



Standard Guide for the Determination of Technetium-99 in Soil¹

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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.

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

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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.

6.2.1 *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 When no tracer is available, 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.

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 *High Purity 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 to 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.

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 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

⁵ Prepacked columns from EICHRM Industries (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 Analytix, 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.

¹⁰ TEVA resin from EICHRM Industries has been found satisfactory for the purposes listed. No other commercial sources of equivalent material are known.

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