Designation: ~~D3557 – 12~~ D3557 – 17

Standard Test Methods for Cadmium in Water[1]

This standard is issued under the fixed designation D3557; 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 These test methods cover the determination of dissolved and total recoverable cadmium in water and wastewater by atomic-absorption spectrophotometry and differential pulse anodic stripping voltammetry.[2] Section 44 on Quality Control pertains to these test methods. Four test methods are included as follows:

	Concentration Range	Sections
Test Method A—Atomic Absorption, Direct	0.05 to 2.0 mg/L	7 to 15
Test Method B—Atomic Absorption, Chelation-Extraction	5 to 200 µg/L	16 to 24
Test Method C—Differential Pulse Anodic Stripping Voltammetry	1 to 100 µg/L	25 to 34
Test Method D—Atomic Absorption, Graphite Furnace	2 to 10 µg/L	35 to 43

	~~Concentration Range~~	~~Sections~~
~~Test Method A—Atomic Absorption, Direct~~	~~0.05 to 2.0 mg/L~~	~~7 to 15~~
~~Test Method B—Atomic Absorption, Chelation-Extraction~~	~~5 to 200 µg/L~~	~~16 to 24~~
~~Test Method C—Differential Pulse Anodic Stripping Voltammetry~~	~~1 to 100 µg/L~~	~~25 to 34~~
~~Test Method D—Atomic Absorption, Graphite Furnace~~	~~2 to 10 µg/L~~	~~35 to 43~~

1.2 Test Method B can be used to determine cadmium in brines. It is the user's responsibility to ensure the validity of these test methods for waters of untested matrices.

1.3 ICP-MS or ICP-AES may also be appropriate but at a higher instrument cost. See Test Methods D5673 and D1976.

1.4 The values stated in ~~either~~ SI units ~~or inch-pound units~~ are to be regarded ~~separately~~ as standard. The values ~~stated~~given in ~~each system are mathematical conversions and may not be exact equivalents; therefore, each system shall be used independently of the other.~~parentheses are mathematical conversion to inch-pound units that are provided for information only and are not considered standard.

1.5 *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.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D858 Test Methods for Manganese in Water

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[1] These test methods are under the jurisdiction of ASTM Committee D19 on Water and are the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

Current edition approved ~~Sept. 1, 2012~~June 1, 2017. Published ~~September 2012~~June 2017. Originally approved in 1977. Last previous edition approved in ~~2007~~2012 as ~~D3557 – 02 (2007)~~D3557~~$^{\varepsilon1}$.~~ – 12. DOI: ~~10.1520/D3557-12.~~10.1520/D3557-17.

[2] Platte, J. A., and Marcy, V. M., "A New Tool for the Water Chemist," *Industrial Water Engineering*, May 1965.

[3] 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.

***A Summary of Changes section appears at the end of this standard**

D1066 Practice for Sampling Steam
D1068 Test Methods for Iron in Water
D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D1687 Test Methods for Chromium in Water
D1688 Test Methods for Copper in Water
D1691 Test Methods for Zinc in Water
D1886 Test Methods for Nickel in Water
D1976 Test Method for Elements in Water by Inductively-Coupled Argon Plasma Atomic Emission Spectroscopy
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
D3558 Test Methods for Cobalt in Water
D3559 Test Methods for Lead in Water
D3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry
D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
D5673 Test Method for Elements in Water by Inductively Coupled Plasma—Mass Spectrometry
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

3. Terminology

3.1 ~~*Definitions*—~~*Definitions:* ~~For definitions of terms used in these test methods, refer to Terminology D1129.~~

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *continuing calibration blank, n*—a solution containing no analytes (of interest) which is used to verify blank response and freedom from carryover.

3.2.2 *continuing calibration verification, n*—a solution (or set of solutions) of known concentration used to verify freedom from excessive instrumental drift; the concentration is to cover the range of calibration curve.

3.2.3 *SCE, n*—saturated calomel electrode.

3.2.4 *spiking solution, n*—the standard solution added to the polarographic cell that is used to quantitate the sample.

3.2.5 *stripping peak potential, n*—the applied potential versus SCE at which the stripping peak current is a maximum.

~~3.2.3 *SCE, n*—saturated calomel electrode.~~

3.2.6 *stripping peak signal, n*—the current measured at the stripping peak maximum for a metal.

3.2.7 *total recoverable metal, n*—a descriptive term relating to the metal forms of cadmium recovered in the acid-digestion procedure specified in these test standards.

4. Significance and Use

4.1 The test for cadmium is necessary because it is a toxicant and because there is a limit specified for cadmium in potable water in the National Interim Primary Drinking Water Regulations. This test serves to determine whether the cadmium content of potable water is above or below the acceptable limit.

5. Purity of Reagents

5.1 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.[4] 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 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193, Type I. Other reagent water types may be used, provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely affecting the bias and precision of the test method. Type II water was specified at the time of round-robin testing of this test method.

6. Sampling

6.1 Collect the samples in accordance with the applicable ASTM standard as follows: Practices D3370 and D1066.

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[4] *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.

6.2 Samples shall be preserved with HNO_3 (sp gr 1.42) to a pH of 2 or less immediately at the time of collection, normally about 2 mL/L of HNO_3. If only dissolved cadmium is to be determined, the sample shall be filtered through a 0.45-µm (No. 325) membrane filter before acidification. The holding time for samples may be calculated in accordance with Practice D4841.

NOTE 1—Alternatively, the pH may be adjusted in the laboratory ~~if the sample is returned within 14 days.~~ within 14 days of collection. However, acid must be added at least 24 hours before analysis to dissolve any metals that adsorb to the container walls. This could reduce hazards of working with acids in the field when appropriate.

TEST METHOD A—ATOMIC ABSORPTION, DIRECT

~~7. Scope~~

~~7.1 This test method covers the determination of dissolved and total recoverable cadmium in most waters and wastewaters.~~

~~7.2 This test method is applicable in the range from 0.05 to 2.0 mg/L of cadmium. The range may be extended to concentrations greater than 2.0 mg/L by dilution of the sample.~~

~~7.3 This test method has been used successfully with reagent grade water, river water, wastewater, ground water, tap water, lake water, and refinery effluent. The information on precision and bias may not apply to other water. It is the user's responsibility to ensure the validity of this test method for waters of other matrices.~~

7. Scope

7.1 This test method covers the determination of dissolved and total recoverable cadmium in most waters and wastewaters.

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7.3 This test method has been used successfully with reagent grade water, river water, wastewater, ground water, tap water, lake water, and refinery effluent. The information on precision and bias may not apply to other water. It is the user's responsibility to ensure the validity of this test method for waters of other matrices.

8. Summary of Test Method

8.1 Cadmium is determined by atomic absorption spectrophotometry. Dissolved cadmium is determined by aspirating a portion of the filtered sample directly with no pretreatment. Total recoverable cadmium is determined by aspirating the sample following hydrochloric-nitric acid digestion and filtration. The same digestion procedure may be used to determine total recoverable nickel (Test Methods D1886), chromium (Test Methods D1687), cobalt (Test Methods D3558), copper (Test Methods D1688), iron (Test Methods D1068), lead (Test Methods D3559), manganese (Test Methods D858), and zinc (Test Methods D1691).

9. Interferences

9.1 Calcium concentrations above 1000 mg/L suppress the cadmium absorption. At 2000 mg/L of calcium the suppression is 19 %.

9.2 Sodium, potassium, sulfate, and chloride (9000 mg/L each), magnesium (4500 mg/L), iron (4000 mg/L), nitrate (100 mg/L), and nickel, lead, copper, zinc, cobalt, and chromium (10 mg/L each), do not interfere.

9.3 Background correction or a chelation-extraction procedure (see Test Method B) may be necessary to determine low levels of cadmium in some waters.

NOTE 2—Instrument manufacturer's instructions for use of the specific correction technique should be followed.

10. Apparatus

10.1 *Atomic Absorption Spectrophotometer,* for use at 228.8 nm.

NOTE 3—The manufacturer's instructions shall be followed for all instrumental parameters. A wavelength other than 228.8 nm may be used if it has been determined to be equally suitable.

10.2 *Cadmium Light Source*—Either cadmium hollow-cathode lamps or multielement hollow-cathode lamps, or electrodeless-discharge lamps.

10.3 *Pressure-Reducing Valves*—The supplies of fuel and oxidant shall be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

11. Reagents and Materials

11.1 *Cadmium Solution, Stock* (1 mL = 1.0 mg Cd)—Dissolve 1.000 g of cadmium metal in a minimum quantity of HNO_3 (sp gr 1.42) and dilute to 1 L. A purchased cadmium stock solution of appropriate known purity is also acceptable.

11.2 *Cadmium Solution, Standard* (1 mL = 0.1 mg Cd)—Dilute 100.0 mL of the cadmium stock solution and 1 mL of HNO_3 (sp gr 1.42) to 1000 mL with water.

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

NOTE 4—If the reagent blank concentration is greater than the method detection limit, distill the HCl or use spectrograde acid. ~~(**Warning—**When HCl is distilled, an azeotropic mixture is obtained (approximately 6 *N* HCl.) Therefore, whenever concentrated HCl is specified for the preparation of a reagent or in the procedure, use double the volume specified if distilled acid is used.)~~

(**Warning—**When HCl is distilled, an azeotropic mixture is obtained (approximately 6 *N* HCl). Therefore, whenever concentrated HCl is specified for the preparation of a reagent or in the procedure, use double the volume specified if distilled acid is used.)

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

NOTE 5—If the reagent blank concentration is greater than the method detection limit, distill the HNO_3 or use a spectrograde acid.

11.5 *Nitric Acid* (1 + 499)—Add 1 volume of HNO_3 (sp gr 1.42) to 499 volumes of water.

11.6 *Oxidant:*

11.6.1 *Air,* which has been passed through a suitable filter to remove oil, water, and other foreign substances is the usual oxidant.

11.7 *Fuel:*

11.7.1 *Acetylene*—Standard, commercially available acetylene is the usual fuel. Acetone, always present in acetylene cylinders, can affect analytical results. The cylinder should be replaced at 345 kPa (50 psi). (**Warning—**"Purified" grade acetylene containing a special proprietary solvent rather than acetone should not be used with poly(vinyl chloride) tubing as weakening of the tubing walls can cause a potentially hazardous situation.)

11.8 *Paper Filter*—Purchase suitable filter paper. Typically the filter papers have a pore size of 0.45-µm membrane. Material such as fine-textured, acid-washed, ashless paper, or glass fiber paper are acceptable. The user must first ascertain that the filter paper is of sufficient purity to use without adversely affecting the bias and precision of the test method.

12. Standardization

12.1 Prepare 100 mL each of a blank and at least four standard solutions to bracket the expected cadmium concentration range of the samples to be analyzed by diluting the standard cadmium solution (11.2) with HNO_3 (1 + 499). Prepare the standards each time the test is to be ~~performed.~~performed or as determined by Practice D4841.

12.2 When determining total recoverable cadmium, add 0.5 mL of HNO_3 (sp gr 1.42) to each blank and standard solution and proceed as directed in ~~13.2~~13.3 through ~~13.4~~13.5. After the digestion of the blank and standard solutions has been completed in ~~13.4~~13.5, return to 12.3 to complete the standardization for total recoverable determinations. When determining dissolved cadmium, proceed with 12.3.

12.3 Aspirate the blank and standards and record the instrument readings. Aspirate HNO_3 (1 + 499) between each standard.

12.4 ~~Prepare~~ Read directly in concentration if this capability is provided with the instrument or measure the absorbance of the standards and prepare an analytical curve by plotting the absorbance versus the concentration for each standard on the instrument software. ~~Alternatively, read directly in concentration if this capability is provided with the instrument.~~

13. Procedure

13.1 An effective way to clean all glassware to be used for preparation of standard solutions or in the digestion step, or both, is by soaking the glassware overnight with HNO_3 (1 + 1) and then rinse with reagent.

13.2 Measure 100.0 mL of a well-mixed acidified sample into a 125-mL beaker or flask.

NOTE 6—If only dissolved cadmium is to be determined, start with ~~13.5~~13.6.

13.3 Add 5 mL of HCl (sp gr 1.19) to each sample.

13.4 Heat the samples (between 65°C and 95°C) on a steam bath or hotplate below boiling in a well-ventilated hood until the volume has been reduced to 15 to 20 mL, making certain that the samples do not boil.

NOTE 7—For samples containing appreciable amounts of suspended matter or dissolved solids, the amount of reduction in volume is left to the discretion of the analyst.

NOTE 8—Many laboratories have found block digestion systems a useful way to digest samples for trace metals analysis. Systems typically consist of either a metal or graphite block with wells to hold digestion tubes. The block temperature controller must be able to maintain uniformity of temperature across all positions of the block. The digestion block must be capable of maintaining a temperature between 65°C and 95°C. For trace metals analysis, the digestion tubes should be constructed of polypropylene and have a volume accuracy of at least 0.5 %. All lots of tubes should come with a certificate of analysis to demonstrate suitability for their intended purpose.

13.5 Cool and filter the samples through a suitable filter (11.8) such as fine-textured, acid-washed, ashless, paper into 100-mL volumetric flasks. Wash the filter paper two or three times with water and adjust to volume.

13.6 Aspirate each filtered and acidified sample and determine its absorbance or concentration at 228.8 nm. Aspirate HNO_3 (1 + 499) between each sample.

14. Calculation

14.1 Calculate the concentration of cadmium in the sample, in milligrams per litre, using the analytical curve prepared in 12.4.

15. Precision and Bias[5]

15.1 The precision of this test method was tested by 17 laboratories in reagent water, river water, wastewater, ground water, tap water, lake water, and refinery effluent. The overall bias and precision of this test method, within its designated range, varies with the quantity being measured in accordance with Table 1.

15.2 These data may not apply to waters of the matrices, therefore, it is the responsibility of the analyst to ensure the validity of the test method in other matrices.

15.3 Precision and bias for this test method conforms to Practice D2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777~~ – 08,~~ – 13, these precision and bias data meet existing requirements for interlaboratory studies of Committee D19 test methods.

TEST METHOD B—ATOMIC ABSORPTION, CHELATION-EXTRACTION

~~16. Scope~~

~~16.1 This test method covers the determination of dissolved and total recoverable cadmium in most waters and brines.~~

~~16.2 This test method is applicable in the range from 5 to 200 µg/L of cadmium. The range may be extended to concentrations greater than 200 µg/L by dilution of the sample.~~

~~16.3 This test method has been used successfully with reagent grade water, river water, wastewater, ground water, tap water, lake water, and refinery effluent. The information on precision and bias may not apply to other water.~~

~~16.4 It is the responsibility of the analyst to determine the acceptability of this test method when analyzing other matrices.~~

16. Scope

16.1 This test method covers the determination of dissolved and total recoverable cadmium in most waters and brines.

16.2 This test method is applicable in the range from 5 to 200 µg/L of cadmium. The range may be extended to concentrations greater than 200 µg/L by dilution of the sample.

16.3 This test method has been used successfully with reagent grade water, river water, wastewater, ground water, tap water, lake water, and refinery effluent. The information on precision and bias may not apply to other water.

16.4 It is the responsibility of the analyst to determine the acceptability of this test method when analyzing other matrices.

17. Summary of Test Method

17.1 Cadmium is determined by atomic absorption spectrophotometry. The element, either dissolved or total recoverable, is chelated with pyrrolidine dithiocarbamic acid and extracted with chloroform. The extract is evaporated to dryness, treated with hot nitric acid to destroy organic matter, dissolved in hydrochloric acid, and diluted to a specified volume with water. A portion of the resulting solution is then aspirated into the air-acetylene flame of the spectrophotometer. The digestion procedure summarized in 8.1 is used to determine total recoverable cadmium. The same chelation-extraction procedure may be used to determine nickel (Test Methods D1886), cobalt (Test Methods D3558), copper (Test Methods D1688), iron (Test Methods D1068), lead (Test Methods D3559), and zinc (Test Methods D1691).

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1030. Contact ASTM Customer Service at service@astm.org.

TABLE 1 Determination of Bias and Precision for Cadmium by Atomic Absorption, Direct

Amount Added, mg/L	Amount Found, mg/L	S_T, mg/L	S_O, mg/L	% Bias	Statistically Significant, 95 % Level
Reagent Water					
0.20	0.200	0.033	0.033	0.0	No
0.60	0.592	0.034	0.026	−1.3	No
1.60	1.521	0.111	0.061	−4.9	Yes
Water of Choice					
0.20	0.200	0.033	0.033	0.0	No
0.60	0.589	0.040	0.026	−1.8	No
1.60	1.511	0.114	0.061	−5.6	Yes

18. Interferences

18.1 See Section 9.

19. Apparatus

19.1 All items of apparatus described in Section 10 are required.

20. Reagents and Materials

20.1 *Bromphenol Blue Indicator Solution* (1 g/L)—Dissolve 0.1 g of bromphenol blue in 100 mL of 50 % ethanol or isopropanol.

20.2 *Cadmium Solution, Stock* (1.0 mL = 1.0 mg Cd)—See 11.1.

20.3 *Cadmium Solution, Intermediate* (1.0 mL = 50 µg Cd)—Dilute 50.0 mL of stock cadmium solution and 1 mL of HNO_3 (sp gr 1.42) to 1 L with water.

20.4 *Cadmium Solution, Standard* (1.0 mL = 0.5 µg Cd)—Dilute 10 mL of cadmium intermediate solution and 1 mL of HNO_3 (sp gr 1.42) to 1 L with water.

20.5 *Chloroform* ($CHCl_3$).

20.6 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl) (see Note 4).

20.7 *Hydrochloric Acid* (1 + 2)—Add 1 volume of HCl (sp gr 1.19) to 2 volumes of water.

20.8 *Hydrochloric Acid* (1 + 49)—Add 1 volume of HCl (sp gr 1.19) to 49 volumes of water.

20.9 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3) (see Note 5).

20.10 *Pyrrolidine Dithiocarbamic Acid-Chloroform Reagent*—Add 36 mL of pyrrolidine to 1 L of $CHCl_3$. Cool the solution and add 30 mL of CS_2 in small portions, swirling between additions. Dilute to 2 L with $CHCl_3$. The reagent can be used for several months if stored in a cool, dark place. (**Warning—**All components of this reagent are highly toxic. Carbon disulfide is also highly flammable. Prepare and use in a well-ventilated hood. Avoid inhalation and direct contact.)

20.11 *Sodium Hydroxide Solution* (100 g/L)—Dissolve 100 g of sodium hydroxide (NaOH) in water, cool, and dilute to 1 L.

20.12 *Materials*—Use materials from 11.6, 11.7~~and~~ , and ~~11.7~~11.8.

21. Standardization

21.1 Prepare a blank and sufficient standard containing from 0.0 to 20 µg of cadmium by diluting 0.0 to 40.0-mL portions of cadmium standard solution to 100 mL with water.

21.2 When determining total recoverable cadmium use 125-mL beakers or flasks, add 0.5 mL of HNO_3 (sp gr 1.42) and proceed as directed in ~~22.2~~22.3 through ~~22.15~~22.16. When determining dissolved cadmium, use 250-mL separatory funnels and proceed as directed in ~~22.5~~22.6 through ~~22.15~~22.16.

21.3 ~~Construct an analytical curve by reading concentrations from the instrument software. Alternatively, read directly in concentration if this capability is provided with the instruments.~~Read directly in concentration if this capability is provided with the instrument or measure the absorbance of the standards and construct an analytical curve by reading absorbances from the instrument software.

22. Procedure

22.1 An effective way to clean all glassware to be used for preparation of standard solutions or in the digestion step, or both, is by soaking the glassware overnight with HNO_3 (1 + 1) and then rinse with reagent.

22.2 Measure a volume of a well-mixed acidified sample containing less than 20.0 µg of cadmium (100-mL maximum) into a 125-mL beaker or flask and adjust the volume to 100 mL with water.

NOTE 9—If only dissolved cadmium is to be determined, measure a volume of filtered and acidified sample containing less than 20 µg of cadmium (100-mL maximum) into a 250-mL separatory funnel, and begin with ~~22.5~~22.6.

22.3 Add 5 mL of HCl (sp gr 1.19) to each sample.

22.4 Heat the samples (between 65°C and 95°C) on a steam bath or hotplate below boiling in a well-ventilated hood until the volume has been reduced to 15 to 20 mL, making certain that the samples do not boil.

NOTE 10—When analyzing brine samples and samples containing appreciable amounts of suspended matter or dissolved solids, the amount of reduction in volume is left to the discretion of the analyst.

NOTE 11—Many laboratories have found block digestion systems a useful way to digest samples for trace metals analysis. Systems typically consist of either a metal or graphite block with wells to hold digestion tubes. The block temperature controller must be able to maintain uniformity of temperature of across all positions of the block. The digestion block must be capable of maintaining a temperature between 65°C and 95°C. For trace metals analysis, the digestion tubes should be constructed of polypropylene and have a volume accuracy of at least 0.5 %. All lots of tubes should come with a certificate of analysis to demonstrate suitability for their intended purpose.

22.5 Cool and filter the samples through a suitable ~~filter,~~ filter (11.8), such as fine-textured, acid-washed, ashless paper, into 250-mL separatory funnels. Wash the filter paper two or three times with water and adjust the volume to approximately 100 mL.

22.6 Add 2 drops of bromphenol blue indicator solution and mix.

22.7 Adjust the pH by addition of NaOH (100 g/L) solution until a blue color persists. Add HCl (1 + 49) by drops until the blue color just disappears; then add 2.5 mL of HCl (1 + 49) in excess. The pH at this point should be 2.3.

NOTE 12—The pH adjustment of ~~22.6~~22.7 may be made with a pH meter instead of using an indicator.

22.8 Add 10 mL of pyrrolidine dithiocarbamic acid-chloroform reagent and shake vigorously for 2 min. (**Warning—**See Note 12.~~Warning)—see Note 12.~~)

22.9 Plug the tip of the separatory funnel with cotton, allow the phases to separate, and drain the $CHCl_3$ phase into a 100-mL beaker.

22.10 Repeat the extraction with 10 mL of $CHCl_3$ and drain the $CHCl_3$ layer into the same beaker.

NOTE 13—If color still remains in the $CHCl_3$ extract, reextract the aqueous phase until the $CHCl_3$ layer is colorless.

22.11 Place the beaker on a hotplate set at low heat or on a steam bath, and evaporate to near dryness. Remove beaker from heat and allow residual solvent to evaporate without further heating. (**Warning—**Perform in a well-ventilated hood.~~Warning)—Perform in a well-ventilated hood.~~)

22.12 Hold the beaker at a 45° angle, and slowly add dropwise 2 mL of HNO_3 (sp gr 1.42), rotating the beaker to effect thorough contact of the acid with the residue.

22.12.1 If acid is added to the beaker in a vertical position, a violent reaction will occur, accompanied by high heat and spattering.

22.13 Place the beaker on a hotplate set at low heat or on a steam bath, and evaporate to near dryness. Remove beaker from heat and allow residual solvent to evaporate without further heating.

22.14 Add 2 mL of HCl (1 + 2) to the beaker, and heat, while swirling for 1 min.

22.15 Cool and quantitatively transfer the solution to a 10-mL volumetric flask and adjust to volume with water.

22.16 Aspirate each sample and record the scale readings or concentrations at 228.8 nm.

23. Calculation

23.1 Determine the weight of cadmium in each sample by referring to the analytical curve. Calculate the concentration of cadmium in micrograms per litre as follows:

$$\text{Cadmium, µg/L} = (1000/A) \times B \qquad (1)$$

where:

~~*1000* = 1000 mL / Liter~~
1000 = 1000 mL / L,
A = volume of original sample, mL, and
B = weight of cadmium in sample, µg.

24. Precision and Bias[5]

24.1 The precision of this test method was tested by seven laboratories in reagent water, river water, waste water, ground water, tap water, lake water, and refinery effluent. The overall precision of this test method, within its designated range, varies with the quantity being measured according to Table 2.

TABLE 2 Determination of Bias and Precision for Cadmium by Atomic Absorption, Chelation-Extraction

Amount Added, µg/L	Amount Found, µg/L	S_T, µg/L	S_O, µg/L	% Bias	Statistically Significant, 95 % Level
Reagent Water					
30	30.6	4.3	3.3	+2.1	No
80	76.9	9.9	6.2	−3.9	No
160	151.0	21.3	3.9	−5.6	No
Water of Choice					
30	28.9	7.0	4.5	−3.6	No
80	76.9	10.5	3.6	−3.9	No
160	152.7	19.7	9.1	−4.6	No

24.2 These data may not apply to waters of other matrices, therefore, it is the responsibility of the analyst to ensure the validity of the test method in a particular matrix.

24.3 Precision and bias for this test method conforms to Practice D2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 ~~– 08,~~ – 13, these precision and bias data meet existing requirements for interlaboratory studies of Committee D19 test methods.

TEST METHOD C—DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY

~~25. Scope~~

~~25.1 This test method describes the determination of cadmium in water and wastewaters using differential pulse anodic stripping voltammetry.~~

~~25.2 This test method is applicable up to a concentration of 100 µg/L cadmium. Higher concentrations can be determined by dilution.~~

~~25.3 The lower limit of detection for cadmium is 1.0 µg/L.~~

~~NOTE 14—The lower limit of detection for differential pulse anodic stripping voltammetry is not absolute and can easily be lowered by changing the experimental parameters as described in Appendix X1. However, these variations have not been interlaboratory tested.~~

~~25.4 It is the responsibility of the analyst to determine the acceptability of this test method when analyzing other matrices.~~

25. Scope

25.1 This test method describes the determination of cadmium in water and wastewaters using differential pulse anodic stripping voltammetry.

25.2 This test method is applicable up to a concentration of 100 µg/L cadmium. Higher concentrations can be determined by dilution.

25.3 The lower limit of detection for cadmium is 1.0 µg/L.

NOTE 14—The lower limit of detection for differential pulse anodic stripping voltammetry is not absolute and can easily be lowered by changing the experimental parameters as described in Appendix X1. However, these variations have not been interlaboratory tested.

25.4 It is the responsibility of the analyst to determine the acceptability of this test method when analyzing other matrices.

26. Summary of Test Method

26.1 This test method determines the total recoverable concentration of cadmium in water and wastewater. The same digestion, sample preparation, and analysis procedure may be used to determine total recoverable lead (Test Methods D3559) simultaneously with cadmium.

26.2 The sample is digested with nitric acid in a polarographic cell: 0.2 *M* ammonium citrate buffer (pH 3.0) and 10 % hydroxylamine solution are added. The solution is warmed to dissolve the cadmium. Warming with hydroxylamine eliminates interference from ferric iron by reducing it to ferrous.

26.3 After cooling, this sample is de-aerated, and the cadmium is deposited into a hanging mercury drop electrode with a surface area of 1.5 to 3.0 mm^2 at a constant potential of − 0.80 V versus saturated calomel electrode (SCE). The cadmium is then stripped back into solution using the differential pulse scanning mode, and the current is measured during the stripping step. (**Warning—**Mercury has been designated by many regulatory agencies as a hazardous material that can cause serious medical issues. Mercury, or its vapor, has been demonstrated to be hazardous to health and corrosive to materials. Caution should be taken when handling mercury and mercury containing products. See the applicable product Safety Data Sheet (SDS) for additional information. Users should be aware that selling mercury and/or mercury containing products into your state or country may be prohibited by law.)

26.4 The stripping peak height is proportional to the concentration of the cadmium, and the stripping peak potential is a qualitative measure of the cadmium in solution.

27. Interferences

27.1 Selenium does not interfere up to 50 µg/L. Interferences from selenium concentration up to 1000 µg/L may be overcome by adding ascorbic acid which reduces selenium (IV) to selenium metal and eliminates the interference.

27.2 When ferric ions are present at levels greater than cadmium, interference may occur from oxidizing the deposited metal out of the amalgam. Interference by ferric iron at concentrations as high as 20 mg/L is eliminated by warming with hydroxylamine. Ferric ions are reduced to ferrous ions by the hydroxylamine, and the interference caused by the presence of iron is eliminated.

27.3 The presence of a neighboring stripping peak which is <100 mV from that of cadmium will interfere.

28. Apparatus

28.1 *Polarographic Instrumentation* capable of performing differential pulse work.[6]

28.2 *Hanging Mercury Drop Electrode.* [7]

28.3 *Reagent Purifier System.* [8]

28.4 *Counter Electrode,* platinum.

28.5 *Salt Bridge,* with slow leakage fritted glass tip,[9] to isolate saturated calomel electrode from the test solution.

28.6 *Magnetic Stirrer*—The magnetic stirrer used must have a separate On/Off switch, so that uniform rotational speed can be maintained. A0.5-in. (13-mm) magnetic stirring bar is also required.

28.7 *pH Meter.*

28.8 *Hot ~~Plate.~~ Plate or Hot Block Digestion System.*

28.9 *Micropipettes* incorporating disposable plastic tips are used. The sizes required are 10, 20, 50, and 100 µL.

29. Reagents and Materials

29.1 *Purity of Reagents*—The ammonium citrate solution and redistilled nitric acid are purified or purchased to contain less than 1 µg/L of cadmium.

29.2 *Ammonium Citrate Buffer*—Dissolve 42 g of citric acid in 800 mL of water and add enough ammonium hydroxide to bring the pH to 3.0 ± 0.2. Dilute to 1000 mL with water and place in the cell of the reagent purifier system. Purify for a minimum of 36 h at a potential of − 1.3 V versus SCE at a mercury pool working electrode. De-aerate the supporting electrolyte during the purification process. If the buffer contains less than 1 µg/L of cadmium, the purification step may be omitted, providing new buffer is prepared every 2 weeks. The electrolyzed buffer is stable against bacterial growth for at least 1 month.

NOTE 15—To prevent bacterial growth in the unpurified buffer for a month, sterilize by autoclaving for 15 min at 121°C and ~~1.03 × 10~~103.4~~^{5}~~ ~~Pa~~kPa (15 psi).

29.3 *Aqua Regia* (1 + 1)—Add 1 volume of nitric acid (sp gr 1.42) to 4 volumes of water. Then add 3 volumes of hydrochloric acid (sp gr 1.19). (**Warning—**Toxic fumes may be released. Prepare and use in a ventilated hood.~~Warning~~)~~—Toxic fumes may be released. Prepare and use in a ventilated hood.)~~

29.4 *Ascorbic Acid* (100 g/L)—Dissolve 10.0 g of *L*-ascorbic acid in reagent water and dilute to 100 mL.

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

29.6 *Hydroxylamine Solution* (100 g/L)—Dissolve 5.00 g of hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) in reagent water and dilute to 50 mL.

29.7 *Nitric Acid* (sp gr 1.42) [10]—Redistilled concentrated nitric acid (HNO_3).

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

29.9 *Nitric Acid* (1 + 160)—Add 1 volume of nitric acid to 160 volumes of water.

29.10 *Nitric Acid* (2 + 3)—Add 2 volumes of nitric acid, reagent grade,[4] to 3 volumes of water.

29.11 *Purified Nitrogen*—Nitrogen employed for de-oxygenation must be sufficiently oxygen-free so that a differential pulse polarographic scan from − 0.20 to − 0.80 V versus SCE of the ammonium citrate buffer solution, after 10-min de-aeration at 10^5 mm^3/min, gives a signal no more than 0.1 µA. See Appendix X2 to learn methods of gas purification.

29.12 *Standard Solutions*—Obtain standard 100 mg/L reference solution for cadmium[11] or prepare from cadmium metal.

29.12.1 *Cadmium Solution, Stock* (1 mL = 1.0 mg Cd)—Dissolve 1.000 g cadmium metal in a minimum quantity of HNO_3 (sp gr 1.42) and dilute to 1000 mL. A purchased cadmium stock solution of appropriate known purity is also acceptable.

29.12.2 *Cadmium Solution, Standard* (1 mL = 0.1 mg Cd)—Dilute 100.0 mL of cadmium stock solution and 1 mL of HNO_3 (sp gr 1.42) to 1000 mL with water.

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[6] Two instruments that have been found satisfactory for this purpose are the polarographic analyzer with mechanical drop timer, Model 174A, and the Houston Omnigraphic X-Y Recorder, Model 2200-3-3, available from Princeton Applied Research, Princeton, NJ. Another instrument, the Charge Transfer Analyzer, Model 3040, available from Environmental Sciences Associates (ESA), Bedford, MA, has also been found satisfactory for this purpose. For settings on ESA Model 3040 equivalent to those in 33.10, see ESA Application Note CTA-AN-1.

[7] The hanging mercury drop electrode, Model 9323, or the automated hanging mercury drop electrode, Model 314, manufactured by Princeton Applied Research, have been found satisfactory for this purpose.

[8] Both the Electrolyte Purification System, Model 9500, available from Princeton Applied Research, and the PM Reagent Cleaning System, Model 2014, available from ESA, have been found satisfactory for this purpose.

[9] A Vycor tip, available from Corning Glass Works, Corning, NY, has been found satisfactory for this purpose.

[10] Acids that may contain suitably low levels of cadmium (and lead) are the redistilled reagents or equivalent available from G. Frederick Smith Chemical Co., 867 McKinley Ave., Columbus, OH 43223.

[11] Certified Atomic Absorption Standards, (Fisher Scientific Co., Fairlawn, NJ) have been found satisfactory for this purpose.

30. Hazards

30.1 The liquid mercury used for the hanging mercury drop electrode[7] forms a toxic vapor, and the liquid itself is toxic. Handle with gloves in a ventilated hood. (**Warning—**Mercury has been designated by many regulatory agencies as a hazardous material that can cause serious medical issues. Mercury, or its vapor, has been demonstrated to be hazardous to health and corrosive to materials. Caution should be taken when handling mercury and mercury containing products. See the applicable product Safety Data Sheet (SDS) for additional information. Users should be aware that selling mercury and/or mercury containing products into your state or country may be prohibited by law.)

31. Calibration

31.1 After a differential pulse anodic stripping curve is run on the sample solution, the anodic stripping curve is quantitated using the technique of standard additions.

31.2 Prepare 100 mg/L stock solutions by diluting 5.00 mL of the cadmium standard solutions to 50.0 mL with HNO_3 (1 + 160). These can be stored for several weeks if kept in a plastic bottle.

31.3 Prepare spiking solution by diluting 5.00 mL of the cadmium stock solution to 50.0 mL with HNO_3 (1 + 160). Prepare fresh daily. Alternatively, if lead is to be quantified too, both metals may be added to a single spiking solution. The best procedure here is to prepare the spiking solution with each metal in the ratio expected in the sample. (Example: If lead is expected to be 5 times the cadmium, prepare a spiking solution with lead and cadmium in a 5 to 1 ratio).

31.4 Add an appropriate aliquot of the cadmium spiking solution to the sample in the cell. De-aerate for 5 min at 10^5 mm^3/min to mix the solution and remove oxygen added with the spike.

31.5 Repeat the analysis procedure beginning with 32.8.

32. Procedure

32.1 Soak voltammetric cells (or digestion vessels) overnight in concentrated HNO_3, and verify that the reagent blank is less than 1 µg/L for cadmium. Omit the soaking step if the reagent blank of the unsoaked cells is less than 1 µg/L. Clean other glassware with HNO_3 (2 + 3). See Annex A1 for a procedure to clean glassware.

NOTE 16—Soaking the cells of digestion vessels in aqua regia (1 + 1) for 1 h improves blank values.

32.2 Place exactly 10.0 mL of a well-mixed sample containing less than 100 µg/L of cadmium into the cell.

NOTE 17—Concentrations greater than 100 µg/L of cadmium may be determined by dilution.

32.3 Add 2.0 mL of redistilled HNO_3 to each sample.

32.4 Evaporate the samples ~~without boiling~~ (between 65°C and 95°C) on a hot plate or steam bath below boiling in a well-ventilated hood until the sample just reaches dryness (do not "bake" as this may cause losses due to volatilization). 32.3 and 32.4 may be repeated if necessary for samples containing large amounts of organic matter.

32.5 Cool, add 5.0 mL of ammonium citrate buffer, and 100 µL of hydroxylamine solution. Warm the solution 15 min to reduce the ferric iron and to effect dissolution of the metals in the buffer.

32.6 Bring to volume of 10 to 12 mL with ammonium citrate buffer (pH 3.0). The exact volume need not be known because the standard additions method will be used to quantitate.

32.6.1 To overcome selenium at levels up to 1000 µg/L, add 1 mL of ascorbic acid.

32.7 De-aerate for 10 min at 10^5 mm^3/min with an oxygen-free stream of nitrogen.

32.8 After de-aeration is complete, extrude with the hanging mercury drop electrode a mercury droplet whose area is 1.5 to 3 mm^2, as determined in Annex A2.[12] Turn on the magnetic stirrer and adjust the stirring rate so that the solution beneath the mercury droplet is well stirred but there is no visible movement of the mercury droplet. The stirrer is turned on 15 s prior to deposition to assure uniform rotational speed. (**Warning—**Mercury has been designated by many regulatory agencies as a hazardous material that can cause serious medical issues. Mercury, or its vapor, has been demonstrated to be hazardous to health and corrosive to materials. Caution should be taken when handling mercury and mercury containing products. See the applicable product Safety Data Sheet (SDS) for additional information. Users should be aware that selling mercury and/or mercury containing products into your state or country may be prohibited by law.)

32.9 Connect the cell. Deposit at −0.80 V versus SCE for exactly 2 min, switch off stirrer, and wait exactly 30 s before beginning the scan. The quiescent period between deposition and scan allows convection to cease.

32.9.1 Annex A3 gives typical stripping curve shapes, peak potential, and sensitivities (in µA/5 µg/L) for cadmium deposited into a mercury droplet with a 2.9-mm^2 area for 2 min with stirring plus 30 s without stirring.

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[12] With the Model 9323 hanging mercury drop electrode manufactured by Princeton Applied Research, a mercury droplet with suitable surface area is formed by rotating the micrometer six small vertical divisions.