



Standard Guide for the Determination of Technetium-99 in Soil¹

This standard is issued under the fixed designation C 1387; 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.

1. Scope

1.1 This document is intended to serve as a reference for laboratories wishing to perform Tc-99 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 Tc-99 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 Tc-99 in soil, there is insufficient data to support a single method written as a standard method.

2. Referenced Documents

2.1 ASTM Standards:

C 998 Sampling Surface Soil for Radionuclides²

C 999 Soil Sample Preparation for the Determination of Radionuclides²

D 1193 Standard Specification for Reagent Water³

E 11 Specification for Wire-cloth Sieves for Testing Purposes⁴

3. Summary of Guide

3.1 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, TcO_4^- . Technetium-99 is a long-lived (half-life 213,000 years), weak beta (beta max of 293 keV) emitting radioisotope.

3.2 For the analysis of Tc-99 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.

4. Significance and Use

4.1 This guide offers several options for the determination of Tc-99 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.

5. Interferences

5.1 Any radionuclide not completely removed by the extraction chromatography column that has a beta decay energy similar to or higher than Tc-99 will interfere when counting techniques are used for quantification of the Tc-99 activity.

5.2 Any elements with a mass-to-charge ratio (m/z) of 99 (that is, naturally occurring isotope of Ru-99, or other artificially produced elements of sufficient half-life with similar m/z) can interfere when using mass spectrometry for quantification of the Tc-99 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.

5.3 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.

6. Apparatus

6.1 Apparatus for the Extraction of Tc from Sample Matrix:

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

¹ This guide is under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Test. Current edition approved July 10, 2003. Published August 2003. Originally approved in 1998. Last previous edition approved in 1998 as C 1387-98.

² Annual Book of ASTM Standards, Vol 12.01.

³ Annual Book of ASTM Standards, Vol 11.01.

⁴ Annual Book of ASTM Standards, Vol 14.02.

6.2 Apparatus for the Purification of Tc from the Soil Extract:

6.2.1 *Extraction column*—with a bed volume of several milliliters for the extraction chromatography resin.⁵

6.2.2 *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.

6.2.3 *Column rack*—to hold columns such that several extractions can be performed simultaneously.

6.3 Apparatus for the Quantification of Tc-99:

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

7. Reagents

7.1 *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.⁶ 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.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water, as defined by Type I of Specification D 1193.

7.3 Tracer:

7.3.1 Isotope Dilution Yield Determination:

7.3.1.1 *Radiometric Yield Determination*—Tc-95m⁷ or Tc-99m⁸ have been used to monitor the chemical yield of the extraction and purification of Tc-99 prior to quantification. [Example: Add 10 nCi of Tc-99m as a yield tracer when determining yield by gamma spectrometry.]

7.3.1.2 *Mass Spectrometric Yield Determination*—Tc-97 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 Tc-99 (1).⁹ [Example: Add 1 ng of Tc-97 as a yield tracer for mass spectrometry.]

7.3.2 Duplicate Sample Analysis to Monitor Chemical Yield:

7.3.2.1 Duplicate samples may be analyzed, one spiked with a known amount of Tc-99 and one unspiked. The chemical recovery of the spiked sample is then used to correct the unspiked sample to obtain the original sample activity.

⁵ Prepacked columns from EICRoM Technologies (Darien, IL) or BioRad (Richmond, CA) poly prep columns have been found satisfactory for this purpose.

⁶ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, D. C. For suggestions on the testing of reagents not listed by the American Chemical Society, Washington, D. C. 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., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention (USPC), Rockville, MD.

⁷ Tc-95m may be obtained from Analytics, Inc., Atlanta, GA, or other suitable supplier.

⁸ Tc-99m may be obtained from a local medical pharmacy supplier or other suitable supplier.

⁹ The boldface numbers in parentheses refer to the list of references at the end of this standard.

7.4 Reagents for the Extraction of Tc-99 from Sample Matrix:

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

7.5 Reagents for the Purification of Tc from the Sample Matrix:

7.5.1 *Extraction Chromatography Resin*—TEVA Resin.¹⁰

7.5.2 *Prefilter Resin*—a nonionic acrylic ester polymer resin used to remove residual organic matter prior to the extraction chromatography resin column.¹¹

7.5.3 *Hydrogen Peroxide*—30 %.

7.5.4 *Nitric Acid*—(HNO₃) concentrated, specific gravity 1.42.

7.5.5 *1M Nitric Acid*—Add 63 mL of high purity HNO₃ to 900 mL of DI water, dilute to a final volume of 1 liter.

7.5.6 *4M Nitric Acid*—Add 250 mL of high purity HNO₃ to 600 mL of DI water, dilute to a final volume of 1 liter.

7.6 Reagents for the Quantification of Tc-99:

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

8. Procedure

8.1 Collect samples in accordance with Specification C 998.

8.2 Soil or Sediment Preparation:

8.2.1 Oven dry samples at a temperature not to exceed 105°C and homogenized in accordance with Specification C 999.

8.2.2 *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 (2-4). If desired, it is suggested that 5–10 g of the sample be weighed 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 (4), or for 30–60 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 (2).

8.3 *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.

8.3.1 *Acid Leaching*—There are many reported acid leaching techniques in the literature (2, 3, 5-9); however, only those that are easily coupled to the extraction chromatography purification are described in 8.3.1.1-8.3.1.4. These methods are summarized in the following four sections

8.3.1.1 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 nitric acid. After cooling, remove residual solid matter from the sample by centrifugation. Add

¹⁰ TEVA Resin from EICRoM Technologies has been found satisfactory for the purposes listed. No other commercial sources of equivalent material are known.

¹¹ Prefilter columns are available from EICRoM Technologies or Amberchrom GC-71CD resin has been found satisfactory for this purpose.

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 using ammonium hydroxide (dilute with water to a final sample volume of approximately 500 mL) (5).

8.3.1.2 Add the desired yield monitor to 5–10 g of sample, which is then ashed using step 8.2.2. Leach the sample twice with hot 8M 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 water to approximately 500 mL (6).

8.3.1.3 Weigh out up to 200 grams of sample. Add the desired yield monitor. Ash using step 8.2.2. Transfer the sample to a decomposition vessel. Add 6M nitric acid. Decompose the sample at 100–120°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 nitric acid (at least 500 mL) (7).

8.3.1.4 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 to a final volume of approximately 250–500 mL (8).

8.3.2 *Soil Fusion*—The following two methods have been used for Tc-99.

8.3.2.1 Weigh out four grams of sample. Add the desired yield monitor and ash using step 8.2.2. When cool, transfer the sample to a Ni crucible. Add 20 gram of the flux mixture (Na_2CO_3 , K_2CO_3 and 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 over set at 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 mL (10).

8.3.2.2 It is suggested that the sample be ground to pass through a 45 micron standard test sieve as defined in Specification E 11. 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 Zr 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. 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 mL with water (11).

8.3.3 *Microwave Digestion*—The following two methods have been used for Tc-99.

8.3.3.1 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 nitric acid to the bomb and swirl to mix the contents. Place the bomb in a microwave and heat at moderate power for 30–60 minutes.¹² 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 mL such that the final acid solution is less than 0.5M (12).

8.3.3.2 Weigh out up to 0.5 gram of sample to a tared Teflon 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 liners into the microwave digestion vessels and place in the microwave oven¹³ in accordance with the manufacturers specifications. Heat the samples in stages up to a maximum of 200°C and 600 psi. Allow the samples to cool to less than 30 psi and 80°C. The vessels are manually vented and the sample solution transferred 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 in nitric acid, about 350 mL (13).

8.4 *Tc Purification by Extraction Chromatography Separation* (5):

8.4.1 Place a column in the column rack for each sample to be analyzed. Prefilled extraction chromatography columns are available⁵ 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.

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

8.4.3 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 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 1L as long as the acidity of the solution is less than 0.5M HNO_3 . Rinse the sample container with a few mL of water and add to the column reservoir.

8.4.4 Allow the entire sample to pass through the column, then rinse only the extraction column with 25–50 mL of 1M nitric acid.¹⁴

8.4.4.1 *If the resin is to be counted directly by liquid scintillation spectrometry*, rinse the column with 2 mL of 0.1M nitric acid to reduce the acidity on the column prior to adding the extraction resin to the liquid scintillation cocktail.

8.4.4.2 *If the sample is to be analyzed by beta proportional techniques or mass spectrometry techniques*, elute the technetium to a clean beaker by passing 30 mL of 4M nitric acid through the column or only 20 mL of 8–12M nitric acid through the column.

¹² Heating at 40 % power for 30 minutes has been found satisfactory when four CEM Teflon bombs are used in the CEM microwave oven, the oven having a 600 watt power output.

¹³ A CEM MDS-2100 Microwave Digestion System has been found satisfactory; this unit consists of a 950 watt microwave power supply, a fluoropolymer coated microwave cavity, a cavity exhaust fan and tubing, a direct drive turntable, and the capacity to monitor pressure and temperature in a closed vessel.

¹⁴ 25 mL of wash acid is sufficient for most counting techniques; however, 50 mL is suggested for mass spectrometry techniques.

8.5 Activity Determination—Liquid scintillation spectrometry (LSC) and inductively coupled plasma mass spectrometry (ICP-MS) are the most common techniques used for determination of the Tc-99 activity in sample; however, beta proportional counting is also possible (14), though not discussed below.

8.5.1 Liquid Scintillation Spectrometry:

8.5.1.1 Transfer the extraction resin to a liquid scintillation vial with a few mL of 0.1M nitric acid or water by inverting the column over a liquid scintillation vial and pushing the resin out from the bottom with the liquid, or by cutting off the bottom of the column and rinsing the resin into the scintillation vial. Add an appropriate amount of liquid scintillation cocktail to fill the vials used. Cap the vial and shake well.

8.5.1.2 Submit the samples along with the appropriate quality control (QC) samples to the counting room for LSC analysis.

8.5.1.3 Set up the scintillation counting window to measure an optimum region to minimize low energy noise and encompass the E_{max} of Tc-99, for example, from 18.6 to 300 keV, or alternate window as desired.

8.5.1.4 If the quenching between samples and QC samples varies greatly, a quench curve should be prepared.

8.5.1.5 Count each sample and QC sample the time required to obtain the counting statistics and detection limit required. Typically, samples are counted 30–150 minutes.

8.5.1.6 If Tc-99m was used as the tracer, an initial LSC count must be made very quickly to determine the yield, and the count repeated after the tracer has decayed.

8.5.1.7 If Tc-95m was used as the tracer, the sample must be counted by gamma spectrometry to determine the chemical yield.

8.5.2 Inductively Coupled Plasma Mass Spectrometry:

8.5.2.1 Refer to the instrument operating manual or other laboratory-specific procedures for setup and calibration procedures for the instrument.

8.5.2.2 Program the instrument to monitor the desired masses and perform the appropriate isotopic abundance corrections.

Example 1: Tc-97 used as an isotope dilution yield monitor—Monitor m/z of 95, 97, 99, 101; m/z 95 is monitored to make corrections to the Tc-97 for any molybdenum interference; m/z 101 is monitored to make corrections to the Tc-99 for any ruthenium interference (1).

Example 2: Rhenium used as an internal standard—Monitor m/z of 99, 101, 187; m/z 101 is monitored to make corrections to the Tc-99 for any ruthenium interference; 187 is monitored as the internal standard to correct for chemical yield, matrix suppression of the sample on the plasma ionizing properties, and any instrument drift in sensitivity (11).

8.5.2.3 Program the instrument to perform the analysis in terms of dwell time, number of passes, number of analyses per sample, etc.

8.5.2.4 Program the instrument to analyze the samples and QC samples as defined by the laboratory or customer requirements.

9. Calculation

9.1 The user should refer to the Reference list for the equations to calculate sample activity and associated error.

9.2 Repeat measurements on (known) samples will be necessary to estimate the precision and bias of the method.

10. Keywords

10.1 extraction chromatography; liquid scintillation spectrometry; mass spectrometry; microwave digestion; soil; soil fusion; technetium

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