Designation: D4785 – 08 (Reapproved 2013)$^{\varepsilon 1}$

Standard Test Method for
Low-Level Analysis of Iodine Radioisotopes in Water[1]

This standard is issued under the fixed designation D4785; 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.

ε^1 NOTE—Warning notes were editorially updated throughout in June 2013.

1. Scope

1.1 This test method covers the quantification of low levels of radioactive iodine in water by means of chemical separation and counting with a high-resolution gamma ray detector. Iodine is chemically separated from a 4-L water sample using ion exchange and solvent extraction and is then precipitated as cuprous iodide for counting.

1.2 The values stated in SI units are to be regarded as standard. The values given in parentheses are provided for information purposes only.

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.* For specific hazard statements, see 8.17, 8.18, 8.19, Section 9, and 13.2.11.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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
D3370 Practices for Sampling Water from Closed Conduits
D3648 Practices for the Measurement of Radioactivity
D3649 Practice for High-Resolution Gamma-Ray Spectrometry of Water
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D1129.

4. Summary of Test Method

4.1 Sodium iodide is added as a carrier prior to performing any chemical separations. The samples undergo an oxidation-reduction process to ensure exchange between the carrier and the radioactive iodide. Hydroxylamine hydrochloride and sodium bisulfite are added to convert all the iodine to iodide which is then removed by anion exchange. Subsequent elution of the iodide is followed by oxidation-reduction to elemental iodine. The elemental iodine is purified by solvent extraction, reduced to iodide, and precipitated as cuprous iodide. The chemical recovery is determined from the recovery of the iodide carrier.

5. Significance and Use

5.1 This test method was developed for measuring low levels of radioactive iodine in water. The results of the test may be used to determine if the concentration of several radioisotopes of iodine in the sample exceeds the regulatory statutes for drinking water. With a suitable counting technique, sample size, and counting time, a detection limit of less than 0.037 Bq/L (1 pCi/L) is attainable by gamma-ray spectroscopy. This method was tested for ^{131}I . Other iodine radioisotopes should behave in an identical manner in this procedure. However, other iodine radioisotopes have not been tested according to Practice D2777. The user of this method is responsible for determining applicability, bias, and precision for the measurement of other iodine radioisotopes using this method.

5.2 This procedure addresses the analysis of iodine radioisotopes with half-lives greater than 2 hours, which include ^{121}I, ^{123}I, ^{124}I, ^{125}I, ^{126}I, ^{129}I, ^{130}I, ^{131}I, ^{132}I, ^{133}I, and ^{135}I.

6. Interferences

6.1 Stable iodine in the sample will interfere with the chemical recovery determination. One milligram of ambient iodine would produce a bias of about −4 %.

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[1] This test method 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.

6.2 There are numerous characteristic iodine X-rays at and below 33.6 keV which are indicative of iodine, but not a specific radioisotope of iodine. It is recommended that only discreet gamma energy lines at and above 35.5 keV be used for identification and quantification of iodine radioisotopes.

7. Apparatus

7.1 *Analytical Balance,* readable to 0.1 mg.

7.2 *Flexible Polyvinyl Chloride (PVC) Tubing,* 6.35 mm (¼ in.) outside diameter, 1-m length.

7.3 *Gamma-Ray Spectrometry System*—High resolution gamma spectrometer (high purity germanium or equivalent) with a useful energy range of approximately 30 keV to 1800 keV (see Practice D3649).

7.4 *Glass Fiber Filter Paper,* 11.5-cm diameter.

7.5 *Ion Exchange Column,* glass tube, 35 ± 2-mm inside diameter, 150-mm length, fitted with No. 8 one-hole rubber stoppers and perforated disk.

7.6 *Membrane Filters,* 0.4 or 0.45-µm pore size, 25-mm diameter, with suitable filter holder and vacuum filter flask.

7.7 *Peristaltic Tubing Pump,* variable speed, fitted with vinyl or silicone tubing.

7.8 *pH Meter.*

7.9 *Sintered Glass Filter,* Büchner funnel, 150-mL size, medium or coarse porosity with suitable one-hole stopper and vacuum filter flask.

7.10 *Vacuum Desiccator.*

7.11 *Vortex Mixer.*

8. Reagents and Materials

8.1 *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.[3] Other grades may be used provided they are of sufficiently high purity to permit their use without reducing the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Specification D1193, Type III.

8.3 *Radioactive Purity*—Radioactive purity shall be such that the measured radioactivity of blank samples does not exceed the calculated probable error of the measurement.

8.4 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide (NH_4OH).

8.5 *Ammonium Hydroxide* (1.4 *M*)—Mix one volume of concentrated NH_4OH (sp gr 0.90) with nine volumes of water.

8.6 *Anion Exchange Resin*—Strongly basic, styrene, quarternary ammonium salt, 20–50 mesh, chloride form, Dowex 1-X8, or equivalent.

8.7 *Cuprous Chloride Solution* (approximately 10 mg CuCl/mL)—Dissolve 10 g of CuCl (99.99 %) in 26 mL of concentrated HCl (sp gr 1.19). Add this solution to 1000 mL of NaCl solution (1 *M*) slowly with continuous stirring. Add a small quantity of metallic copper (for example, 5 to 10 copper metal shot) to the solution for stabilization.[4] Store the CuCl in a desiccator.

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

8.9 *Hydrochloric Acid Solution* (0.3 *M*)—Dilute 25 mL of concentrated HCl to 1000 mL with water.

8.10 *Hydroxylamine Hydrochloride* ($NH_2OH:HCl$)—Crystals.

8.11 *Iodide Carrier Solution* (25 mg I/mL)—Dissolve 14.76 g of NaI in approximately 80 mL of water in a 500-mL volumetric flask and dilute to volume. Standardize using the procedure in Section 10.

8.12 *Iodine-131 Standardizing Solution*—National standardizing body such as National Institute of Standards and Technology (NIST), traceable solution with a typical concentration range from 1 to 10 kBq/mL.

8.13 *Nitric Acid* (sp gr 1.42)—Concentrated HNO_3.

8.14 *Nitric Acid* (1.4 *M*)—Mix 1 volume of concentrated HNO_3 (sp gr 1.42) with 10 volumes of water.

8.15 *Sodium Bisulfite Solution,* (2 *M*)—Dissolve 104.06 g of $NaHSO_3$ in approximately 300 mL of water in a 500-mL volumetric flask and dilute to volume.

8.16 *Sodium Chloride Solution* (1 *M*)—Dissolve 58.45 g of NaCl in approximately 500 mL of water in a 1000 mL volumetric flask and dilute to volume.

8.17 *Sodium Hydroxide Solution* (12.5 *M*)—Dissolve 500 g of NaOH in 800 mL of water and dilute to 1 L. (**Warning—**The dissolution of sodium hydroxide may produce excessive heat.)

8.18 *Sodium Hypochlorite* (NaOCl)—Approximately 5 to 6 %. Commercially available bleach is acceptable. (**Warning—**Acidification of NaOCl produces toxic chlorine gas and must be handled in a fume hood.)

8.19 *Toluene.* (**Warning—**Toluene is a carcinogen and must be handled and disposed of in an approved manner.)

8.20 *Calibration Standard(s)*—Known amounts of ^{125}I, ^{129}I, and ^{131}I are used for calibration when determining these radionuclides. A mixed-gamma standard, for example, ^{241}Am, $_{109}Cd$, ^{57}Co, ^{141}Ce, ^{113}Sn, ^{137}Cs, ^{88}Y, and ^{60}Co, is used for calibration over an extended energy range as required for the

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[3] *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 *Annual 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.

[4] CuCl solution is not stable. It can be oxidized to the Cu^{+2} state by air after a period of time, when the solution will turn dark green. If this happens, prepare a fresh solution. The shelf life of the solution can be extended by displacing the air over the remaining solution with nitrogen or argon gas after each use and then closing the container promptly.

determination of additional radioisotopes of iodine. These standards should be mounted on the filter as described in 7.6. The known amounts of the radionuclides must be traceable to a national standardizing body such as NIST in the USA. The standard may be prepared by the laboratory performing this method or by a commercial supplier of such standards. Alternate radionuclides may be used for calibration provided that they have gamma ray energies covering the range of interest for the iodine radionuclides to be analyzed.

9. Hazards

9.1 Due to the potential health effects from handling these compounds, the steps utilizing NaOCl and toluene must be carried out in a fume hood. Toluene is a carcinogen and acidification of NaOCl liberates toxic Cl_2 gas.

10. Standardization of Iodide Carrier

10.1 Pipet 1.0 mL of iodide carrier reagent into each of five 100-mL centrifuge tubes containing 50 mL of deionized water.

10.2 Add 0.1 mL of 2 *M* $NaHSO_3$ to each solution and stir vigorously using a vortex mixer. Add 5.0 mL of freshly prepared CuCl solution.

10.3 Using a pH meter, check the pH of each solution and adjust the pH to between 2.40 to 2.50 with 0.3 *M* HCl or 1.4 *M* NH_4OH.

10.4 Place each solution in a warm (approximately 50 to 60°C) water bath for 5 to 10 min, stirring occasionally.

10.5 Rinse each CuI precipitate onto a separate preweighed 0.45-µm membrane filter mounted in a vacuum filtration assembly. Rinse the walls of the filter holder with approximately 50 mL of water.

10.6 Dry all samples in a vacuum desiccator for a minimum of 60 min or to constant weight. Remove and weigh the filter and precipitate. Record all data.

10.7 Determine the net weight of each CuI precipitate.

10.8 Use the mean of the five weights for the standard weight. The relative standard deviation of the mean should not exceed 0.025.

11. Calibration of High-Resolution Gamma-Ray Spectroscopy System

11.1 Accumulate an energy spectrum using the calibration standard (8.20) traceable to a national standards body, in the geometrical position representing that of the samples to be analyzed. Accumulate sufficient net counts (total counts minus the Compton baseline) in each full-energy gamma-ray peak of interest to obtain a relative standard counting uncertainty of ≤1 %.

11.2 Using the gamma-ray emission data from the calibration standard and the peak location data from the calibration spectrum, establish the energy per channel relationship (energy calibration) as:

$$En = Offset + (Ch \times Slope) \tag{1}$$

where:

En = peak energy (keV),
$Offset$ = energy offset for the energy calibration equation (keV),
Ch = peak location channel number, and
$Slope$ = energy calibration equation slope (keV per channel).

NOTE 1—Most modern spectroscopy software packages perform this calculation, and may include higher-order polynomial terms to account for minor non-linearity in the energy calibration.

11.3 Using the gamma emission data from the calibration standard and the peak resolution data from the calibration spectrum, establish the resolution versus energy relationship (energy calibration) as:

$$FWHM = Offset + (Ch \times Slope) \tag{2}$$

where:

$FWHM$ = full width of the peak at one-half the maximum counts in the centroid channel (keV),
$Offset$ = width offset for the resolution calibration equation (keV),
En = peak energy (keV), and
$Slope$ = resolution calibration equation slope (keV/keV).

NOTE 2—Most modern spectroscopy software packages perform this calculation, and may include higher-order polynomial terms to account for non-linearity in the resolution calibration.

11.4 For each gamma-ray photopeak, calculate the full-energy peak efficiency, ε_f, as follows:

$$\varepsilon_f = \frac{R_n}{R_\gamma \times DF} \tag{3}$$

where:

ε_f = full-energy peak efficiency (counts per gamma ray emitted),
R_n = net gamma-ray count rate in the full-energy peak of interest, counts per second (s^{-1}),
R_γ = gamma-ray emission rate, in gamma-rays per second (s^{-1}), as of the reference date and time of the calibration standard,
DF = decay factor for the calibrating radionuclide, $e^{-\lambda(t_1-t_0)}$),
λ = (ln 2) / $t_{1/2}$,
$t_{1/2}$ = half-life of calibrating radionuclide (half-life unit must match that used for the time difference, $t_1 - t_0$),
t_0 = reference date and time of the calibration standard, and
t_1 = midpoint of sample count (date and time).

11.5 Many modern spectrometry systems are computerized and the determination of the gamma-ray detection efficiencies is performed automatically at the end of an appropriate counting interval. Refer to the manufacturer instructions for specific requirements and capabilities.

11.6 Plot the values for the full-energy peak efficiency (as determined in Section 11.5) versus gamma-ray energy. Compare the efficiency curve to the typical efficiency curve for the detector type. The curve should be smooth, continuous and have a shape similar to the detector being used. The plot will allow the determination of efficiencies at energies throughout the range of the calibration energies and will show that the algorithms used in computerized systems are providing valid efficiency calibrations. Select the fit that has the best 95 % confidence limit around the fitted curve, has all data points