Designation: D8026 – 16

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

This standard is issued under the fixed designation D8026; 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 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 $^{99}$Tc 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 $^{99}$Tc in Water by Solid Phase Extraction Disk
D7902 Terminology for Radiochemical Analyses

## 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, $TcO_4^-$, which is an analog to nitrate and can be taken up by living organisms. Monitoring of $^{99}$Tc 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+5years), 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 $^{99}$Tc in soil.

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[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] 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.

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,* anonionic 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 $HNO_3$),* concentrated, specific gravity 1.42, high purity.

8.7 *1M Nitric Acid*—Add 63 mL of $HNO_3$ (8.6) to 900 mL of water, dilute to a final volume of 1 L.

8.8 *8M Nitric Acid*—Add 500 mL of $HNO_3$ (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

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[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.

[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 vender 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.

hours to break down organic matter. Let the sample cool to room temperature prior to the column extraction.

10.1.3 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 dissolved organic matter, it is recommended to place a prefilter resin column in series prior to the extraction chromatography column.

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

10.1.5 Add a column extension funnel to each column and then pour the prepared sample through the columns. Technetium and rhenium will be retained by the extraction chromatography resin at volumes up to 1 L 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.

NOTE 2—A vacuum box or similar apparatus may be used to pull the solution through the column but flow rates should not exceed 5 mL per minute.

10.1.6 Allow the entire sample to pass through the column. If a prefilter column was used it should be removed and discarded in accordance with applicable regulations. Rinse the extraction column with 25–50 mL of 1M nitric acid, under gravity flow rate, or up to 2 mL per minute. This will remove Mo and Ru which are similar in mass to Tc thereby providing a more stable baseline in the Tc mass analysis region.

10.1.7 Place a clean container under the column and elute the Tc and Re with 30 mL of 8 M $HNO_3$.

10.1.8 Reduce the solution volume to near dryness using low heat (~100–120°C). Reconstitute the sample in ~20 mL of 2% nitric acid. (**Warning—**Do not heat the sample to complete dryness as this may result in the volatilization and loss of the Tc.)

## 11. Analysis by Inductively Coupled Plasma Mass Spectrometry

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

11.1.1 Typically a calibration curve will be generated by the analysis of calibration solutions with known and varying amounts of Tc and a constant amount of Re, which is monitored as the internal standard.

11.1.2 Blank correction should not be performed automatically by the instrument.

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

11.2.1 For example, monitor m/z of 99, 101, 185 and 187; m/z 101 is monitored to make corrections to the $^{99}$Tc for any ruthenium interference; 185 and 187 are 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.

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

11.4 When the instrument is programmed to monitor Re as the internal standard it can be programmed to report the Tc concentration in each sample analyzed. When converting the Tc concentration to activity units ensure reference is made to the source used for the half-life of $^{99}$Tc.

## 12. Quality Control

12.1 The following recommendations are based on the requirements of Practice D5847.

12.2 *Initial Demonstration of Laboratory Capability:*

12.2.1 If the laboratory or analyst has not previously performed this method, a precision and bias study must be performed to demonstrate laboratory capability.

12.2.2 Analyze seven replicates of a standard solution prepared from an independent reference material containing $^{99}$Tc spiked at a concentration in the mid-range of the calibration curve. The matrix used for the demonstration should represent a water sample typical for which the method will be used, (for example, surface water). The total dissolved solids of the matrix should approximate the levels expected in normal use.

12.2.3 Calculate the mean and standard deviation of the seven values. The study should be repeated until precision and bias meet desired limits.

12.2.4 Analyze three replicates of a blank solution matrix. The matrix used for the demonstration should represent a water sample typical for which the method will be used (for example, surface water). The total dissolved solids of the matrix should approximate that which may be encountered in normal use.

12.2.5 Calculate the $^{99}$Tc activity for each of these three blank solutions. The study should be repeated until the $^{99}$Tc result of each of the three blank solutions is below one-half the associated MDC.

12.3 *Laboratory Control Sample (LCS):*

12.3.1 To ensure that the test method is in control, analyze an LCS with each batch of no more than 20 samples. The activity added to reagent water should be appropriate for the type of samples analyzed and should produce results of sufficient precision to ensure meaningful assessment of accuracy. The LCS must be taken through all the steps of the analytical method including sample preservation and pretreatment.

12.3.2 The result obtained for the LCS shall fall within the limit of 25 % of the expected value, or meets the desired limits. If the result is not within these limits reporting of the results is halted until the problem is resolved. An indication of the occurrence should accompany the reported results.

12.4 *Method Blank (Blank):*

12.4.1 Analyze a reagent water test blank with each batch of no more than 20 samples. The concentration of analytes found in the blank should be less than the critical level concentration. If the result is not within these limits reporting of the results is halted until the problem is investigated and resolved. An indication of the occurrence should accompany the reported results.

12.5 *Matrix Spike (MS):*

12.5.1 A matrix spike should be performed with each batch of samples. Add a known amount of $^{99}$Tc to a blank sample or a reagent blank, add the Re tracer, and process the matrix spike through the chemical separation steps.

12.5.2 If the resulting calculated $^{99}$Tc activity concentration is not within the desired limits there may be a fractionation of the Tc and Re. Analyses should be halted until the cause is identified and corrected.

12.6 *Duplicate:*

12.6.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch of no more than 20 samples. Document the statistical agreement between the two results to verify the measurement is within the desired limits.

12.6.2 In those cases where there is insufficient sample volume to allow performance of a duplicate sample analysis, a duplicate LCS shall be performed.

12.6.3 If the result is not within these limits reporting of the results is halted until the problem is resolved. An indication of the occurrence should accompany the reported results.

12.7 *Independent Reference Material (IRM):*

12.7.1 In order to verify the quantitative value produced by the test method, analyze an IRM submitted on at least a single-blind basis (if practical) to the laboratory at least once per quarter. The concentration of analyte in the traceable reference material should be appropriate to the typical purpose for which the method is used. The value obtained shall demonstrate acceptable performance as defined by the program or the outside source.

## 13. Precision and Bias

13.1 This practice is provided for users to develop their own precision and bias statements when using this method. As sufficient labs become familiar with the method ASTM International will seek volunteers to participate in an interlaboratory study to develop a precision and bias statement consistent with Practice D2777.

## 14. Keywords

14.1 extraction chromatography; ICP-MS; rhenium; technetium