



Designation: E 417 - 75

## Standard Method for COLORIMETRIC DETERMINATION OF TECHNETIUM IN AQUEOUS SOLUTIONS<sup>1</sup>

This Standard is issued under the fixed designation E 417; 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.

*This method, which has been superseded by E 321, is being balloted for withdrawal by the sponsoring committee.*

### INTRODUCTION

This method<sup>2</sup> was developed for the determination of technetium in solutions of nuclear fuel that contain radioactive nuclides. The need for this method arose in laboratories of the nuclear energy industry where a wide variety of nuclear-fuel solutions containing technetium are encountered. The tetrapropylammonium-thiocyanate method is described for the determination of technetium in aqueous solutions.

#### 1. Scope

1.1 This method covers quantitative determination of technetium in known volumes of aqueous solutions of nuclear fuel that contain radioactive nuclides. These solutions are from the processing of irradiated nuclear fuel and from the laboratory studies on irradiated nuclear fuel.

1.2 The method as described is applicable to solutions that contain a minimum of 5  $\mu\text{g}$  of technetium per sample, but it will detect as little as 0.4  $\mu\text{g}$ . At concentrations above 200  $\mu\text{g}/\text{ml}$ , dilutions must be made. The absorbance is linear from 1 to 20  $\mu\text{g}$  of technetium in the final solution. The method as described is limited to sample volumes of 2 ml or less, but reagent volumes can be scaled to accommodate larger sample aliquots.

1.3 Photometers and photometric practice prescribed in this method shall conform to ASTM Recommended Practice E 60, for Photometric Methods for Chemical Analysis of Metals.<sup>3</sup>

NOTE 1—The values stated in U.S. customary units are to be regarded as the standard. The metric equivalents of U.S. customary units may be approximate.

#### 2. Summary of Method

2.1 This method is based upon the measurement of the absorbance of the technetium-

thiocyanate complex in chloroform. All the technetium in the measured volume of sample is first oxidized to technetium (VII) by basic hydrogen peroxide. The alkalinity of the solution must be between 2.6 and 3.5  $M$  for quantitative extraction of the technetium-tetrapropyl ammonium ion-association complex into the chloroform solvent. To assure complete extraction and recovery of the technetium, two extractions are necessary with careful washing of the aqueous phase with chloroform. Color development is made in the chloroform phase with the addition of strong sulfuric acid, tetrapropylammonium hydroxide, and potassium thiocyanate. The colored chloroform phase is transferred to a volumetric flask. After diluting to volume, a portion of the solution is placed in a clean 1-cm absorption cell and its absorbance measured against a reagent blank. The colored complex absorbs at 513 nm, has a molar extinction coefficient of 46,000, and is stable for several hours. The concentration of technetium in the

<sup>1</sup>This method is under the jurisdiction of ASTM Committee E-10 on Nuclear Applications and Measurement of Radiation Effects.

Current edition approved Jan. 24, 1975. Published March 1975. Originally published as E 417 - 70 T. Last previous edition E 417 - 70 T.

<sup>2</sup>Foster, R. E., Macek, W. J., and Rein, J. E., *Analytical Chemistry*, ANCHA, Vol. 39, 1967, p. 39.

<sup>3</sup>*Annual Book of ASTM Standards*, Part 12.

sample is determined from two comparison standards bracketing the unknown and processed concurrently, or from a standard curve.

### 3. Interferences

3.1 This method is highly specific for technetium. No metal ion interference has been found from aluminum, vanadium, chromium (III), manganese (II), iron (III), cobalt, nickel, copper, strontium, zirconium, niobium (also known as columbium), molybdenum, ruthenium, rhodium, palladium, silver, cadmium, tin, antimony, lanthanum, tantalum, tungsten, rhenium, platinum, gold, mercury, bismuth, thorium, and uranium. Technetium can be successfully determined in solutions of aluminum-clad uranium fuel, aluminum-uranium alloy fuel, Zircaloy-clad uranium fuel, stainless steel clad uranium fuel, and fissium fuel. The tolerance limit (no interference at the 95 percent confidence limit), expressed as the weight ratio of metal ion to technetium, is greater than  $4.5 \times 10^3$  for aluminum and greater than  $5.3 \times 10^3$  for uranium. The tolerance limit is greater than  $3.5 \times 10^3$  for iron (III) and zirconium, when diethylenetriaminepentaacetic acid (DTPA) is used as a complexing agent during the solvent extraction of technetium. The tolerance limit expressed as the mole ratio of anion to technetium is greater than  $1.2 \times 10^3$  for chloride,  $2.7 \times 10^4$  for fluoride,  $2.2 \times 10^4$  for bromide,  $8.8 \times 10^4$  for sulfate,  $7.2 \times 10^4$  for phosphate,  $2.4 \times 10^4$  for citrate,  $1.0 \times 10^4$  for oxalate,  $1.0 \times 10^4$  for ethylenediaminetetraacetic acid (EDTA), and  $2.4 \times 10^4$  for DTPA. Perchlorate interferes above  $1 \times 10^3$  and nitrate interferes above  $3.1 \times 10^4$ . With greater than 3 millimoles of nitrate in the original sample aliquot, absorbance measurements are low, and the stability of the colored technetium-thiocyanate complex is decreased. The tolerance limit for free acid is 16 meq in the sample aliquot.

### 4. Apparatus

4.1 *Shielded Facility* for sampling, diluting the solution of irradiated fuel, and for extraction of technetium from other fission products.

4.2 *Spectrophotometer*.<sup>4</sup>

4.3 *Absorption Cells*, 1-cm path length.<sup>5</sup>

4.4 *Büchner Funnel*, sintered glass, 15-ml capacity, coarse porosity.

4.5 *Tube Furnace*, 1-in. (25-mm) diameter capable of reaching a temperature of 1112 F (600 C). The furnace should be fitted with a quartz tube which extends 3 in. (75 mm) beyond both ends of the furnace.

4.6 *Quartz Boats*, 2 in. (50 mm) long by  $\frac{1}{2}$  in. (13 mm) wide.

4.7 *Erlenmeyer Flask*, 125 ml, fitted with a  $\frac{29}{32}$  standard-taper joint.

4.8 *Reflux Condenser*, straight-tube, fitted with a  $\frac{29}{32}$  standard taper joint.

### 5. Reagents and Materials

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>6</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to ASTM Specification D 1193, for Reagent Water<sup>7</sup>, Type IV.

5.3 *Chloroform (Density 1.471 to 1.474 at 77 F (25 C))*—Distill the chloroform using a simple flask and condenser. Discard the first one sixth and the last one sixth of the distillate.

5.4 *Diethylenetriaminepentaacetic Acid (DTPA) 0.5 M*—Using water that has been made slightly alkaline with dilute sodium hydroxide, pH 9 to 10, dissolve 19.7 g of DTPA and dilute to 100 ml. Should the DTPA fail to dissolve, add 1 M sodium hydroxide solution dropwise and shake until solution is complete. The final pH of this solution should be 8 to

<sup>4</sup>A Beckman Model DU Spectrophotometer obtainable from Beckman Instruments, Inc., Fullerton, Calif., has been found satisfactory for this purpose.

<sup>5</sup>Absorption cells from American Instrument Co., Silver Spring, Md., have been found satisfactory.

<sup>6</sup>"Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D.C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Roan, D. Van Nostrand Co., Inc., New York, N.Y., and the "United States Pharmacopeia."

<sup>7</sup>Annual Book of ASTM Standards, Parts 20, 21, 22, 29, 31, 37, and 40.



10. If this solution is cloudy, filter using a soft, open, rapid-filtering paper.

5.5 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

5.6 *Hydrogen Peroxide* ( $H_2O_2$ ) (30 Volume percent).

5.7 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid ( $HNO_3$ ).

5.8 *Phenolphthalein Solution*—Dissolve 1 g of phenolphthalein in 50 ml of ethanol and dilute to 100 ml with water.

5.9 *Potassium Thiocyanate Solution* (2 M)—Dissolve 19.42 g of potassium thiocyanate (KSCN) in water and dilute to 100 ml with water.

5.10 *Sodium Hydroxide Solution* (10 M)—Dissolve 400 g of sodium hydroxide (NaOH) pellets in water and dilute to 1 liter with water.

5.11 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid ( $H_2SO_4$ ).

5.12 *Sulfuric Acid* (9 N)—Add 250 ml of concentrated sulfuric acid ( $H_2SO_4$ ) (sp gr 1.84) carefully with stirring to water to make 1 liter.

5.13 *Tank Hydrogen*.

5.14 *Technetium Metal*.<sup>a</sup>

5.15 *Tetrapropyl Ammonium Hydroxide* (10 percent in water) (0.47 M).

## 6. Cell Matching

6.1 Absorption cells should be matched or have correction factors determined within 0.001 absorbance units at the working wavelength of 513 nm.

6.2 Fill two clean cells with a solution prepared by processing a technetium standard as described in Section 7, and place in the spectrophotometer.

6.3 Designate the cell with the lowest absorbance reading as the reference cell.

6.4 Adjust the instrument to 0.000 absorbance reading with the reference cell in position.

6.5 Determine the absorbance value for the other cell. This absorbance value is the cell correction. Subtract this from the sample absorbance readings to give corrected readings.

6.6 Determine these corrections each time samples are analyzed.

## 7. Calibration and Standardization

7.1 *Preparation of Technetium Standard Solution*—The technetium is prepared by the

reduction of chemically pure ammonium pertechnetate (less than 0.1 percent other metal impurities) to the metal with hydrogen (see Note 2). During storage it oxidizes slowly and that material which is sold as metal may contain as much as 5 percent oxygen. For this reason, it must be reduced to the metal with hydrogen prior to its use as an analytical standard.

NOTE 2: Caution—Particularly stringent precautions should be exercised when handling the technetium metal. The radioactive nature of the material ( $1.5 \times 10^{10}$  disintegrations/min·g), the difficulties of detection (ordinary surveying equipment does not respond to its 0.29-MeV beta emissions), and its powdery form combine to make the material particularly difficult to handle. The material should be handled only in a well-ventilated hood and when being handled a program of close surveillance with a thin-windowed beta counter should be carried out to prevent the spread of activity into the laboratory.

7.1.1 Insert the quartz boat into a closable secondary vial and weigh to the nearest 0.1 mg on an analytical balance.

7.1.2 In the hood (see Note 2) remove the boat from the secondary vial and transfer about 100 mg of technetium metal to the boat.

7.1.3 Insert the boat into the quartz furnace tube. **Do not preheat the furnace!**

7.1.4 Pass hydrogen through the furnace tube at the rate of 25 to 50 ml/min. Be sure that the hydrogen is vented to the hood exhaust.

7.1.5 After the hydrogen has been passed through the furnace for about 15 min, bring the furnace temperature to about 1112 F (600 C).

7.1.6 After 6 h, turn off the furnace and allow the furnace to cool to room temperature.

7.1.7 After the furnace has cooled, terminate the hydrogen flow. Remove the boat from the furnace tube, insert the boat into the secondary vial, close the vial, and weigh it to the nearest 0.1 mg on the analytical balance.

7.1.8 Transfer the boat and its contents to the Erlenmeyer flask and attach the reflux condenser.

7.1.9 With cold water circulating through the reflux condenser, add successively 40 ml of concentrated HCl and 10 ml of concentrated  $HNO_3$ . Let stand for 24 h.

<sup>a</sup> Available from Isotope Sales Department, Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830.