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## Standard Guide for the Determination of Technetium-99 in Soil<sup>1</sup>

This standard is issued under the fixed designation C1387; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This guide is intended to serve as a reference for laboratories wishing to perform <sup>99</sup>Tc analyses in soil. Several options are given for selection of a tracer and for the method of extracting the Tc from the soil matrix. Separation of Tc from the sample matrix is performed using an extraction chromatography resin. Options are then given for the determination of the <sup>99</sup>Tc activity in the original sample. It is up to the user to determine which options are appropriate for use, and to generate acceptance data to support the chosen procedure.

1.2 Due to the various extraction methods available, various tracers used, variable detection methods used, and lack of certified reference materials for <sup>99</sup>Tc in soil, there is insufficient data to support a single method written as a standard method.

1.3 ~~The values stated in SI units are to be regarded as standard. No other standard, except where the non-SI unit of molar,  $M$ , units of measurement are included in this is used for the concentration of chemicals and reagents. The values given in parentheses after SI units are provided for information only and are not considered standard.~~

~~1.4 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.~~

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~~1.5 This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.~~

### 2. Referenced Documents

#### 2.1 ASTM Standards:<sup>2</sup>

- C859 Terminology Relating to Nuclear Materials
- C998 Practice for Sampling Surface Soil for Radionuclides
- C999 Practice for Soil Sample Preparation for the Determination of Radionuclides
- D1193 Specification for Reagent Water
- D7168 Test Method for <sup>99</sup>Tc in Water by Solid Phase Extraction Disk

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<sup>2</sup> 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.

D8026 Practice for Determination of Tc-99 in Water by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)  
E11 Specification for Woven Wire Test Sieve Cloth and Test Sieves

### 3. Terminology

3.1 For definitions of terms in this guide, refer to Terminology **C859**.

### 4. Summary of Guide

4.1 There are no stable isotopes of technetium. Technetium-99 is produced by the fission of uranium and plutonium, and has been released to the environment via nuclear weapons testing and nuclear materials processing. In an oxidizing environment, it exists as the very mobile pertechnetate ion,  $\text{TcO}_4^-$ . Technetium-99 is a long-lived (half-life of  $2.1 \times 10^5$  years), weak beta (maximum beta energy of 293 keV) emitting radioisotope.

4.2 For the analysis of  $^{99}\text{Tc}$  in soil, a tracer is added to the sample matrix, or spiked duplicate samples are prepared, and then the Tc is extracted from the soil matrix by one of several methods, including acid leaching or one of various fusion methods. The resulting solution is passed through an extraction chromatography column. Technetium is known to be retained by the extraction chromatography material while most other elements pass through the column. The column is washed with dilute acid to remove any remaining interferents. The resin may then be counted directly by adding it to a liquid scintillation cocktail and counting by liquid scintillation spectrometry, or the Tc may be eluted from the resin for alternative counting or mass spectrometric techniques.

### 5. Significance and Use

5.1 This guide offers several options for the determination of  $^{99}\text{Tc}$  in soil samples. Sample sizes of up to 200 g are possible, depending on the method chosen to extract Tc from the soil matrix. It is up to the user to determine if it is appropriate for the intended use of the final data.

### 6. Interferences

6.1 Any radionuclide not completely removed by the extraction chromatography column that has a beta decay energy similar to or higher than  $^{99}\text{Tc}$  will interfere when counting techniques are used for quantification of the  $^{99}\text{Tc}$  activity.

6.2 Any elements with a mass-to-charge ratio ( $m/z$ ) of 99 (that is, naturally occurring isotope of  $^{99}\text{Ru}$  or other artificially produced elements of sufficient half-life with similar  $m/z$ ) can interfere when using mass spectrometry for quantification of the  $^{99}\text{Tc}$  mass activity. Any element with the same  $m/z$  as the isotope used as an isotope dilution tracer or internal standard will cause a bias in the yield correction. Corrections should be included in the mass spectrometry data reduction for known interferences.

6.3 Additional interferences may be encountered, depending on the tracer and measurement technique chosen. It is up to the user to determine and correct for any additional interferences.

### 7. Apparatus

7.1 *Apparatus for the Extraction of Tc from Sample Matrix:*

7.1.1 See the individual extraction method descriptions to compile a list of the equipment needed for the chosen extraction method.

7.2 *Apparatus for the Purification of Tc from the Soil Extract:*

7.2.1 *Extraction column*—with a bed volume of several milliliters for the extraction chromatography resin.

7.2.2 *Column extension funnels*—that can be added to the extraction column such that a few hundred milliliters of solution can be added to the column at one time.

7.2.3 *Column rack*—holds columns such that several extractions can be performed simultaneously.

7.3 *Apparatus for the Quantification of  $^{99}\text{Tc}$ :*

7.3.1 See the individual detection method descriptions to compile a list of the equipment needed for the chosen detection method.

## 8. Reagents

8.1 *Purity of Reagents*—All chemicals should, at a minimum, be of reagent grade and should conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.<sup>3</sup> High Purity reagents are suggested if mass spectrometry is chosen as the detection method. Other grades of reagents may be used provided it is first determined that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water, as defined by Type I of Specification **D1193**.

8.3 *Tracer:*

8.3.1 *Isotope Dilution Yield Determination:*

8.3.1.1 *Radiometric Yield Determination*—<sup>95m</sup>Tc or <sup>99m</sup>Tc<sup>4</sup> have been used to monitor the chemical yield of the extraction and purification of <sup>99</sup>Tc prior to quantification. [Example: Add ~~10 nCi~~ 370 Bq (10 nCi) of <sup>99m</sup>Tc as a yield tracer when determining yield by gamma spectrometry.]

8.3.1.2 *Mass Spectrometric Yield Determination*—<sup>97</sup>Tc may be produced in a nuclear reactor in very limited quantities to be used as an isotope dilution tracer for the mass spectrometric determination of <sup>99</sup>Tc **(1)**.<sup>5</sup> [Example: Add 1 ng of <sup>97</sup>Tc as a yield tracer for mass spectrometry.]

8.3.1.3 *Rhenium as a Mass Spectrometric Yield Monitor*—The chemical behavior of Re and Tc are similar enough on the extraction resin that Re may be used as a tracer for Tc when using ICP-MS as a detection method **(2)**. Practice **D8026** provides additional information on this option.

8.3.2 *Duplicate Sample Analysis to Monitor Chemical Yield:*

8.3.2.1 Duplicate samples may be analyzed, one spiked with a known amount of <sup>99</sup>Tc and one unspiked. The chemical recovery of the spiked sample is then used to correct the unspiked sample to obtain the original sample activity. (See Test Method **D7168** for an example of this method.)

8.4 *Reagents for the Extraction of <sup>99</sup>Tc from Sample Matrix:*

8.4.1 See the individual extraction method descriptions to compile a list of the reagents needed for the chosen extraction method.

8.5 *Reagents for the Purification of Tc from the Sample Matrix:*

8.5.1 *Extraction Chromatography Resin*—TEVA Resin.

8.5.2 *Prefilter Resin*—a nonionic acrylic ester polymer resin used to remove residual organic matter prior to the extraction chromatography resin column.

8.5.3 *Hydrogen Peroxide*—30 %.

8.5.4 *Nitric Acid*—(16 M HNO<sub>3</sub>) concentrated, specific gravity 1.42.

<sup>3</sup> *Reagent Chemicals, American Chemical Society Specifications, ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, American Chemical Society, Washington, D.C.: 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.; U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

<sup>4</sup> <sup>99m</sup>Tc may be obtained from a local medical pharmacy supplier or other suitable supplier.

<sup>5</sup> The boldface numbers in parentheses refer to the list of references at the end of this standard.

8.5.5 ~~1M~~ 1 M Nitric Acid—Add ~~6364~~ 6364 mL of concentrated HNO<sub>3</sub> (15.7 M, mass fraction of 70.0 %) to 900 mL of ~~DH~~-water, dilute to a final volume of ~~1 liter~~ 1 L.

8.5.6 ~~4M~~ 4 M Nitric Acid—Add ~~250255~~ 250255 mL of concentrated HNO<sub>3</sub> (15.7 M, mass fraction of 70.0 %) to 600 mL of ~~DH~~-water, dilute to a final volume of ~~1 liter~~ 1 L.

## 8.6 Reagents for the Quantification of <sup>99</sup>Tc:

8.6.1 See the individual detection method descriptions to compile a list of the reagents needed for the chosen detection method.

## 9. Procedure

9.1 Collect samples in accordance with Specification C998.

### 9.2 Soil or Sediment Preparation:

9.2.1 Oven dry samples at a temperature not to exceed ~~105°C~~ 105 °C and homogenize in accordance with Specification C999.

9.2.2 *Optional*—Samples may be placed in a muffle oven to decompose organic matter prior to the extraction of Tc. The muffling techniques reported vary significantly (**3-5**). If desired, weigh ~~5–10 g~~ 5 to 10 g of the sample and place in a high temperature crucible. Add the chosen yield monitor and mix the sample. Wet the sample with concentrated ammonium hydroxide and mix, then dry under a heat lamp. It has been found that ammonium hydroxide will prevent the loss of the volatile Tc at higher temperatures. Place the sample in a muffle oven for 24 hours at ~~500°C~~ 500 °C (**5**), or for ~~30–60 minutes~~ 30 minutes to 60 minutes at 600 °C followed by the addition of a few grams of ammonium nitrate and 10 more minutes of heating if traces of carbon remain (**3**).

9.3 *Tc Extraction*—These discussions are summaries from available literature. The user must read the primary reference for a complete discussion of the method prior to its use.

9.3.1 *Acid Leaching*—There are many reported acid leaching techniques in the literature (**3, 4, 6-10**); however, only those that are easily coupled to the extraction chromatography purification are described in 9.3.1.1 – 9.3.1.4. These methods are summarized in the following four ~~sections~~ sections:

9.3.1.1 Weigh out up to 10 grams of soil to a 250 mL glass beaker along with the desired yield monitor. Cover and heat the sample in the presence of ~~1M~~ 1 M nitric acid. After cooling, remove residual solid matter from the sample by centrifugation. Add hydrogen peroxide and sodium vanadate to each sample to destroy residual organic matter. Finally, reduce the acidity of the sample to less than ~~0.5M~~ 0.5 M using ammonium hydroxide (dilute with water to a final sample volume of approximately 500 mL) (**6**).

9.3.1.2 Add the desired yield monitor to ~~5–10 g~~ 5 to 10 g of sample, which is then ashed using step 9.2.2. Leach the sample twice with hot ~~8M~~ 8 M nitric acid and hydrogen peroxide, combining the leachates. Adjust the pH to 7 with sodium hydroxide and filter the solution through a glass fiber filter. Dilute the filtrate to approximately 500 mL (**7**).

9.3.1.3 Weigh out up to 200 grams of sample. Add the desired yield monitor. Ash using step 9.2.2. Transfer the sample to a decomposition vessel. Add ~~6M~~ 6 M nitric acid. Decompose the sample at ~~100–120°C~~ 100 °C to 120 °C for one hour. Filter the sample through a glass fiber filter then dilute with water until the acid concentration is less than ~~0.5M~~ 0.5 M nitric acid (at least 500 mL) (**8**).

9.3.1.4 Weigh out one gram of the dried, unashed sample to a 250 mL conical flask. Add the desired yield monitor. Add concentrated nitric acid and fit into a reflux condenser. Reflux the sample until the brown fumes cease and all the organic matter is dissolved. Cool the flask and pour the solution into water. Neutralize the solution with sodium hydroxide, filter out any undissolved residue, and dilute with water until the acid concentration is less than ~~0.5M~~ 0.5 M nitric acid and to a final volume of ~~250–500~~ 250 mL to 500 mL (**9**).

9.3.2 *Soil Fusion*—The following two methods have been used for <sup>99</sup>Tc.

9.3.2.1 Weigh out four grams of sample. Add the desired yield monitor and ash using step 9.2.2. When cool, transfer the sample

to a nickel crucible. Add 20 ~~gram~~grams of the flux mixture ( $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$  and  $\text{NaNO}_3$  in a 3.92:5.08:1.00 weight ratio; the flux-to-sample ratio should be 5:1). Start the fusion by heating the crucible with the sample over a burner at high heat. When no further reaction is visible, cover the crucible and place in a muffle oven set at ~~900°C~~900 °C for 30 minutes. Remove the sample from the oven and cool. Cover the crucible with a watch glass and add about 25 mL of water to the crucible to start dissolving the cake. Transfer the solution to a beaker and continue rinsing the crucible with water until all the cake is rinsed into the beaker. Cover the beaker and warm slightly if needed to complete the dissolution. Dilute with water to a final volume of about ~~200–250~~ 200 mL to 250 mL (11).

9.3.2.2 It is suggested that the sample be ground to pass through a 45 ~~micron~~micrometer standard test sieve as defined in Specification E11. This will result in a homogeneous sample with a particle size that can be attacked by the fusion procedure. Weigh out 0.25 gram of sample to a zirconium crucible. Add the desired yield monitor. Add 2.25 gram of sodium peroxide and mix well. Place the crucible in a muffle oven preheated to ~~470°C~~470 °C. Heat for 30 minutes. Remove from the oven. When cool, add about 40 mL of water. Allow the mixture to dissolve for approximately one hour. Add 4 mL of concentrated nitric acid to the crucible and dilute the solution to a final volume of approximately ~~150–200~~ 150 mL to 200 mL with water such that the final acid solution is less than 0.5 M (12).

9.3.3 *Microwave Digestion*—The following two methods have been used for  $^{99}\text{Tc}$ .

9.3.3.1 Weigh out 0.5 gram of sample into a microwave digestion vessel. Add the desired yield monitor to the vessel. Add 20 mL of ~~4M~~ 4 M nitric acid to the vessel and swirl to mix the contents. Place the vessel in a microwave oven and heat at moderate power for ~~30–60~~ 30 minutes to 60 minutes. Let the vessels cool completely before venting and opening. Pour the solution to a beaker. Rinse the vessel with water and add to the sample beaker. Dilute to a final volume of ~~200–250~~ 200 mL to 250 mL such that the final acid solution is less than ~~0.5M~~ 0.5 M (13).

9.3.3.2 Weigh out up to 0.5 gram of sample to a tared Teflon<sup>®</sup>PTFE liner. Add the desired yield monitor to each sample. Add 10 mL of concentrated nitric acid to each sample. Allow the samples to predigest in the open vessel for at least 15 minutes. Place the Teflon<sup>®</sup>PTFE liners into the microwave digestion vessels and place in the microwave oven in accordance with the manufacturers specifications. Heat the samples in stages up to a maximum of ~~200°C and 600 psi~~ 200 °C and 4.1 MPa (600 psi). Allow the samples to cool to less than ~~30 psi and 80°C~~ 0.2 MPa (30 psi) and 80 °C. Manually vent the vessel and transfer the sample solution to a labeled container with water. Any undigested residue is removed by centrifugation. Dilute the final solution with water such that the final acid concentration is less than ~~0.5M~~ 0.5 M in nitric acid, about 350 mL mL (14).

#### 9.4 *Tc Purification by Extraction Chromatography Separation* (6):

9.4.1 Place a column in the column rack for each sample to be analyzed. Prefilled extraction chromatography columns are available or add about 2 mL of extraction resin to a standard column geometry. For samples containing residual organic matter, it is recommended to place a prefilter resin column in series prior to the extraction chromatography column.

9.4.2 Condition each extraction column by adding 5 mL of ~~0.1M~~ 0.1 M nitric acid to each column, and allow to drain.

9.4.3 Add the column extension funnels to each column and then pour the solution obtained above in the Tc extraction section through the columns. Solution volumes of ~~100~~ 100 mL to over 500 mL are generated by the Tc extraction procedures above. Technetium will be retained by the extraction chromatography resin at volumes up to ~~1 L~~ 1 L as long as the acidity of the solution is less than ~~0.5M~~ 0.5 M  $\text{HNO}_3$ . Rinse the sample container with a few mL milliliters of water and add to the column reservoir.

9.4.4 Allow the entire sample to pass through the column, then rinse only the extraction column with ~~25–50~~ 25 mL to 50 mL of ~~1M~~ 1 M nitric acid.<sup>6</sup>

9.4.4.1 If radiometric detection is planned for the final activity determination, the following steps are recommended to address elution of other potential beta emitters (for example,  $^{234}\text{Th}$ ) from the resin. These steps should be used in lieu of the ~~1M~~ 1 M  $\text{HNO}_3$  wash in step 9.4.4.

(1) Rinse the extraction column with 5 mL of 0.01 M  $\text{HNO}_3$ .

(2) Rinse the extraction column with 25 mL of ~~0.5M~~ 0.5 M HF/0.02M  $\text{HNO}_3$  or 40 mL of ~~0.25M~~ 0.25 M NaF/0.02M NaF/0.02 M  $\text{HNO}_3$  or 25 mL of ~~1M~~ 1 M NaF/0.02M NaF/0.02 M  $\text{HNO}_3$ .

9.4.5 Rinse the extraction column with 5 mL of ~~0.1M~~ 0.1 M  $\text{HNO}_3$ .

<sup>6</sup> 25 mL of wash acid is sufficient for most counting techniques; however, 50 mL is suggested for mass spectrometry techniques.