



Standard Test Method for Determination of Technetium-99 in Uranium Hexafluoride by Liquid Scintillation Counting¹

This standard is issued under the fixed designation C 1539; 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 test method is a quantitative method used to determine technetium-99 (^{99}Tc) in uranium hexafluoride (UF_6) by liquid scintillation counting.

1.2 *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:

C 787 Specification for Uranium Hexafluoride for Enrichment²

C 996 Specification for Uranium Hexafluoride Enriched to Less than 5 % ^{235}U ²

C 1215 Guide for Preparing and Interpreting Precision and Bias Statements in Test Method Standards Used in the Nuclear Industry²

2.2 Other Document:

USEC-651 Uranium Hexafluoride: A Manual of Good Handling Practices³

3. Terminology

3.1 Definitions:

3.1.1 *quench standard curve*—a relationship between sample quench and detection efficiency. A quench curve for an isotope in a given cocktail and vial combination is developed by counting a series of standards containing the same activity of that isotope, but each with different quench. Sample quench is typically quantified by a variety of parameters.

4. Summary of Test Method

4.1 A measured portion of hydrolyzed uranium hexafluoride (UF_6) containing approximately 0.8 to 1.2 g of uranium or a volume of sample less than or equal to 30 mL is transferred to a centrifuge tube. The uranium is precipitated using ammonium hydroxide. After centrifuging, the decanted supernatant is acidified with sulfuric acid and extracted with tributyl phosphate. An aliquot of the extract is transferred to a scintillation vial, where stannous chloride in hydrochloric acid and liquid scintillation cocktail are added. The ^{99}Tc beta activity is then determined by liquid scintillation counting.

5. Significance and Use

5.1 Uranium hexafluoride is a basic material used to prepare nuclear reactor fuel. To be suitable for this purpose, the material must meet the criteria for technetium composition. This test method is designed to determine whether the material meets the requirements described in Specifications C 787 and C 996.

5.2 Using the specified instrumentation and parameters, this method has a lower detection limit of $0.0004\mu\text{gTc/gU}$.

NOTE 1—Different instrumentation or parameters may provide varying detection limits, as calculated in 11.4.

6. Apparatus

6.1 *Liquid Scintillation Counter*⁴, with alpha/beta discrimination and enhanced low level discrimination over the entire energy range of 0 to 2000 keV.

6.2 *Centrifuge*.

6.3 *Analytical Balance*, 1 mg sensitivity.

6.4 *Separatory Funnel*, 125 mL volume.

6.5 *Liquid Scintillation Vials*, 20 mL.

6.6 *Centrifuge Tubes with Caps*, 50 mL.

6.7 *Laboratory Wipes*, lint free disposable.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that

¹ This test method 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.

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² *Annual Book of ASTM Standards*, Vol 12.01.

³ Available from U.S. Enrichment Corporation, 6903 Rockledge Drive, Bethesda, MD 20817.

⁴ Packard Tri-Carb Model 1905 AB/LA has been found to be acceptable.

all reagents conform to the specifications of the Committee of Analytical Reagents of the American Chemical Society where specifications are available.⁵

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean laboratory accepted deionized water.

7.3 *Ammonium Hydroxide* (NH₄OH), concentrated (14.5M).

7.4 *Hydrochloric Acid* (HCl), concentrated (12M).

7.5 *Hydrochloric Acid* (HCl)(1M). Add 82 mL of concentrated (12M) HCl to 900 mL of water, dilute to a final volume of 1000 mL, and mix.

7.6 *Liquid Scintillation Cocktail*⁶.

7.7 *Potassium Permanganate* (KMnO₄), 1 % W/V in water. Dissolve 1 g of KMnO₄ in 100 mL of water, and mix.

7.8 *Stannous Chloride* (SnCl₂), 20 % (W/V) SnCl₂ in concentrated hydrochloric acid. Dissolve 20 g of SnCl₂ in 100 mL of concentrated hydrochloric acid, and mix.

7.9 *Sulfuric Acid* (H₂SO₄), concentrated 18M.

7.10 *Sulfuric Acid* (H₂SO₄). 9M. Add 500 mL concentrated H₂SO₄ (18M) to 400 mL water, dilute to a final volume of 1000 mL, and mix.

7.11 *Sulfuric Acid* (H₂SO₄). 3M. Add 168 mL of concentrated H₂SO₄ (18M) to 800 mL of water, dilute to a final volume of 1000 mL, and mix.

7.12 *Sulfuric Acid* (H₂SO₄). 1M. Add 56 mL of concentrated H₂SO₄ (18M) to 900 mL of water, dilute to a final volume of 1000 mL, and mix.

7.13 *Technetium Standard(s) in a Basic Aqueous Solution*.

7.14 *Tributyl Phosphate* (TBP C₁₂H₂₇O₄P), saturated solution. Equilibrate 500 mL TBP with 500 mL 3M H₂SO₄. Shake for approximately 2 min. Allow to separate and discard aqueous layer.

8. Hazards

8.1 Since UF₆ is radioactive, toxic, and highly reactive, especially when reducing substances and moisture are present (see USEC-651), appropriate facilities and practices must be provided.

9. Procedure

9.1 Transfer an aliquot up to 30 mL of one of the following solutions, as applicable, to a 50 mL centrifuge tube:

9.1.1 *Hydrolyzed UF₆ Sample*—Unknown UF₆ sample hydrolyzed in water.

9.1.2 *Standard*—Laboratory control sample with a known ⁹⁹Tc concentration.

9.1.3 *Spike Solution*—UF₆ sample spiked with a known concentration of ⁹⁹Tc (approximately ten times the sample activity).

9.2 Add 2 drops of potassium permanganate solution (1 % W/V) and swirl to mix.

9.3 Dilute with water to approximately 35 mL and swirl to mix.

9.4 Add 5 mL concentrated ammonium hydroxide to precipitate uranium.

9.5 Dilute with deionized water to 50 mL.

9.6 Cap and shake vigorously to break up large particles of ammonium diuranate.

9.7 Centrifuge for approximately 10 min at approximately 1500 rpm.

9.8 Add 25 mL 9M H₂SO₄ to a clean 125-mL separatory funnel.

9.9 Decant the supernatant containing the technetium into the 125-mL separatory funnel.

NOTE 2—The precipitated uranium remains in the centrifuge tube.

9.10 Add 5 mL of TBP solution to the separatory funnel.

9.11 Stopper or cap the funnel and shake for approximately 60 s.

9.12 Allow phases to separate a minimum of 5 min.

9.13 Drain off aqueous (lower) phase into a waste beaker.

9.14 Add 20 mL of 3M H₂SO₄.

9.15 Stopper or cap the funnel and shake for approximately 30 to 45 s.

9.16 Allow phases to separate for a minimum of 5 min.

9.17 Drain off aqueous (lower) phase into a waste beaker.

9.18 Pipette up to 4 mL of the extract from the funnel into a 20 mL scintillation vial.

9.19 Pipette 0.2 mL stannous chloride solution into the vial.

9.20 Pipette 12 mL liquid scintillation cocktail into the vial.

NOTE 3—This test method has proven acceptable for 12 mL of liquid scintillation cocktail, but up to 16 mL can be added depending on the user's instrumentation.

9.21 Cap the vial and shake vigorously for approximately 5 to 10 s.

9.22 Wipe the outside of the vial with a damp laboratory wipe to remove static electricity, if necessary.

9.23 Place the vial in the liquid scintillation counter.

9.24 Allow vial to stand for approximately 15 min prior to counting.

10. Counting

10.1 Program the liquid scintillation counter according to the manufacturer's guidelines.⁷

10.2 Place reagent blank in position one and allow instrument to subtract background counts to obtain net counts per minute (cpm), as needed.

10.3 Count vial for three consecutive 10 min counts, and average (avg).

10.4 Calculate counting efficiency by spiking a known amount of ⁹⁹Tc into vial containing 4 mL of TBP, 0.2 mL of SnCl₂, and 12 mL of liquid scintillation cocktail.

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*, Merck Ltd., Poole, Dorset, U.K. and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD, or equivalent.

⁶ Insta-Gel[®] has been found to be acceptable.

⁷ Packard Tri-Carb Model 1905 AB/LA uses a 0.8 to 293 keV counting window.

$$\frac{\text{Net cpm}}{\text{dpm of the known reference value}} = \text{Efficiency (expressed as a decimal)} \quad (1)$$

where:

dpm = disintegrations per minute

10.5 Convert cpm to dpm for the unspiked samples prior to performing calculations.

$$\text{Avg dpm} = \frac{\text{Avg cpm}}{\text{Efficiency (expressed as a decimal)}} \quad (2)$$

11. Calculations

11.1 Calculate the ^{99}Tc concentration:

$$\frac{\mu\text{g}^{99}\text{Tc}}{\text{gU}} = \frac{A \times \bar{y}}{(B \times \text{Aliq}) \times C \times 37830} \quad (3)$$

where:

A = volume (mL) of TBP added to the separatory funnel in 9.10,

B = uranium concentration in gU/mL of the hydrolyzed UF_6 ,

C = aliquot (mL) of extract taken from the separatory funnel in 9.18,

Aliq = sample (mL) from 9.1.1,

37830 = specific activity of ^{99}Tc in dpm/ $\mu\text{g}^{99}\text{Tc}$, and

\bar{y} = average dpm of sample as obtained in 10.4 and 10.5.

11.2 Manual Calculation of Spike Recovery⁸

$$\text{Spike Recovery (\%)} = \frac{[\text{Spiked Sample(dpm)} - \text{Sample(dpm)}]}{\text{Spike Concentration(dpm)}} \times 100 \quad (4)$$

11.3 Calculate the minimum detectable activity (MDA) when the background and sample run times are equal.

$$\text{MDA} = \frac{[3 + 4.66 \times \sqrt{\text{gross counts}}] \times A}{T \times B \times \text{Aliq} \times C \times 37830 \times K} = \frac{\mu\text{g}^{99}\text{Tc}}{\text{gU}} \quad (5)$$

where:

4.66 = Currie's Factor (a constant to achieve 2 σ error),

T = time in min,

gross counts = background cpm \times T, and

K = counting yield or counting efficiency expressed as a decimal.

NOTE 4—Below is an example of some typical values. Please note that some values will vary depending on the instrumentation used, instrument setup, cocktail used, and lower detection limits.

T = 30 min as designated in 10.3

K = 0.93 to 0.95

B = 0.8 to 1.2 g of uranium or a volume of sample \leq 30 mL

C = 4 mL

11.4 Calculate the minimum detectable activity (MDA) when the background and sample run times are not equal.

$$\text{MDA} = \frac{[3 + 3.29 \times \sqrt{R_b t_g (1 + t_g/t_b)}] \times A}{t_g \times B \times \text{Aliq} \times C \times 37830 K} = \frac{\mu\text{g}^{99}\text{Tc}}{\text{gU}} \quad (6)$$

where:

R_b = background, cpm,

t_g = gross counting time, min, and

t_b = background counting time, min.

12. Precision and Bias

12.1 Data⁹—Data are presented for three ^{99}Tc controls having certified reference values traceable to recognized national standards. The three standards were 229 ± 3.05 dpm ^{99}Tc , 1146 ± 15.24 dpm ^{99}Tc , and 1923 ± 21.92 dpm ^{99}Tc , where the \pm quantities are at the 2 σ error for the reference values. The standard designations, function, reference values and uncertainties are listed in Table 1. The lowest (229 dpm) and highest (1923 dpm) controls were each prepared as a laboratory control sample (LCS) in deionized water to assess the overall process for an inherent bias. In addition, the 1146 dpm ^{99}Tc control was prepared as a spike in UF_6 samples to indicate the appropriateness of the method by measuring ^{99}Tc recovery in UF_6 . The UF_6 samples contained uranium concentrations ranging from 0.0493 to 0.0675 gU/mL and ^{99}Tc concentrations (prior to spiking) ranging from 0.0001 to 0.0301 $\mu\text{g}^{99}\text{Tc/gU}$. Each of the three standards was analyzed over two months by different analysts in the same laboratory resulting in a total of at least 30 test results for each standard. Three different analysts analyzed the 229 dpm ^{99}Tc and 1923 dpm ^{99}Tc laboratory control standards, with five different analysts analyzing the 1146 dpm ^{99}Tc laboratory control sample. The data were used to quantify precision and bias.

12.2 Due to difficulties in movement and ownership of nuclear materials, as referred to in Section 1.4 of Guide C 1215, interlaboratory testing is not practical. The reproducibility was obtained by treating the analysts as different laboratories. This should be taken into account when considering the reproducibility results.

12.3 Precision—Table 2 summarizes the statistical results for precision, giving both the repeatability and reproducibility results obtained using standard analysis of variance (ANOVA) techniques. The absolute standard deviation increases with ^{99}Tc concentration indicating the precision is a function of the test results (in this case, the relative standard deviation is the more appropriate measure of precision). The relative repeatability

⁹ Supporting data, including raw data and statistical analysis, have been filed at ASTM Headquarters and may be obtained by requesting Research Report C26:1009.

TABLE 1 Reference Values

Identity	Function	Value	Uncertainty (2 σ)
SRM 4288A (NIST)	LCS ^A	1923 dpm ^{99}Tc	1.14 %
Amersham Labs ^B	LCS	229 dpm ^{99}Tc	1.33 %
Amersham Labs	UF_6 spike	1146 dpm ^{99}Tc	1.33 %

^A LCS = laboratory control sample.

^B Amersham Laboratories meets quality assurance requirements of Nuclear Regulatory Commission for achieving implicit traceability.

⁸ Spike Recovery is used for Laboratory QA/QC purposes to monitor the quality of the analysis.

TABLE 2 Precision and Bias Test Results

Results	Reference Values			
	229 dpm ⁹⁹ Tc	1146 dpm ⁹⁹ Tc (=0.03724 µgTc/gU) ^A	1923 dpm ⁹⁹ Tc	Average
Sample size	30	36	30	...
Mean	227.6	1045.4 (=0.03396 µgTc/gU)	1934.5	...
SD _r ^B	5.94	22.0	33.3	...
SD _R ^C	5.99	25.2	36.4	...
%RSD _r ^D	2.61 %	2.10 %	1.72 %	2.14 %
%RSD _R ^E	2.63 %	2.40 %	1.88 %	2.30 %
Repeatability limit ^F	7.31 %	5.88 %	4.82 %	6.00 %
Reproducibility limit ^G	7.36 %	6.72 %	5.26 %	6.45 %
% Difference ^H	-0.61 %	-8.80 %	0.60 %	-2.94 %

^A The 1146 dpm⁹⁹Tc control was used as a matrix spike (spiked into the UF₆ sample) and equates to a true value of 0.03724 µgTc/gU (based on 0.0545 gU/mL).

^B SD_r = repeatability standard deviation (single analyst).

^C SD_R = reproducibility standard deviation (different analysts).

^D %RSD_r = relative repeatability standard deviation (percent) = 100*(SD_r/Mean).

^E %RSD_R = relative reproducibility standard deviation (percent) = 100*(SD_R/Mean).

^F Repeatability limit = 2.8 %RSD_r. This represents the 95 % confidence limits for the difference between two measurements taken by the same analyst.

^G Reproducibility limit = 2.8 %RSD_R. This represents the 95 % limits for the difference between two measurements obtained by different analysts.

^H % Difference = 100*[(Mean-reference value)/reference value].

standard deviation (single analyst) has been determined to be 2.14 % (averaged over the three standards) while the reproducibility standard deviation (between analysts) was determined to be 2.30 % in the same manner. The between analysts variation was not statistically significant at the 99 % level.

12.4 *Bias*—Table 2 also summarizes the statistical results for bias estimation. The relative difference of the mean result on each standard from its reference value, averaged over the

three standards, is -2.94 %, indicating an average recovery of 97.1 % on the standards. This difference is an indication of bias.

13. Keywords

13.1 scintillation counter; technetium-99; uranium hexafluoride

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