat the sample on a hotplate at approximately 80°C for about 1 hour or until any visible reaction has subsided. Allow the sample to cool to ambient temperature before proceeding with subsequent steps.

13.1.6 Using forceps, carefully position a disc on the filter stand. Secure the funnel reservoir over the disc.

13.1.7 Precondition the disc by allowing 25 mL of water to pass through the disc by gravity. Check the filter funnel for leaks.

13.1.8 Add the sample to the funnel reservoir and allow to pass through the disc by gravity flow (nominal flow rate should not exceed ~100 mL/min). If needed vacuum may be used to maintain adequate flow.

13.1.9 Rinse the disc with 25 mL of 0.5M HCl.

13.1.10 Rinse the disc with 100 mL of water.

13.1.11 Apply vacuum to the filtration apparatus to remove residual liquid from the disc.

13.1.12 Detach the reservoir from the filter apparatus.

13.1.13 Using forceps, remove and carefully roll the disc and transfer to a scintillation vial.

13.1.14 Add 15 mL of liquid scintillation cocktail.

13.1.15 Cap and shake the contents of the vial, to allow the disc to disintegrate. A vortex mixer may be used.

13.1.16 Count the sample test source (STS) in a liquid scintillation counter using an optimized energy window within the range of 20 to 292 keV for a period of time adequate to achieve the required detection limit.

13.2 *Method Variation B*—For use with PTFE Extraction Membranes:

13.2.1 For each sample and QC sample to be processed, transfer duplicate 1 L aliquants of sample to each of two beakers.