



Standard Practice for Determination of Tc-99 in Water by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)¹

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1. Scope

1.1 Technetium is separated and concentrated from a water sample by extraction chromatography using its chemical analog, rhenium, as a tracer. The ratio of technetium to rhenium is measured by inductively coupled plasma mass spectrometry (ICP-MS) to then quantify the ⁹⁹Tc concentration.

1.1.1 This practice is provided as an alternative to Test Method D7168 which provides for a different separation media geometry and measurement by liquid scintillation spectrometry. Similar detection limits should be attainable by this method.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*²

C1387 Guide for the Determination of Technetium-99 in Soil

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

D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

D7168 Test Method for ⁹⁹Tc in Water by Solid Phase Extraction Disk

D7902 Terminology for Radiochemical Analyses

¹ This practice 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.

3. Terminology

3.1 Definitions:

3.1.1 For definitions of terms used in this standard, refer to Terminologies D1129 and D7902.

4. Summary of Practice

4.1 A known quantity of Re is added to a known volume of a filtered water sample. The sample is heated in the presence of peroxide to ensure the Tc and Re are in the oxidized form. The Tc and Re are then extracted from the sample using an extraction chromatography resin loaded in a column.^{3, 4} The resin is rinsed of some co-retained elements and then the Tc and Re are co-eluted from the resin.

4.2 An ICP-MS is used to determine the ratio of Tc relative to the Re tracer; the Re is used as an internal standard to monitor instrument response as well as to correct for chemical yield of the Tc through the column separation.

5. Significance and Use

5.1 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, TcO₄⁻, which is an analog to nitrate and can be taken up by living organisms. Monitoring of ⁹⁹Tc in waters around nuclear processing facilities is part of a complete environmental monitoring program.

5.2 Technetium-99 is a long-lived (half-life 2.1E+5 years), weak beta (maximum beta energy of 293 keV) emitting radioisotope. There are no stable isotopes of Tc. Thus the determination of its activity concentration presents unique challenges to traditional radiochemical determination methods. This method provides an alternative to the spiked/unspiked replicate method of Method D7168 and uses options presented in Guide C1387 for the determination of ⁹⁹Tc in soil.

³ Tagami, K., and Uchida, S., *Analytica Chimica Acta*, Vol 405, 2000, pp. 227–229.

⁴ Kabai, E., Beyermann, M., Seeger, J., Savkin, B. T., Stanglmaier, S., and Hiersche, L., *Applied Radiation and Isotopes*, Vol 81, 2013, pp. 6–41.

6. Interferences

6.1 Any element with a mass-to-charge ratio (m/z) of 99 (that is, naturally occurring isotope of ^{99}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}Tc activity. Any element with the same m/z as the isotope used as an isotope dilution tracer or internal standard, that is, m/z of 185 or 187, will cause a bias in the yield correction. Corrections should be included in the mass spectrometry data reduction for known interferences.

6.2 High levels of nitrate in the sample could lead to saturating the active sites on the resin and cause low recovery of the Tc and Re. They should be equally affected by this and therefore observed as a low signal for the Re in the ICP-MS analysis.

6.3 Most other elements will not be retained by the extraction resin at the low acidity suggested in this practice. The user should determine if any elements exist at high enough concentration to affect the retention of the Tc and Re, and if they cause a bias in the effective retention of the two elements of interest.

7. Apparatus

7.1 *Extraction column*, a standard geometry column to hold ~2 mL of resin and allow connection to an extension funnel.

7.2 *Column extension funnels*, that can be added to the extraction column such that a few hundred mL of solution can be added to the column at one time.

7.3 *Column rack*, holds columns such that several extractions can be performed simultaneously.

7.4 *Vacuum pump, vacuum box, or other vacuum filtration apparatus (optional)*—to facilitate the flow through the column.

7.5 *Inductively Coupled-Plasma Mass Spectrometer*, with all associated hardware and software for sample analysis.

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.⁵ High Purity reagents are suggested when mass spectrometry is the detection method.

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

⁵ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, 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., and the United States Pharmacopeia and National Formulary, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.3 *Extraction chromatography resin*, an aliphatic quaternary amine which is mainly used for Tc analysis as well as for the separation of tetravalent actinides.^{6, 7}

NOTE 1—If using the purchased prepared resin, the large particle size should be used; back extraction from the small particle resin may not be equivalent for the Tc and the Re.

8.4 *Prefilter Resin*, anionionic acrylic ester polymer resin used to remove residual organic matter prior to the extraction chromatography resin column.

8.5 *Hydrogen Peroxide*, 30 %.

8.6 *Nitric Acid (16M HNO₃)*, concentrated, specific gravity 1.42, high purity.

8.7 *1M Nitric Acid*—Add 63 mL of HNO₃ (8.6) to 900 mL of water, dilute to a final volume of 1 L.

8.8 *8M Nitric Acid*—Add 500 mL of HNO₃ (8.6) to 400 mL of water, dilute to a final volume of 1 L.

8.9 *Rhenium tracer solution*, commercially available as a mass spectrometry solution standard, diluted to a known volume to provide the desired mass to the test sample in a convenient delivery volume.

8.10 *Technetium-99 standard solution*, traceable solution, diluted to a useful activity concentration, for method validation and instrument calibration. Available from commercial suppliers of radioactive materials.

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. Procedure

10.1 The following steps are provided as guidance for performing this Practice. The laboratory should define finite values when performing method validation and sample testing.

10.1.1 Collect a water sample according to prescribed methods. The sample should be analyzed within a few days of collection or preserved by refrigeration at less than 6°C, but not freezing, until analysis. The sample should be filtered prior to analysis to remove debris that could adversely impact the column flow.

10.1.2 Transfer a known volume of water, up to 1 L, to a large glass beaker. Add a known amount of Re as the tracer, nominally 10 ng, to the beaker. Add ~10 mL of hydrogen peroxide and heat the sample to ~80°C with stirring for a few

⁶ The sole source in the United States of the Eichrom TEVA resin known to the committee at this time is Eichrom Technologies, LLC, in Lisle, IL, 60532, and it can be purchased from the appropriate vendor based on international location. 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, which you may attend.

⁷ See also Horwitz, P., Dietz, M., Chiarizia, R., Diamond, H., "Separation and preconcentration of actinides by extraction chromatography using a supported liquid anion exchanger: application to the characterization of high-level nuclear waste solutions," *Anal. Chim. Acta*, Vol 310, 1995, pp. 63–78.