



## Standard Test Method for Low-Level Iodine-131 in Water <sup>1</sup>

This standard is issued under the fixed designation D 4785; 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 covers the quantification of low levels of iodine-131 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 problems, 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 Note 1, Note 2, Note 7, and Section 9.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 1129 Terminology Relating to Water<sup>2</sup>

D 1193 Specification for Reagent Water<sup>2</sup>

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water<sup>2</sup>

D 3370 Practices for Sampling Water from Closed Conduits<sup>2</sup>

D 3648 Practices for the Measurement of Radioactivity<sup>3</sup>

D 3649 Practice for High-Resolution Gamma-Ray Spectrometry of Water<sup>3</sup>

### 3. Terminology

3.1 **Definitions**—For definitions of terms used in this test method, refer to Terminology D 1129.

### 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 so-

dium bisulfite are added to convert all the iodine to iodide which is then removed by anion exchange. Subsequent elution of the iodide followed by oxidation-reduction yields elemental iodine. The elemental iodine is purified by solvent extraction, reduced to iodide, and precipitated as cuprous iodide. The chemical yield 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 iodine-131 in water. The results of the test may be used to determine if the concentration of iodine-131 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.

### 6. Interferences

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

6.2 Iodine isotopes other than iodine-131 will cause erroneously high results if the activity is determined using beta counting.

### 7. Apparatus

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

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

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

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

7.5 **pH Meter**.

7.6 **Vortex Mixer**.

7.7 **Vacuum Desiccator**.

7.8 **Gamma-Ray Spectrometry System**—high resolution using a high-purity germanium or lithium-drifted germanium detector (see Practice D 3649).

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

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

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.04 on Methods of Radiochemical Analysis.

Current edition approved April 15, 1993. Published June 1993. Originally published as D 4785 – 88. Last previous edition D 4785 – 88.

<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.02.

## 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.<sup>4</sup> 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 D 1193, 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<sub>4</sub>OH).

8.5 *Ammonium Hydroxide* (1 + 9)—Mix one volume of concentrated NH<sub>4</sub>OH (sp gr 0.90) with nine volumes of water.

8.6 *Anion Exchange Resin*—Strongly basic, styrene, quaternary ammonium salt, 20–50 mesh, chloride form, Dowex 1-X8,<sup>5</sup> or equivalent.

8.7 *Cuprous Chloride Solution* (CuCl) (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.<sup>6</sup> Store the CuCl in a desiccator.

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

8.9 *Hydrochloric Acid Solution* (1 + 40) (0.3 M)—Dilute 25 mL of concentrated HCl to 1000 mL with water.

8.10 *Hydroxylamine Hydrochloride* (NH<sub>2</sub>OH: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 *Nitric Acid* (sp gr 1.42)—Concentrated HNO<sub>3</sub>.

8.13 *Nitric Acid* (1 + 10)—Mix 1 volume of HNO<sub>3</sub> (sp gr 1.42) with 10 volumes of water.

8.14 *Sodium Bisulfite Solution* (2 M)—Dissolve 104.06 g of NaHSO<sub>3</sub> in approximately 300 mL of water in a 500 mL volumetric flask and dilute to volume.

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

8.16 *Sodium Hydroxide Solution* (500 g/L)—Dissolve 500 g of NaOH in 800 mL of water and dilute to 1 L.

8.17 *Sodium Hypochlorite* (NaOCl)—Approximately 5 to

6 %. Commercially available bleach is acceptable.

NOTE 1—**Warning:** Acidification of NaOCl produces toxic chlorine gas and must be handled in a fume hood.

### 8.18 Toluene.

NOTE 2—**Warning:** Toluene is a carcinogen and must be handled and disposed of in an approved manner.

## 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<sub>2</sub> 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<sub>3</sub> 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 to 2.45 using dilute HCl or NH<sub>4</sub>OH.

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. Sampling

11.1 Collect a sample in accordance with Practice D 3370.

## 12. Procedure

### 12.1 Sample Preparation:

12.1.1 Measure or weigh 4 L of the sample into a suitable plastic container. While stirring, add 1.0 mL of I<sup>−</sup> carrier and 5.0 mL of 5 to 6 % NaOCl. Stir approximately 3 to 5 min.

12.1.2 Add 2.0 g of NH<sub>2</sub>OH:HCl, stir, and add 5.0 mL of 2 M NaHSO<sub>3</sub>. Adjust the pH to 6.5 using (500 g/L) NaOH or (1 + 10) NHO<sub>3</sub>. Stir for 30 min.

12.1.3 Filter the sample through a glass fiber filter and discard the residue.

### 12.2 Anion Exchange Separation:

12.2.1 Slurry 100 mL (wet volume) of washed anion exchange resin into a 35-mm inside diameter glass column fitted at the lower end with a one-hole rubber stopper, perforated disk, and a short length of 5-mm glass tubing connecting to the inlet side of the peristaltic pump (see Fig. 1).

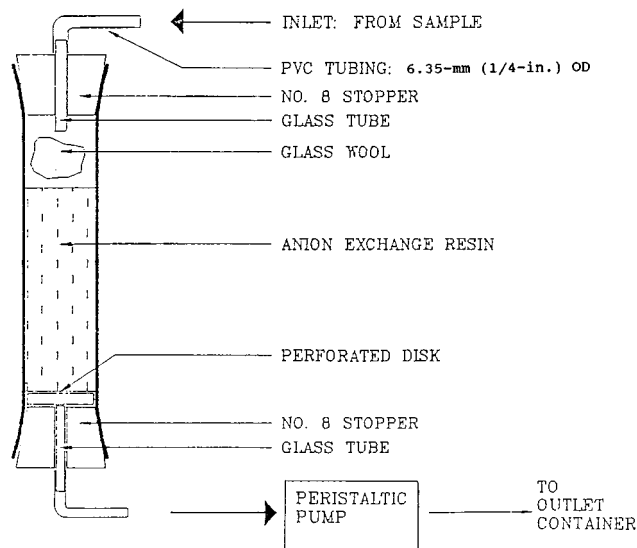
NOTE 3—The resin should be washed with water until the wash water shows no change in pH. This is most conveniently done by batch sequential washing of a relatively large quantity of resin and storing the washed resin as a slurry.

<sup>4</sup> "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., 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, and the "United States Pharmacopeia."

<sup>5</sup> Available from Dow Chemical USA, Midland, MI 48640.

<sup>6</sup> CuCl solution is not stable. It can be oxidized to the Cu<sup>+2</sup> state by air after a period of time, when the solution will turn dark green. If this happens, prepare a fresh solution.

# IODINE PROCEDURE: ION EXCHANGE



**FIG. 1 Iodine Procedure: Ion Exchange**

12.2.2 Leave approximately 25 mL of water on top of the resin bed and insert a glass wool plug, being careful not to touch the resin. Place a one-hole rubber stopper, fitted with a short length of 5-mm glass tubing, in the top of the column and connect it to a 1 m length of flexible PVC tubing.

NOTE 4—If a peristaltic pump is not available, the sample can be passed through the column by gravity flow using an appropriate reservoir.

12.2.3 Pump approximately 100 mL of water through the resin-packed column and check the final effluent pH with pH paper. Repeat the wash if the test indicates residual activity. Be sure to leave approximately 25 mL of water standing on top of the resin bed in the glass column or be certain that the feed tube remains full of water in order to prevent air from entering the resin bed before the sample reaches the column.

12.2.4 Place the flexible PVC inlet tube into the sample container. It may be desirable to attach a 250 to 300 mm length of glass tubing to the sample container end of the PVC to facilitate removal of the sample from the container.

12.2.5 Place the pump discharge tube into a beaker or bottle to collect the column effluent.

12.2.6 Start the pump and vary the speed control to give a flow rate of 40 mL/min.

NOTE 5—It is necessary to calibrate the variable speed control of the peristaltic pump by timing the flow of known liquid quantities at each setting of the control.

12.2.7 When the sample container is empty, remove the upper stopper, and glass wool plug from the top of the column and pour the resin into a 600-mL beaker.

12.2.8 Wash the resin with three successive 100 mL portions of water. Stir briefly and allow the resin to settle to the bottom of the beaker. Decant and discard the wash water.

12.2.9 Place a magnetic stirring bar in the beaker with the washed resin and add 250 mL of 5 to 6 % NaOCl. Place the beaker on a magnetic stirrer and stir for 10 min. Allow the resin to settle. Filter the NaOCl solution by suction through a glass fiber filter supported in a sintered glass Büchner-type funnel.

NOTE 6—The NaOCl solution oxidizes the iodide absorbed on the resin to periodate which is released to the solution.

12.2.10 Add 250 mL of fresh 5 to 6 % NaOCl solution to the resin remaining in the beaker and stir for another 10 min. Allow the resin to settle and filter the NaOCl solution into the Büchner funnel.

12.2.11 Add 50 mL of water solution to the resin remaining in the beaker and stir for 5 min. Filter the solution and resin into the Büchner funnel and rinse the resin thoroughly with water. Transfer the NaOCl solution into a 2000-mL beaker and discard the resin.

NOTE 7—**Precaution:** Chlorine Gas Released. Acidification of the residual NaOCl decomposes it, releasing chlorine gas (green color) which is highly toxic. This destroys residual NaOCl which would interfere in the reduction of iodate to elemental iodine. All subsequent steps through 12.2.16 are to be performed in a well-ventilated fume hood.

12.2.12 In an adequate fume hood, slowly add concentrated HNO<sub>3</sub> (sp gr 1.42) to the NaOCl solution from 12.2.11 until the pH is brought to 1. (Approximately 45 mL of HNO<sub>3</sub> are required.) Stir magnetically until the bulk of the chlorine gas has evolved from the solution.

12.2.13 Pour the acidified solution into a 1000-mL separatory funnel containing 100 mL of toluene and 2 g of NH<sub>2</sub>OH·HCl.

NOTE 8—Hydroxylamine hydrochloride is a mild reducing agent capable of reducing iodate to iodine (I<sup>0</sup>). Iodine is preferentially soluble in the toluene phase and can be separated by solvent extraction. When NH<sub>2</sub>OH·HCl is added, some gas evolution will occur and the solution color will darken (straw to amber) due to the formation of the complex ions I<sub>3</sub><sup>-</sup> (a combination of I<sub>2</sub> and I<sup>-</sup>).

12.2.14 Shake the separatory funnel for a total of 2 min, relieving the pressure occasionally. Allow the phases to separate. Drain off the lower aqueous phase into a second clean 1000-mL separatory funnel containing 2 g of hydroxylamine hydrochloride, and 100 mL of toluene. Allow a few drops of the toluene to drain off with the aqueous phase. Save the toluene in the first separatory funnel.

NOTE 9—It is necessary to relieve the pressure at the beginning of shaking and a few times during the 2-min shaking. As the iodine transfers to the toluene phase, the dark color of the aqueous phase will be replaced by a violet color in the toluene due to dissolved elemental iodine.

12.2.15 Shake the second separatory funnel for 2 min, relieving the pressure occasionally. Allow the phases to separate, and discard the lower aqueous phase (a third extraction can be performed if desired). Combine this toluene with the first toluene fraction in the first separatory funnel.

12.2.16 To the combined toluene in the separatory funnel, add 50 mL of water containing 0.1 mL of 2 M NaHSO<sub>3</sub>. Shake for 2 min. Allow the phases to separate and drain off the lower aqueous phase into a 100-mL centrifuge tube until the toluene phase enters the stopcock bore. Discard the toluene in an appropriate hazardous waste container.

NOTE 10—The NaHSO<sub>3</sub> reduces the iodine to iodide which is not soluble in toluene. The color in the toluene fades rapidly as the iodine is extracted into the aqueous phase. Remove any remaining toluene drops in the centrifuge tube.

## 12.3 CuI Precipitation and Mounting:

12.3.1 Add 5 mL of the CuCl solution and stir thoroughly.

Adjust the pH to between 2.40 to 2.50 with HCl (1 + 40) or NH<sub>4</sub>OH solution as required.

NOTE 11—The proper pH during the CuI precipitation is crucial. A pH of less than 2.4 causes incomplete iodide precipitation. A pH value of greater than 2.6 will cause a yellow to green color to appear in the precipitate and the coprecipitation of some form of the excess copper, resulting in artificially high chemical yields.

12.3.2 Allow the precipitate to stand with occasional mixing for 5 to 10 min.

NOTE 12—12.3.3 through 12.3.6 presuppose that the radioactivity will be determined using gamma-ray spectrometry. Suitable adjustments may be made if beta-gamma coincidence counting is used (see Practice D 3648).

12.3.3 Mount a preweighed filter (0.4 or 0.45 µm pore size or equivalent) on a suction filtration apparatus and filter the CuI precipitate. Wash down the walls of the filter holder and the precipitate with water.

12.3.4 Place the sample into the vacuum dessicator and dry under vacuum for a minimum of 60 min or to constant weight. Remove the sample, weigh it, and record the weight.

12.3.5 Mount the sample for counting in a reproducible geometrical arrangement for which the gamma-ray spectrometry system has been or will be calibrated for counting efficiency.

12.3.6 Using the high resolution gamma-ray spectrometry system, determine the net counting rate for the 364.48 KeV gamma ray line.

### 13. Calculations

13.1 Calculate the concentration,  $X$ , of radioactive iodine-131 corrected to sample time as follows:

$$X = \frac{C}{\epsilon Y V e^{-\lambda t}}$$

where:

$X$  = concentration of iodine-131 in the water, Bq/L (pCi/L),

$C$  = net gamma photopeak counting rate of the sample,

$\epsilon$  = absolute counting efficiency of the counting apparatus, counts per disintegration,

$Y$  = the fraction of the total iodine carrier recovered from the sample, (weight of sample determined in 12.3 divided by the weight of standardized carrier found in 10.8),

$V$  = sample volume, liters,

$\lambda$  = decay constant for iodine-131, days<sup>-1</sup>, and

$t$  = time from sample collection to time of counting in days.

13.2 The absolute counting efficiency is determined as follows:

$$\epsilon = R_c/R_d$$

where:

$R_c$  = net counting rate for the 364.48 KeV gamma ray line of a standard iodine-131 source in the same chemical form and geometrical arrangement as is used for the sample and

$R_d$  = disintegration rate of the standard iodine-131 source at the time of counting.

### 14. Precision and Bias <sup>7</sup>

14.1 The collaborative test conducted of this test method included 6 laboratories each with one operator. Three activity levels between 0.74 Bq/L (20 pCi/L) and 149 Bq/L (4020 pCi/L) were tested with three replicates per level. The determination of the precision and bias statements were made in accordance with D2777.

14.2 These collaborative test data were obtained using reagent grade water.

14.3 The overall precision  $S(T)$  and single-operator precision  $S(O)$  have been found to vary with level in a manner according to Fig. 2.

14.4 The bias of this test method, based upon the collaborative test data, was found to vary with level according to Table 1.

### 15. Keywords

15.1 iodine-131; ion exchange; low-level activity; radioactivity; water

<sup>7</sup> Supporting data are available from ASTM Headquarters. Request Research Report RR:D-19-1136.

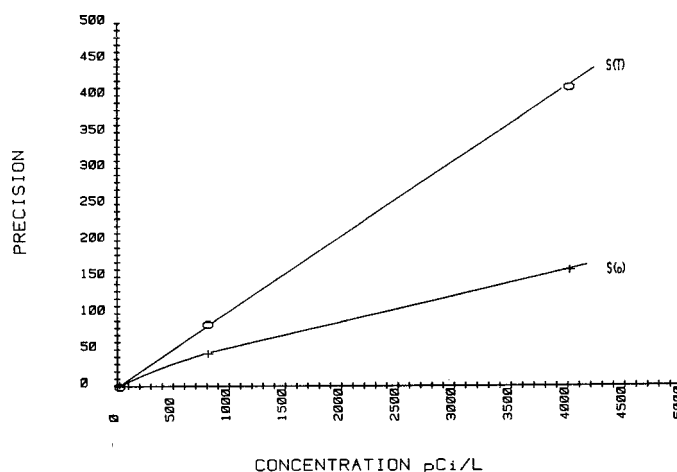


FIG. 2  $S(T)$  and  $S(O)$  versus Concentration

**TABLE 1 Iodine-131 Precision and Bias Data <sup>A</sup>**

Amount Added		Amount Found		Per- cent Bias	Rela- tive Pre- ci- sion
Bq/L	pCi/L	Bq/L	pCi/L		
0.74 ± 0.01	20.2 ± 0.4	0.78 ± 0.12	21.1 ± 3.1	4.4	14.7
30 ± 1	809 ± 17	29.6 ± 4	802 ± 94	- 0.8	11.7
149 ± 9	4020 ± 82	152 ± 16	4100 ± 426	1.9	10.4

<sup>A</sup> For the 0.74 Bq/L (20 pCi/L) sample, the random uncertainty associated with counting statistics ranged up to 10 % at the 2-sigma level.

*The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.*

*This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 100 Barr Harbor Drive, West Conshohocken, PA 19428.*