Designation: D 3557 – 02

An American National Standard

Standard Test Methods for Cadmium in Water[1]

This standard is issued under the fixed designation D 3557; 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] 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

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 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 858 Test Methods for Manganese in Water[3]
D 1066 Practice for Sampling Steam[3]
D 1068 Test Methods for Iron in Water[3]
D 1129 Terminology Relating to Water[3]
D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits[3]
D 1193 Specification for Reagent Water[3]
D 1687 Test Methods for Chromium in Water[3]
D 1688 Test Methods for Copper in Water[3]
D 1691 Test Methods for Zinc in Water[3]
D 1886 Test Methods for Nickel in Water[3]
D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D19 on Water[3]
D 3370 Practices for Sampling Water from Closed Conduits[3]
D 3558 Test Methods for Cobalt in Water[3]
D 3559 Test Methods for Lead in Water[3]
D 3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry[3]
D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents[3]
D 5810 Guide for Spiking into Aqueous Samples[3]
D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis[4]

3. Terminology

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

3.2 *Definitions of Terms Specific to This Standard:*

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

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

3.2.3 *SCE*—saturated calomel electrode.

3.2.4 *stripping peak signal*—the current measured at the stripping peak maximum for a metal.

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

[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.

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

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 11.02.

conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.[5] 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 D 1193, 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 D 3370, Practice D 1066, and Specification D 1192.

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 D 4841.

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.

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 D 1886), chromium (Test Methods D 1687), cobalt (Test Methods D 3558), copper (Test Methods D 1688), iron (Test Methods D 1068), lead (Test Methods D 3559), manganese (Test Methods D 858), and zinc (Test Methods D 1691).

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 1—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 2—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.

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 3—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.)

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

NOTE 4—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

[5] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Phamracopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

replaced at 50 psig (345 kPa). (**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.)

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.

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 through 13.4. After the digestion of the blank and standard solutions has been completed in 13.4, 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 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 Measure 100.0 mL of a well-mixed acidified sample into a 125-mL beaker or flask.

NOTE 5—If only dissolved cadmium is to be determined, start with 13.5.

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

13.3 Heat the samples on a steam bath or hotplate 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 6—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.

13.4 Cool and filter the samples through a suitable filter 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.

13.5 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 [6]

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 D 2777-77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D 2777-98, 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.

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 D 1886), cobalt (Test Methods D 3558), copper (Test Methods D 1688), iron (Test Methods D 1068), lead (Test Methods D 3559), and zinc (Test Methods D 1691).

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

[6] Supporting data are available from ASTM International Headquarters. Request RR: D19-1030.

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 3).

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 4).

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 and 11.7.

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 through 22.15. When determining dissolved cadmium, use 250-mL separatory funnels and proceed as directed in 22.5 through 22.15.

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.

22. Procedure

22.1 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 7—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.

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

22.3 Heat the samples on a steam bath or hotplate 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 8—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.

22.4 Cool and filter the samples through a suitable filter, 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.

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

22.6 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 9—The pH adjustment of 22.6 may be made with a pH meter instead of using an indicator.

22.7 Add 10 mL of pyrrolidine dithiocarbamic acid-chloroform reagent and shake vigorously for 2 min. (**Warning**— see Note 9.)

22.8 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.

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

NOTE 10—If color still remains in the $CHCl_3$ extract, reextract the aqueous phase until the $CHCl_3$ layer is colorless.

22.10 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.)

22.11 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.

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

22.12 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.

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

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

22.15 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:

$$\text{Cadmium, } \mu g/L = (1000/A) \times B$$

where:

A = volume of original sample, mL, and
B = weight of cadmium in sample, µg.

24. Precision and Bias [6]

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.

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 D 2777-77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D 2777-98, 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 11—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.

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

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 D 3559) 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 deaerated, 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.

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.[7]

28.2 *Hanging Mercury Drop Electrode*. [8]

28.3 *Reagent Purifier System*. [9]

[7] 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.

[8] 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.

[9] 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.

28.4 *Counter Electrode*, platinum.

28.5 *Salt Bridge*, with slow leakage fritted glass tip,[10] 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*.

28.9 *Micropipets* 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. Deaerate 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 12—To prevent bacterial growth in the unpurified buffer for a month, sterilize by autoclaving for 15 min at 121°C and 1.03×10^5 Pa (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.)

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) [11]—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,[5] to 3 volumes of water.

29.11 *Purified Nitrogen*—Nitrogen employed for deoxygenation 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 deaeration 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[12] 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.

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.

30. Hazards

30.1 The liquid mercury used for the hanging mercury drop electrode[8] forms a toxic vapor, and the liquid itself is toxic. Handle with gloves in a ventilated hood.

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. Deaerate 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 13—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 14—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.

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

[11] 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.

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

32.4 Evaporate the samples without boiling on a hot plate or steam bath 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 Deaerate for 10 min at 10^5 mm^3/min with an oxygen-free stream of nitrogen.

32.8 After deaeration 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.[13] 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.

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.

32.10 The following typical settings are for polarographic instrumentation capable of performing differential pulse work:[7] electrode, hanging mercury drop electrode (area 1.5 to 3 mm^2); initial potential, − 0.80 V versus SCE; scan rate, 5 mV/s; scan direction, " + "; modulation amplitude, 25 mV; current range, 1 to 20 µA; drop time, 0.5 s; display direction,"−"; low pass filter, off; mode, differential pulse; deposition time, 2 min with stirring plus 30 s quiescent; scan range, stop − 0.20 V.

32.10.1 The linearity of this test method has been tested up to currents of 20 µA. If the sample gives stripping peaks with currents larger than 20 µA, one may decrease the deposition time (see Appendix X1), although this technique has not been interlaboratory tested. The recommended procedure is to dilute the sample and proceed as in 32.2 through 32.10.

32.11 To obtain a blank, place exactly 10.0 mL of Type IV water into the cell and proceed as in 32.2 through 32.10.

33. Calculation

33.1 Calculate the concentration of cadmium determined by the standard addition procedure as follows:

$$C_u = \frac{i_1 v C_s}{i_1 v + (i_2 - i_1)V}$$

where:

i_1 = stripping peak height for the sample,
i_2 = stripping height for the sample plus standard,
v = volume of standard taken for spiking,
V = volume of sample before digestion,
C_s = concentration of standard used in spike, mg/L, and
C_u = concentration of the unknown in the sample, mg/L.

33.2 The following is a sample calculation using this equation:

$$i_1 = 0.459$$

$$A_{i_2} = 1.24$$

$$A_v = 0.02$$

$$V = 10.0 \text{ mL}$$

$$C_s = 10.0 \text{ mg/L}$$

$$C_u = \frac{(0.459)(0.02)(10)}{(1.24)(0.02) + (1.24 - 0.459)(10)} = 0.01172 \text{ mg/L}$$

TABLE 3 Determination of Precision and Bias for Cadmium by Differential Pulse Anodic Stripping Voltammetry

Amount Added, µg/L	Amount Found, µg/L	S_T, µg/L	S_O, µg/L	% Bias	Statistically Significant, 95 % Level
Reagent Water					
10	10.3	2.30	1.38	+ 3.0	No
30	27.4	3.22	1.96	− 8.7	Yes
70	68.9	9.81	8.83	− 8.8	No
Water of Choice					
10	10.0	3.00	2.38	0.0	No
30	29.6	4.97	3.95	− 1.3	No
70	69.1	9.09	7.87	− 1.3	No

34. Precision and Bias [14]

34.1 *Precision*—The overall and single-operator precisions (standard deviations, S_T and S_O, respectively) of this test method within its designated range for cadmium in reagent water and selected water matrices vary in accordance with Table 3. Eight operators from seven laboratories participated in this study by determining three replicates at each concentration level.

34.2 *Bias*—The bias of this test method for cadmium is listed in Table 3. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

34.3 Precision and bias for this test method conforms to Practice D 2777-77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D 2777-98, these precision and bias data meet existing requirements for interlaboratory studies of Committee D19 test methods.

TEST METHOD D—ATOMIC ABSORPTION, GRAPHITE FURNACE

35. Scope

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

[13] 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.

[14] Supporting data are available from ASTM International Headquarters. Request RR: D19-1047.

35.2 This test method is applicable in the range from 2 to 10 µg/L of cadmium, based on a 20-µL sample size. The range can be increased or decreased by varying the volume of sample injected or the instrumental settings. High concentrations may be diluted, or should be analyzed by an alternate technique.

35.3 The precision and bias for this test method has been obtained on reagent water, tap water, waste treatment plant effluent, lake water, river water, condensate from a medium Btu coal-gasification process, well water, and production plant process water. It is the responsibility of the analyst to determine the acceptability of this test method when analyzing other matrices.

35.4 The analyst is encouraged to consult Practice D 3919 for a general discussion of interferences and sample analysis procedures for graphite furnace atomic absorption spectrophotometry.

36. Summary of Test Method

36.1 Cadmium is determined by an atomic-absorption spectrophotometer used in conjunction with a graphite furnace. A sample is placed in a graphite tube, evaporated to dryness, charred (pyrolyzed or ashed), and atomized. Since the graphite furnace uses the sample much more efficiently than flame atomization, the detection of low concentrations of elements in small sample volumes is possible. Finally, the absorption signal during atomization is recorded and compared to standards. A general guide for the application of the graphite furnace is given in Practice D 3919.

36.2 Dissolved cadmium is determined on a filtered sample with no pretreatment.

36.3 Total recoverable cadmium is determined following acid digeston and filtration. Because chlorides interfere with furnace procedures for cadmium, the use of hydrochloric acid or perchloric acid in any digestion and solubilization step is to be avoided. If suspended material is not present, this digestion and filtration may be omitted.

37. Interferences

37.1 For a complete discussion on general interferences with furnace procedures, the analyst is referred to Practice D 3919.

38. Apparatus

38.1 *Atomic-Absorption Spectrophotometer*, for use at 228.8 nm with background correction.

NOTE 15—A wavelength of 326.1 nm may be used if it has been determined to be suitable. Greater linearity may be obtained at high concentrations by using a less sensitive wavelength.

NOTE 16—The manufacturer's instructions should be followed for all instrumental parameters.

38.2 *Cadmium Light Source*—Cadmium hollow cathode lamp. A single element lamp is preferred, but multielement lamps may be used. Electrodeless discharge lamps have also been found to be satisfactory.

38.3 *Graphite Furnace*, capable of reaching temperatures sufficient to atomize the element of interest.

38.4 *Graphite Tubes*, compatible with furnace device. Pyrolytically coated graphite tubes are recommended.

38.5 *Pipets*, microlitre with disposable tips. Sizes may range from 1 to 100 µL, as required.

38.6 *Data Storage and Reduction Devices and Computer- and Microprocessor-Controlled Devices, or strip chart Recorders* shall be utilized for collection, storage, reduction, and problem recognition (such as drift, incomplete atomization, changes in sensitivity, etc.).

38.7 *Automatic Sampling* should be used.

39. Reagents and Materials

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

39.2 *Cadmium Solution, Intermediate* (1.0 mL = 10.0 µg)—Dilute 10.0 mL of cadmium solution, stock (39.1), and 1 mL of HNO_3 (sp gr 1.42) to 1 L with water.

39.3 *Cadmium Solution, Standard* (1.0 mL = 0.10 µg)—Dilute 10.0 mL of cadmium solution, intermediate (39.2), and 1 mL of HNO_3 (sp gr 1.42) to 1 L water. This standard is used to prepare working standards at the time of the analysis.

39.4 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3). (See Note 3.)

39.5 *Argon*, standard, welders grade, commercially available. Nitrogen and hydrogen may also be used if recommended by the instrument manufacturer.

40. Standardization

40.1 Initially, set the instrument in accordance with the manufacturer's specifications. Follow the general instructions as provided in Practice D 3919.

41. Procedure

41.1 Clean all glassware to be used for preparation of standard solutions or in the digestion step, or both, by rinsing first with HNO_3 (1 + 1) and then with water. Alternatively, soaking the glassware overnight in (1 + 1) HNO_3 is useful for cadmium.

NOTE 17—Due to the extreme sensitivity of this test method, reagents and glassware must be examined for excessive cadmium contamination.

41.2 Measure 100.0 mL of each standard and well-mixed sample into a 125-mL beaker or Erlenmeyer flask.

41.3 For total recoverable cadmium add 5 mL HNO_3 (sp gr 1.42) to each standard sample and proceed as directed in 41.4 through 41.6. If only dissolved cadmium is to be determined, filter the sample through a 0.45-µm membrane filter and proceed to 41.6.

41.4 Heat the samples at 95°C on a steam bath or hotplate in a well-ventilated fume hood until the volume has been reduced to 15 to 20 mL, making certain that the samples do not boil. (See Note 5.)

41.5 Cool and filter the sample through a suitable filter such as fine-textured, acid-washed, ashless paper, into a 100-mL volumetric flask. Wash the filter paper 2 or 3 times with water and bring to volume.

NOTE 18—If suspended material is not present, this filtration may be omitted.

41.6 Inject a measured aliquot of sample into the furnace device following the directions as provided by the particular instrument manufacturer. Refer to Practice D 3919.

42. Calculation

42.1 Determine the concentration of cadmium in each sample by referring to Section 12 of Practice D 3919.

43. Precision and Bias

43.1 The precision and bias of this test method was tested by 16 laboratories in reagent water, and 12 laboratories in tap water, water treatment plant effluent, lake water, river water, condensate from a medium Btu coal gasification process, well water, and production plant process water. Although multiple injections may have been made, the report sheets allowed only for reporting single values. Thus, no single-operation precision data can be calculated. The overall precision within its designated range varies with the quantity being tested in accordance with Table 4.

43.2 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.

43.3 Precision and bias for this test method conforms to Practice D 2777-77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D 2777-98, these precision and bias data meet existing requirements for interlaboratory studies of Committee D19 test methods.

44. Quality Control

44.1 In order to be certain that analytical values obtained using this test method are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing cadmium by any of these test methods.

NOTE 19—44.6 is unnecessary for method C since the method is performed as standard additions.

44.2 *Calibration and Calibration Verification*:

44.2.1 Analyze at least three working standards containing concentrations of cadmium that bracket the expected sample concentration prior to analysis of samples to calibrate the instrument.

44.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The results shall fall within 10% of the results from the calibration.

44.2.3 If calibration cannot be verified, recalibrate the instrument.

44.3 *Initial Demonstration of Laboratory Capability*:

TABLE 4 Determination of Bias, Cadmium Graphite Furnace Atomic Absorption

Amount Added µg/L	Amount Found µg/L	S_T	Bias, µg/L	% Bias	Statistically Significant 95 % Confidence Level
Reagent Water, Type II					
1.30	1.400	1.490	+ 0.100	+ 7.7	no
2.50	2.544	0.257	+ 0.044	+ 1.8	no
6.00	6.520	1.990	+ 0.520	+ 8.7	no
Water of Choice					
1.30	1.533	1.293	+ 0.233	+ 17.9	no
2.50	2.191	1.347	− 0.309	− 12.4	no
6.00	6.690	3.078	+ 0.690	+ 11.5	yes

44.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., a precision and bias study must be performed to demonstrate laboratory capability.

44.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-concentration range of cadmium. This level will vary depending on which test method is used. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps. The replicates may be interspersed with samples.

44.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias inTables 1-4 above. This study should be repeated until the single operator recoveries are within the limits given in the table above. If a concentration other than the recommended concentration is used, refer to Test Method D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

44.4 *Laboratory Control Sample (LCS)*:

44.4.1 To ensure that the test method is in control, analyze a LCS containing a mid-range concentration of cadmium with each batch or 10 samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every 10 samples. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for the LCS shall fall within ± 15 % of the known concentration.

44.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the samples in the batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

44.5 *Method Blank*:

44.5.1 Analyze a reagent water test blank with each batch. The concentration of cadmium found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of cadmium is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

44.6 *Matrix Spike (MS)*:

44.6.1 1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each batch by spiking an aliquot of the sample with a known concentration of cadmium and taking it through the analytical method.

44.6.2 The spike concentration plus the background concentration of cadmium must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample 2 to 5 times the analyte concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

44.6.3 Calculate the percent recovery of the spike (P) using the following formula:

$$P = \frac{100\,[A(V_s + V) - B\,V_s]}{C\,V} \quad (1)$$

where

A = Analyte Concentration (µg/L) in Spiked Sample
B = Analyte Concentration (µg/L) in Unspiked Sample
C = Concentration (µg/L) of Analyte in Spiking Solution
V_s= Volume (mL) of Sample Used
V = Volume (mL) added with Spike

44.6.4 The percent recovery of the spike shall fall within the limits based on analyte concentration listed in Guide D 5810, Table 1. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 20—acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D 5810 for additional information.

44.7 *Duplicate*:

44.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch. If the concentration of the analyte is less than five times the detection limit for the analyte, an MSD should be used.

44.7.2 Calculate the standard deviation of the duplicate values and compare to the appropriate precision data in the collaborative study using an F test. Refer to 6.4.4 of Test Method D 5847 for information on applying the F test.

44.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

44.8 *Independent Reference Material (IRM)*:

44.8.1 In order to verify the quantitative value produced by the test method, analyze an IRM submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the reference material should be in the middle of the concentration range of the specific test method chosen. The value obtained must fall within the control limits established by the laboratory.

45. Keywords

45.1 atomic absorption; cadmium; chelation; differential pulse anodic stripping; flame; graphite furnace; voltammetry; water

ANNEXES

(Mandatory Information)

A1. PROCEDURE TO CLEAN GLASSWARE

A1.1 Leach the voltammetric cells in concentrated HNO_3 for at least 24 h prior to use. During the leaching period for the cells, fill other glassware with the HNO_3 (2 + 3), cover by a sheet of plastic film [15] to prevent contamination by trace metals in atmospheric particles, and soak for at least 24 h. Clean all glassware that may contact the sample solution. This includes the voltammetric cells, digestion beakers, stirring bars, platinum wire, and outgassing tubes. For very low-level determinations leach instead in aqua regia (1 + 1) for 1 h prior to use.

A1.2 After the leaching period, rinse the glassware with reagent water and place in an oven to dry. Exclude the oven drying step for the platinum wire and outgassing tube. Clean the reference electrode salt bridge tube initially by soaking for 24 h with HNO_3 (2 + 3) but thereafter keep it immersed in a small amount of the purified buffer solution. Again, use plastic film [15] to cover any areas that might tend to accumulate dust.

A1.3 Remember when performing trace analyses that any solution or any equipment which is left open to the air can become contaminated by the trace metals from atmospheric particles. Care should be taken to prevent this from happening by liberal use of plastic film.

[15] Parafilm available from Fisher Scientific Co., Fairlawn, NJ, has been found satisfactory for this purpose.

A2. DETERMINATION OF HANGING MERCURY DROP AREA

A2.1 Place 4 mL of water into a 5-mL beaker and submerge a hanging mercury drop electrode (HMDE) capillary tip under the surface of water.

A2.2 Extrude and dislodge 10 drops from HMDE into the 5-mL beaker.

A2.3 Decant the water and rinse with three 3-mL portions of acetone.

A2.4 Obtain the weight of the beaker plus the mercury *(W_T)*.

A2.5 Discard the mercury and obtain the weight of the beaker *(W_B)*.

A2.6 Calculate the mercury drop area (assuming a spherical drop) as follows:

A2.6.1 $WHg = (W_T - W_B)/10$ = weight of a single mercury drop.

A2.6.2 Obtain the density of mercury at room temperature, ρHg, from the following table. If the room temperature used is not listed here, find the density at the correct temperature from a suitable reference source.

Temperature, °C	ρHg, g/mL[16]
20	13.5462
21	13.5438
22	13.5413
23	13.5389
Temperature,°C	ρHg, g/mL
24	13.5364
25	13.5340
26	13.5315
27	13.5291
28	13.5266
29	13.5242
30	13.5217

[16] Reproduced from *Handbook of Chemistry and Physics*, 44th edition, The Chemical Rubber Publishing Co., Cleveland, OH, 1963, p. 2199.

A2.6.3

$$\text{Area of Hg drop} = 4\,\pi\,(3W_{Hg}/4\pi\rho_{Hg})^{2/3}$$

A2.7 *Sample Calculation:*

$$W_{Hg} = 0.006228 \text{ for 1 Hg drop}$$

$$\text{Area of 1 Hg drop} = 4\pi\left(\frac{(3)(0.006228\text{ g})}{4\pi(0.0135438\text{ g/mm}^3)}\right)^{2/3}$$

$$= 12.56636\,(1.0978 \times 10^{-1})^{2/3}$$

$$= 2.881\text{ mm}^2$$

A2.8 Tabulated here are typical surface areas for each small vertical division on a manually operated hanging mercury drop electrode.[8]

Surface Area, mm²	Reading, Small Vertical Division
1.42	2
1.86	3
2.23	4
2.60	5
2.92	6
3.23	7

A3. VOLTAMMOGRAM

A3.1 The voltammogram shown in Fig. A3.1 gives typical stripping curve shapes, peak potentials, and sensitivities (in µA per 5 µg/L) for cadmium and lead deposited into a mercury droplet with a 2.9-mm² area for 2 min with stirring plus 30 s without stirring.

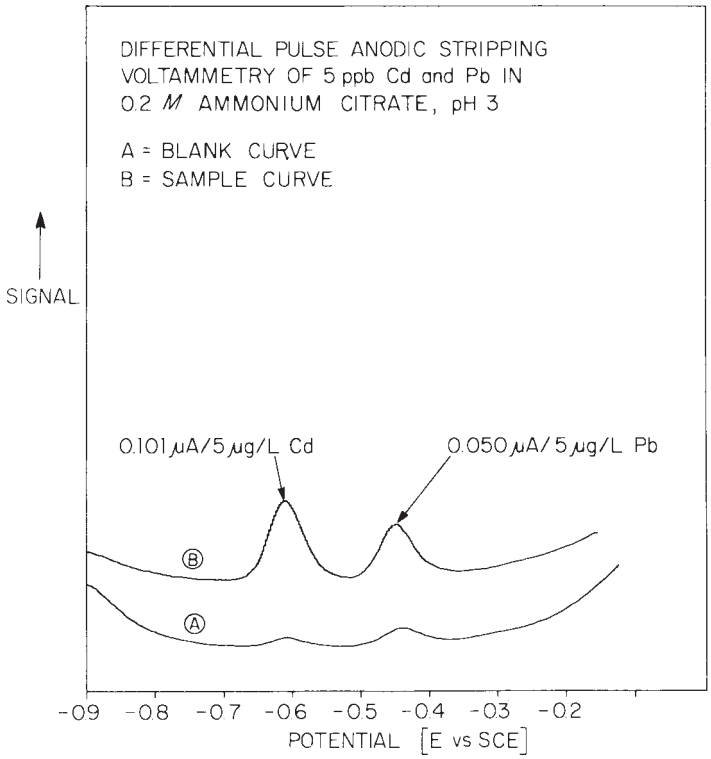

FIG. A3.1 Differential Pulse Anodic Stripping Voltammetry

APPENDIXES

(Nonmandatory Information)

X1. THE SENSITIVITY OF DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY

X1.1 The sensitivity of DPASV is dependent upon a number of factors and thus can be varied if so desired. The experimental conditions chosen for this work are those that are best suited for the concentration range covered by the samples which were analyzed. Experimental settings that can be varied to improve the sensitivity include: hanging mercury drop electrode size, deposition time, modulation amplitude, instrument gain, and stirring rate.

X1.2 The size of the mercury drop can be decreased to increase the sensitivity of this method. The recommended mercury droplet size is six divisions (see Annex A1), but mercury droplets of eight divisions can be used. [8] Droplets larger than this are not practical because they are very easily dislodged from the capillary.

X1.3 The sensitivity of DPASV is variable over a wide range by increasing the deposition time. A deposition time of 2 min is chosen for the concentration range investigated because this time gives adequate sensitivity in a reasonable length of time. The use of deposition times as long as 30 min has been reported in the literature when detection limits below 0.1 µg/L (ppb) were required. When sensitivity such as this is required, the additional time required is well spent.

X1.4 Another procedure to improve the sensitivity is to use larger pulse modulation amplitudes. For typical differential pulse polarographic instrumentation, [7] the pulse modulation amplitude may be increased to 50 mV with no significant loss of resolution.

X1.5 One may also change the gain on the instrument to improve the sensitivity. The highest gain that can be used in this experiment gives a current of 0.1 µA/in. This gain can be increased by a factor of 2 to 5, and sensitivity is increased by a corresponding amount. When using the higher gain on the instrument, it should be noted that the current at the beginning of the deposition may be well above the limiting value and the instrument overload light will be on. This does not mean the instrument is malfunctioning and the experiment can be allowed to proceed as planned. It may also be necessary to use offset to bring the curves on scale because, without the offset, the d-c current may be larger than the maximum current which the recorder will accept at thatparticular gain setting.

X1.6 The final procedure that increases the sensitivity is to increase the rate of stirring during the deposition step. The maximum stirring rate that is practical depends on the kind of stirrer and the geometry of the cell.

X1.7 The variable sensitivity is one of the major advantages of differential pulse anodic stripping voltammetry. The sensitivity can be conveniently increased or decreased to meet the needs of the experiment by changing the deposition time, mercury droplet size, instrument gain, stirring rate, and pulse modulation amplitude. However, no factor that affects the sensitivity should be changed between the time the sample and spiked sample are analyzed.

X2. METHODS FOR REMOVING OXYGEN FROM NITROGEN GAS

X2.1 Remove oxygen from nitrogen by any one of a variety of techniques. It is recommended that the nitrogen be scrubbed with 0.1 *M* chromous chloride in 2.4 *M* HCl containing amalgamated zinc [17] with a 0.8 to 3.2-mm pore size [18] or be scrubbed with vanadous chloride [17], which is a less suitable technique because of the critical dependence of the scrubbing efficiency on the acid concentration. Note that several commercial systems are available for removing oxygen at room temperature [19] or at high temperatures. [20]

[17] Meites, L., *Polarographic Techniques*, 2nd edition, Interscience Publishers, New York, NY, 1967, pp. 89–90.

[18] Amalgamated zinc with a pore size of 0.8 to 3.2 mm for a Jones reductor (Fisher Scientific Co., Fairlawn, NJ) has been found satisfactory for this purpose.

[19] One system that has been found satisfactory for this purpose is available from Applied Science Laboratories, State College, PA. It removes oxygen at room temperature with a Dow gas purifier preceded by a Hydro-Purge Unit.

[20] Hewlett-Packard, Avondale, PA, Model 19046A gas purifier uses a furnace at 475°C that is packed with copper, and Supelco (Bellefonte, PA) Model 02-2315 gas purifier uses a furnace at 600°C containing a special catalytic converter.