Designation: D3559 – 15

Standard Test Methods for Lead in Water[1]

This standard is issued under the fixed designation D3559; 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.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope*

1.1 These test methods cover the determination of dissolved and total recoverable lead in water and waste water by atomic-absorption spectrophotometry[2] and differential pulse anodic stripping voltammetry. Four test methods are included as follows:

	Concentration Range	Sections
Test Method A—Atomic Absorption, Direct	1.0 to 10 mg/L	7 to 15
Test Method B—Atomic Absorption, Chelation-Extraction	100 to 1000 µg/L	16 to 24
Test Method C—Differential Pulse Anodic Stripping Voltammetry	1 to 100 µg/L	25 to 35
Test Method D—Atomic Absorption, Graphite Furnace	5 to 100 µg/L	36 to 44

1.2 Test Method B can be used to determine lead in brines. Test Method D has been used successfully with reagent water, lake water, well water, filtered tap water, condensate from a medium Btu coal gasification process, waste treatment plant effluent, and a production plant process water.

1.3 It is the user's responsibility to ensure the validity of these test methods for waters of untested matrices.

1.4 The values stated in SI units are to be regarded as standard. The values given in parentheses are mathematical conversions 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.* For specific hazards statements, see Note 3, *11.3, 11.4, 11.8.1, 21.8, 21.9, 21.12, 23.7, 23.10, 32.2.1, and 33.1*.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D858 Test Methods for Manganese in Water
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
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
D3557 Test Methods for Cadmium in Water
D3558 Test Methods for Cobalt 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
E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry
E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

3. Terminology

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

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *total recoverable lead, n*—a descriptive term relating to the lead forms recovered in the acid-digestion procedure specified in these test methods.

[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. Brown, E., Skougstad, M. W., and Fishman, M. J., "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases," *Techniques of Water-Resources Investigations of the U. S. Geological Survey*, Book 5, 1970, p. 115.

[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**

4. Significance and Use

4.1 The test for lead is necessary because it is a toxicant and because there is a limit specified for lead in potable water in the National Interim Primary Drinking Water Regulations. This test serves to determine whether the lead 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 Practice D1066 and Practices D3370, as applicable.

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 lead is to be determined, the sample shall be filtered through a 0.45-µm membrane filter before acidification.

NOTE 1—Alternatively, the pH may be adjusted in the laboratory if the sample is returned within 14 days. 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 lead in most waters and wastewaters.

7.2 The test method is applicable in the range from 1.0 to 10 mg/L of lead. The upper limits of detectability can be increased to concentrations greater than 10 mg/L by dilution of the sample.

8. Summary of Test Method

8.1 Lead is determined by atomic absorption spectrophotometry. Dissolved lead is determined by aspirating the filtered and preserved sample directly with no pretreatment. Total recoverable lead is determined by aspirating the sample following hydrochloric-nitric acid digestion and filtration. The same digestion procedure may be used to determine total recoverable cadmium (Test Methods D3557), chromium (Test Methods D1687), cobalt (Test Methods D3558), copper (Test Methods D1688), iron (Test Methods D1068), manganese (Test Methods D858), nickel (Test Methods D1886), and zinc (Test Methods D1691).

9. Interferences

9.1 Other metals usually do not interfere in the determination of lead by increasing or decreasing the amount of absorbed radiation. The most common interference is caused by a chemical reaction in the flame that prevents conversion of the lead to the atomic state.

9.2 High concentrations of calcium, such as those connected with the coal industry, will give lead concentrations higher than which actually exist. This can be corrected by using a background correction technique, or by the chelation-extraction procedure (Test Method B).

9.2.1 The equipment manufacturer's instructions for use of specific correction technique shall be followed.

10. Apparatus

10.1 *Atomic Absorption Spectrophotometer,* for use at 283.3 nm.

NOTE 2—The manufacturer's instructions shall be followed for all instrumental parameters. Wavelengths other than 283.3 nm may be used if they have been determined to be equally suitable.

10.2 *Lead Light Source,* hollow-cathode lamps or electrodeless-discharge lamps have been found satisfactory.

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 *Filter Paper*—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.

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

11.3 *Lead Solution, Stock* (1 mL = 1 mg lead)—Commercially purchase or dissolve 1.5999 g of lead nitrate ($Pb(NO_3)_2$) in a mixture of 10 mL of HNO_3 (sp gr 1.42) and 100 mL of water. Dilute to 1 L with water. A purchased lead stock solution of appropriate known purity is also acceptable.

[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.

(**Warning—**Lead salts are toxic. Handle with care and avoid personal contamination.)

11.4 *Lead Solution, Standard* (1 mL = 0.1 mg lead)—Dilute 100.0 mL of stock lead solution to 1 L with HNO_3 (1 + 499). Store all solutions in polyethylene bottles. (**Warning—**Lead salts are toxic. Never pipette by mouth. Pipette with the end of a suction device or employ other conventional means of quantitative measurement.)

11.5 *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 trace metal grade acid.

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

11.7 *Oxidant:*

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

11.8 *Fuel:*

11.8.1 *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).

11.8.1.1 **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 walls can cause a potential hazardous situation.

12. Standardization

12.1 Prepare 100 mL each of a blank and at least four standard solutions to bracket the expected lead concentration range to be analyzed by diluting the lead standard solution (11.4) with HNO_3 (1 + 499) (11.6). Analyze at least four working standards containing concentrations of lead that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument. Prepare the standards each time the test is to be performed or as determined by Practice D4841.

12.2 When determining total recoverable lead, add 0.5 mL of HNO_3 (sp gr 1.42) (11.5) 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 lead, proceed with 12.3.

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

12.4 Prepare an analytical curve by plotting the absorbance versus the concentration for each standard on linear graph paper. Alternatively, read directly in concentration if this capability is provided with an 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 lead is to be determined, start with 13.5.

13.2 Add 5 mL of HCl (sp gr 1.19) (11.2) to each sample.

13.3 Heat the samples on a steam bath or hot plate 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 having appreciable amounts of suspended matter or dissolved matter, the amount of reduction in volume is left to the discretion of the analyst.

NOTE 7—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. 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.

13.4 Cool and filter (11.1) 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 283.3 nm. Aspirate HNO_3 (1 + 499) between samples.

14. Calculation

14.1 Calculate the concentration of lead in each sample, in milligrams per litre, using the calibration curve established in 12.4.

15. Precision and Bias[5]

15.1 Fourteen operators from nine laboratories participated in this study. One operator performed the analysis in quadruplicate, twelve in triplicate and one in duplicate at each concentration level.

15.2 The bias of this test method for lead is listed in Table 1.

15.3 These data may not apply to waters of other matrices.

[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, Direct

Amount Added, mg/L	Amount Found, mg/L	S_T, mg/L	S_0, mg/L	Bias, %	Statistically Significant (95 % Confidence Level)
Reagent Water, Type II					
1	1.01	0.08	0.04	+1.00	no
6	6.01	0.28	0.14	+0.17	no
8	8.02	0.34	0.14	+0.25	no
Selected Water Matrices					
1	1.00	0.00	0.06	0.00	no
6	6.11	0.25	0.16	+1.83	yes
8	7.99	0.36	0.23	–0.13	no

15.4 This section on precision and bias conforms to Practice D2777 – 77 which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D2777 – 13, these precision and bias data do meet existing requirements of interlaboratory studies of Committee D19 test methods.

16. Quality Control

16.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing lead.

16.2 *Calibration and Calibration Verification:*

16.2.1 Analyze at least four working standards containing concentrations of lead that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument (12.1). The calibration correlation coefficient shall be equal to or greater than 0.990.

16.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The concentration of a mid-range standard should fall within ±15 % of the known concentration. Analyze a calibration blank to verify system cleanliness.

16.2.3 If calibration cannot be verified, recalibrate the instrument.

16.2.4 It is recommended to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) at a 10 % frequency. The results should fall within the expected precision of the method or ±15 % of the known concentration.

16.3 *Initial Demonstration of Laboratory Capability:*

16.3.1 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.

16.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range concentration of lead. 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.

16.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 1. This study should be repeated until the recoveries are within the limits given in Table 1. If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the *F* test and *t* test in evaluating the acceptability of the mean and standard deviation.

16.4 *Laboratory Control Sample (LCS):*

16.4.1 To ensure that the test method is in control, prepare and analyze a LCS containing a known concentration of lead with each batch (laboratory defined or 20 samples). The laboratory control samples for a large batch should cover the analytical range when possible. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for a mid-range LCS shall fall within ±15 % of the known concentration.

16.4.2 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.

16.5 *Method Blank:*

16.5.1 Analyze a reagent water test blank with each laboratory-defined batch. The concentration of lead found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of lead 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.

16.6 *Matrix Spike (MS):*

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

16.6.2 The spike concentration plus the background concentration of lead must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is 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.

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

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

where:

A = analyte concentration (mg/L) in spiked sample,
B = analyte concentration (mg/L) in unspiked sample,
C = concentration (mg/L) of analyte in spiking solution,
V_s = volume (mL) of sample used, and
V = volume (mL) of spiking solution added.

16.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte concentration, listed in Guide D5810, 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 8—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

16.7 *Duplicate:*

16.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each laboratory-defined batch. If the

concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

16.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an *F* test. Refer to 6.4.4 of Practice D5847 for information on applying the *F* test.

16.7.3 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.

16.8 *Independent Reference Material (IRM):*

16.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

TEST METHOD B—ATOMIC ABSORPTION, CHELATION-EXTRACTION

17. Scope

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

17.2 This test method is applicable in the range from 100 to 1000 µg/L of lead. The range may be extended upward by dilution of the samples.

18. Summary of Test Method

18.1 Lead 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 HCl and diluted to a specified volume with water. The resulting solution is then aspirated into the air-acetylene flame of the spectrophotometer. The digestion procedure summarized in 8.1 is used for total recoverable lead. The same chelation-extraction procedure may be used to determine total recoverable cadmium (Test Methods D3557), cobalt (Test Methods D3558), copper (Test Methods D1688), iron (Test Methods D1068), nickel (Test Methods D1886), and zinc (Test Methods D1691).

19. Interferences

19.1 See Section 9.

20. Apparatus

20.1 All apparatus described in Section 10 are required.

21. Reagents and Materials

21.1 *Bromphenol Blue Indicator Solution* (1 g/L)—Dissolve 0.1 g of bromphenol blue in 100 mL of 50 % ethanol or 2-propanol.

21.2 *Carbon Disulfide* (CS_2).

21.3 *Chloroform* ($CHCl_3$).

21.4 *Filter Paper*—See 11.1.

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

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

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

21.8 *Lead Solution, Stock* (1.0 mL = 200 µg lead)— Commercially purchase or dissolve 0.3198 g of lead nitrate ($Pb(NO_3)_2$) in water containing 1 mL of HNO_3 (sp gr 1.42) and dilute to 1 L with water. A purchased lead stock solution of appropriate known purity is also acceptable. (**Warning—**Lead salts are toxic. Handle with care and avoid personal contamination.)

21.9 *Lead Solution, Intermediate* (1.0 mL = 2.0µ g lead)—Dilute 10 mL of lead stock solution and 1 mL of HNO_3 (sp gr 1.42) to 1 L with water. (**Warning—**Lead salts are toxic. Never pipette by mouth. Pipette with the end of a suction device or employ other convenient means of quantitative measurement.)

21.10 *Lead Solution, Standard* (1.0 mL = 0.2 µg lead)—Immediately before use, dilute 10.0 mL of lead intermediate solution and 1 mL of HNO_3 (sp gr 1.42) to 100 mL with water. This standard is used to prepare working standards at the time of analysis.

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

21.12 *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.)

21.13 *Sodium Hydroxide Solution* (100 g/L)—Dissolve 100 g of sodium hydroxide (NaOH) in water and dilute to 1 L. (**Warning—**This is a very exothermic reaction.)

22. Standardization

22.1 Prepare a blank and sufficient standards from 0.0 to 1000 µg/L lead from the lead standard solution (21.10) by making appropriate dilutions in water. Analyze at least three working standards containing concentrations of lead that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument. Prepare standards immediately prior to use or as determined by Practice D4841.

22.2 When determining total recoverable lead use 125-mL beakers or flasks, add 0.5 mL HNO_3 (21.11) (sp gr 1.42) and proceed as directed in 23.2 – 23.15. When determining dissolved lead use 250-mL separatory funnels and proceed as directed in 23.5 – 23.15.

22.3 Construct an analytical curve by plotting the absorbances of standards versus micrograms of lead. Alternatively, read directly in concentration if this capability is provided with the instrument.

23. Procedure

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

NOTE 9—If only dissolved lead is to be determined, measure a volume of filtered and acidified sample containing less than 100 µg of lead (100-mL maximum) into a 250-mL separatory funnel, and start with 23.5.

23.2 Add 5 mL of HCl (21.5) (sp gr 1.19) to each sample.

23.3 Heat the samples on a steam bath or hot plate 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 brines and samples containing appreciable amounts of suspended matter, 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 across all positions of the block. 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.

23.4 Cool and filter the samples through a suitable filter (21.4) such as fine-textured, acid-washed, ashless paper, into 250-mL separatory funnels. Wash the filter paper two or three times with water and bring to approximately a 100-mL volume.

23.5 Add 2 drops of bromphenol blue indicator solution (21.1) and mix.

23.6 Adjust the pH by addition of NaOH (100 g/L) solution (21.13) until a blue color persists. Add HCl (1 + 49) (21.7) by drops until the blue color just disappears; then add 2.5 mL of HCl (1 + 49) (21.7) in excess. The pH at this point should be 2.3.

NOTE 12—The pH adjustment in 23.6 may be made with a pH meter instead of using an indicator.

23.7 Add 10 mL of pyrrolidine dithiocarbamic acid-chloroform reagent (21.12) and shake vigorously for 20 min (**Warning—**See 21.12.)

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

23.9 Repeat the extraction with 10 mL of chloroform (21.3) and drain the chloroform layer into the same beaker.

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

23.10 Place the beaker on a hot plate at low heat and evaporate just to near dryness. Remove beaker from heat and allow residual solvent to evaporate without further heating. (**Warning—**Perform in a well-ventilated hood.)

23.11 Hold the beaker at a 45° angle and slowly add dropwise 2 mL of HNO_3 (sp gr 1.42) (21.11), rotating the beaker to effect thorough contact of the acid with the residue.

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

23.12 Place the beaker on a hot plate at low heat and evaporate just to dryness.

23.13 Add 2 mL of HCl (1 + 2) (21.6) to the beaker and heat while swirling for 1 min.

NOTE 14—If a precipitate appears when the HCl (1 + 2) is added to the dried residue, obtain a fresh supply of pyrrolidine which has a different lot number or redistill the pyrrolidine just before preparing the pyrrolidine dithiocarbamic acid-chloroform reagent.

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

23.15 Aspirate each sample and record the scale reading or concentration.

24. Calculation

24.1 Determine the weight of lead in each sample by referring to 22.3. Calculate the concentration of lead in micrograms per litre as follows:

$$\text{Lead, } \mu g/L = (1000/A) \times B \qquad (2)$$

where:

1000 = 1000 mL / litre
A = volume of original sample, mL, and
B = weight of lead in sample, µg.

25. Precision and Bias

25.1 Seven operators from six laboratories participated in this study. Five operators performed the analysis in triplicate and two in duplicate at each concentration level.

25.2 The bias of this test method for lead is listed in Table 2.

25.3 These data may not apply to waters of other matrices.

25.4 This section on precision and bias conforms to Practice D2777 – 77 which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D2777 – 13, these

TABLE 2 Determination of Bias, Chelation-Extraction

Amount Added, µg/L	Amount Found, µg/L	S_T, µ g/L	S_0, µg/L	Bias, %	Statistically Significant (95 % Confidence Level)
Reagent Water Type II					
100	86.1	17.7	8	−13.9	yes
400	364	55	27	−9.0	yes
800	674	124	24	−15.8	yes
Selected Water Matrices					
100	83	20	6.5	−17	yes
400	352	51	21	−12	yes
800	669	78	50	−16	yes

precision and bias data do meet existing requirements of interlaboratory studies of Committee D19 test methods.

26. Quality Control

26.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing lead.

26.2 *Calibration and Calibration Verification:*

26.2.1 Analyze at least three working standards containing concentrations of lead that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument (see 22.1). The calibration correlation coefficient shall be equal to or greater than 0.990.

26.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The concentration of a mid-range standard should fall within ±15 % of the known concentration. Analyze a calibration blank to verify the cleanliness of the system.

26.2.3 If calibration cannot be verified, recalibrate the instrument.

26.2.4 It is recommended to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) at a 10 % frequency. The results should fall within the expected precision of the method or ±15 % of the known concentration.

26.3 *Initial Demonstration of Laboratory Capability:*

26.3.1 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.

26.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range concentration of lead. 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.

26.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 2. This study should be repeated until the recoveries are within the limits given in Table 2. If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the *F* test and *t* test in evaluating the acceptability of the mean and standard deviation.

26.4 *Laboratory Control Sample (LCS):*

26.4.1 To ensure that the test method is in control, prepare and analyze a LCS containing a known concentration of lead with each batch (laboratory defined or 20 samples). The laboratory control samples for a large batch should cover the analytical range when possible. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for a mid-range LCS shall fall within ±15 % of the known concentration.

26.4.2 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.

26.5 *Method Blank:*

26.5.1 Analyze a reagent water test blank with each laboratory-defined batch. The concentration of lead found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of lead 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.

26.6 *Matrix Spike (MS):*

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

26.6.2 The spike concentration plus the background concentration of lead must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is 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.

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

$$P = 100\left[A\left(V_s + V\right) - B\ V_s\right]/C\ V \quad (3)$$

where:

A = analyte known concentration (µg/L) in spiked sample,
B = analyte known concentration (µg/L) in unspiked sample,
C = known concentration (µg/L) of analyte in spiking solution,
V_s = volume (mL) of sample used, and
V = volume (mL) of spiking solution added.

26.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte concentration, listed in Guide D5810, Table 2. 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 15—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

26.7 *Duplicate:*

26.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each laboratory-defined batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

26.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an *F* test. Refer to 6.4.4 of Practice D5847 for information on applying the *F* test.

26.7.3 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.

26.8 *Independent Reference Material (IRM):*

26.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

TEST METHOD C—DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY

27. Scope

27.1 This test method describes the determination of lead in water and waste waters using differential pulse anodic stripping voltammetry.

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

27.3 The lower limit of detection for lead is 1.0 µg/L.

NOTE 16—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.

28. Terminology

28.1 *Definitions*——See 3.1.

28.2 *Definitions of Terms Specific to This Standard:*

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

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

28.2.2.1 *SCE, n*—saturated calomel electrode.

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

29. Summary of Test Method

29.1 This test method determines the total recoverable concentration of lead in water and waste water. The same digestion, sample preparation, and analysis procedure may be used to determine total recoverable cadmium (Test Methods D3557) simultaneously with lead.

29.2 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 lead. Warming with hydroxylamine eliminates interference from ferric iron by reducing it to ferrous.

29.3 After cooling, this sample is deaerated, and the lead is deposited into a hanging mercury drop electrode with surface area of 1.5 to 3.0 mm^2 at a constant potential of −0.80 V versus saturated calomel electrode (SCE). The lead 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 or mercury containing products, or both, into your state or country may be prohibited by law.)

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

30. Interferences

30.1 Selenium does not interfere up to 50 µg/L. Interference 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.

30.2 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.

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

31. Apparatus

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

31.2 *Hanging Mercury Drop Electrode.* [7]

31.3 *Reagent Purifier System.* [8]

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[6] Two suitable instruments are the Princeton Applied Research, Princeton, NJ, Model 174A polarographic analyzer with mechanical drop timer, and Houston Omnigraphic X-Y Recorder Model 2200-3-3. An equally suitable instrument is the Environmental Sciences Associates (ESA), Bedford, MA, Model 3040 Charge Transfer Analyzer. For settings on ESA Model 3040 equivalent to those in paragraph 33.10, see ESA Application Note CTA-AN-1. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[7] The Model 9323 hanging, mercury drop electrode or the Model 314 automated hanging mercury drop electrode manufactured by Princeton Applied Research has been found satisfactory. The Metrohm E-410 hanging mercury drop electrode is equally satisfactory. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[8] Both the Model 9500 Electrolyte Purification System (Princeton Applied Research, Princeton, NJ) and the Model 2014 PM Reagent Cleaning System (Environmental Sciences Associates, Bedford, MA) are equally suitable. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

31.4 *Counter Electrode,* platinum.

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

31.6 *Magnetic Stirrer*—The magnetic stirrer used must have a separate on/off switch, so that uniform rotational speed can be maintained. 13-mm (0.5-in.) magnetic stirring bar is also required.

31.7 *pH Meter.*

31.8 *Hot Plate.*

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

32. Reagents

32.1 *Citrate Buffer Solution*—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 lead, 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 17—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).

32.2 *Aqua Regia* (1 + 1)—Add 1 volume of nitric acid (sp gr 1.42), reagent grade, to 4 volumes of water. Then add 3 volumes of hydrochloric acid.

32.2.1 **Warning—**Toxic fumes may be released. Prepare and use in a ventilated hood.

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

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

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

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

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

32.8 *Nitric Acid* (1 + 4)—Add 1 volume of nitric acid (sp gr 1.42) to 4 volumes of water.

32.9 *Nitric Acid* (2 + 3)—Add 2 volumes of nitric acid (sp gr 1.42) reagent grade,[6] to 3 volumes of water.

32.10 *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 citrate buffer solution, after 10 min deaeration at 10^5 mm^3/min, gives a signal no more than 0.1µ A. See Appendix X2 to learn methods of gas purification.

32.11 *Lead Solution, Stock* (1 mL = 0.1 mg Pb)—A purchased lead stock solution of appropriate known purity is acceptable. Alternatively, clean oxide from lead metal with HNO_3 (1 + 4). Wash the cleaned metal with water and dry. Dissolve 0.1000 g of the lead in 25 mL of HNO_3 (1 + 4). Dilute to 1 L with water.

33. Caution/Hazards

33.1 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.

34. Calibration

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

34.2 Prepare spiking solution as directed in 32.11. Alternatively, if cadmium 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).

34.3 Add an appropriate aliquot of the lead spiking solution to the sample in the cell. Analyze at least three working standards containing concentrations of lead that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument. Deaerate for 5 min at $10^5 mm^3$/min to mix the solution and remove oxygen added with the spike.

34.4 Repeat the analysis procedure beginning with 35.8.

35. Procedure

35.1 Soak voltammetric cells (or digestion vessels) overnight in concentrated HNO_3, and verify that the reagent blank is less than 1 µg/L for lead. 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) (32.9). See Annex A1 for a procedure to clean glassware.

NOTE 18—Soaking the cells (or digestion vessels) in aqua regia (1 + 1) (32.2) for 1 h improves blank values.

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

NOTE 19—Concentrations greater than 100 µg/L of lead may be determined by dilution.

35.3 Add 2.0 mL of redistilled HNO_3 (32.6) to each sample.

35.4 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). Steps 35.3 and 35.4 may be repeated if necessary for samples containing large amounts of organic matter.

[9] A Vycor (Corning Glass Works, Corning, NY) tip has been found suitable. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

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

35.5 Cool, add 5.0 mL of citrate buffer (32.1), and 100 µL of hydroxylamine solution (32.5). Warm the solution 15 min to reduce the ferric iron and to effect dissolution of the metals in the buffer.

35.6 Bring to volume of 10 to 12 mL with citrate buffer (pH 3.0) (32.1). The exact volume need not be known because the standard additions method will be used to quantitate.

35.6.1 To overcome selenium at levels up to 1000 µg/L, add 1 mL of ascorbic acid (32.3).

35.7 Deaerate for 10 min at 10^5 mm^3/min with an oxygen-free stream of nitrogen.

35.8 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. 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.

35.9 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.

35.9.1 Appendix X4 gives typical stripping curve shapes, peak potential, and sensitivities (in µA/5 µg/L) for lead deposited into a mercury droplet with a 2.9-mm^2 area for 2 min with stirring plus 30 s without stirring.

35.10 The following typical settings are for polarographic instrumentation capable of performing differential pulse work: [6] 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.

35.10.1 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 µgA, 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 directed in 35.2 through 35.10.

TABLE 3 Determination of Precision and Bias for Lead 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 Type VI					
20	21.6	4.00	2.95	+ 8.00	No
40	38.4	5.70	3.71	– 4.00	No
80	78.5	10.21	9.89	– 1.88	No
Water of Choice					
20	22.4	5.33	4.65	+ 12.0	No
40	40.3	6.59	6.91	+ 0.75	No
80	78.8	10.27	11.10	– 1.50	No

35.11 To obtain a blank, place exactly 10.0 mL of Type IV water into the cell and proceed as directed in 35.2 through 35.10.

36. Calculation

36.1 Calculate the concentration of lead determined by the standard addition procedure as follows:

$$C_u = \frac{i_1 v C_s}{i_2 v + (i_2 - i_1) V} \quad (4)$$

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.

36.2 The following is a sample calculation using this equation:

$$i_1 = 0.459\ \mu A \quad (5)$$

$$i_2 = 1.24\ \mu A$$

$$v = 0.02\ mL$$

$$V = 10.0\ mL$$

$$C_s = 10.0\ mg/L$$

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

37. Precision and Bias[11]

37.1 Eight operators from seven laboratories participated in this study by determining three replicates at each concentration level.

37.2 The precision and bias of this test method for lead is listed in Table 3.

37.3 These data may not apply to waters of other matrices.

37.4 This section on precision and bias conforms to Practice D2777 – 77 which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D2777 – 13, these precision and bias data do meet existing requirements of interlaboratory studies of Committee D19 test methods.

38. Quality Control

38.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing lead.

38.2 *Calibration and Calibration Verification:*

38.2.1 Analyze at least three working standards containing concentrations of lead that bracket the expected sample concentration, prior to analysis of samples, to calibrate the

[11] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1048. Contact ASTM Customer Service at service@astm.org.

instrument (see 34.3). The calibration correlation coefficient shall be equal to or greater than 0.990.

38.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The concentration of a mid-range standard should fall within ±15 % of the known concentration. Analyze a calibration blank to verify system cleanliness.

38.2.3 If calibration cannot be verified, recalibrate the instrument.

38.2.4 It is recommended to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) at a 10 % frequency. The results should fall within the expected precision of the method or ±15 % of the known concentration.

38.3 *Initial Demonstration of Laboratory Capability:*

38.3.1 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.

38.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range concentration of lead. 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.

38.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 3. This study should be repeated until the recoveries are within the limits given in Table 3. If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the *F* test and *t* test in evaluating the acceptability of the mean and standard deviation.

38.4 *Laboratory Control Sample (LCS):*

38.4.1 To ensure that the test method is in control, prepare and analyze a LCS containing a known concentration of lead with each batch (laboratory defined or 20 samples). The laboratory control samples for a large batch should cover the analytical range when possible. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for a mid-range LCS shall fall within ±15 % of the known concentration.

38.4.2 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.

38.5 *Method Blank:*

38.5.1 Analyze a reagent water test blank with each laboratory-defined batch. The concentration of lead found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of lead 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.

38.6 *Matrix Spike (MS):*

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

38.6.2 The spike concentration plus the background concentration of lead must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is 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.

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

$$P = 100[A(V_s + V) - B\,V_s]/C\,V \quad (6)$$

where:

A = analyte known concentration (µg/L) in spiked sample,
B = analyte known concentration (µg/L) in unspiked sample,
C = known concentration (µg/L) of analyte in spiking solution,
V_s = volume (mL) of sample used, and
V = volume (mL) of spiking solution added.

38.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte concentration, listed in Guide D5810, Table 3. 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 D5810 for additional information.

38.7 *Duplicate:*

38.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each laboratory-defined batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

38.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an *F* test. Refer to 6.4.4 of Practice D5847 for information on applying the *F* test.

38.7.3 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.

38.8 *Independent Reference Material (IRM):*

38.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material

TABLE 4 Determination of Bias and Overall Precision in Reagent Water, Graphite Furnace

Amount Added, µg/L	Amount Found, µg/L	S_T	Bias,±	Bias, ± %	Statistically Significant
72	75	7	+ 3	+4.2	No
12	11	2	– 1	–8.3	No
24	25	4	+ 1	+4.0	No

TABLE 5 Determination of Bias and Overall Precision in Water of Choice, Graphite Furnace

Amount Added, µg/L	Amount Found, µg/L	S_T	Bias,±	Bias, ± %	Statistically Significant
72	65	9	–7	–9.7	Yes
12	10	3	–2	–13.3	Yes
24	21	3	–3	–12.5	Yes

(IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

TEST METHOD D—ATOMIC ABSORPTION, GRAPHITE FURNACE

39. Scope

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

39.2 The test method is applicable in the range from 5 to 100 µg/L of lead using a 20-µL injection. The range can be increased or decreased by varying the volume of sample injected or the instrumental settings. High concentrations may be diluted but preferably should be analyzed by direct aspiration atomic absorption spectrophotometry (Test Method A). ICPMS may also be appropriate but at a higher instrument cost. See Test Method D5673.

39.3 This test method has been used successfully with reagent water, lake water, river water, well water, filtered tap water, condensate from a medium Btu coal gasification process, waste treatment plant effluent, and a production plant process water. It is the user's responsibility to assure validity of this test method for untested matrices.

40. Summary of Test Method

40.1 Lead 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. The absorption signal generated during atomization is recorded and compared to standards. A general guide for the application of the graphite furnace is given in Practice D3919.

40.2 Dissolved lead is determined on a filtered and preserved sample with no pretreatment.

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

41. Interferences

41.1 For a complete discussion on general interferences with furnace procedures, the analyst is referred to Practice D3919.

41.2 To suppress sulfate interference (up to 1500 mg/L) lanthanum nitrate is added to both samples and calibration standards. [12]

42. Apparatus

42.1 *Atomic Absorption Spectrophotometer,* for use at 283.3 nm with background correction.

NOTE 21—A wavelength other than 283.3 nm may be used if it has been determined to be suitable.

NOTE 22—The manufacturer's instructions should be followed for all instrumental parameters.

42.2 *Lead Electrodeless Discharge Lamps* are satisfactory.

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

42.4 *Graphite Tubes,* compatible with furnace device.

42.5 *Pipettes,* microlitre with disposable tips. Sizes may range from 5 µL to 100 µL, as required.

42.6 *Data Storage and Reduction Devices, 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.). Strip chart recorders shall have a full scale deflection time of 0.2 s or less to ensure accuracy.

42.7 *Automatic sampling* is recommended if available.

43. Reagents and Materials

43.1 *Filter Paper*—See 11.1.

43.2 *Lanthanum Nitrate Solution*, (1 mL = 50 mg La)—Commercially purchase or dissolve 58.64 g of ACS reagent grade La_2O_3 in 100 mL of concentrated HNO_3 and dilute to 1000 mL with water. This solution is added to the lead calibration standard and to the sample solution as well at a rate of 10 mL per 100 mL of standard or sample solution.

43.3 *Lead Solution, Stock* (1.0 mL = 200 µg Pb)—See 21.8.

43.4 *Lead Solution, Standard* (1.0 mL = 1.0 µg Pb)—Dilute 5.0 mL of lead solution, stock (43.3) and 1 mL of HNO_3 (sp gr 1.42) to 1 L with water.

43.5 *Lead Solution, Working*—Prepare the working standards at the time of analysis by adding various volumes of standard lead solution (43.4) to 50 mL of water containing 0.5

[12] Information regarding sulfate suppression can be found in "Atomic Absorption Newsletter," Vol 15, No. 3, May–June 1976, p. 71.

mL of HNO_3 (sp gr 1.42) adding 10 mL of lanthanum nitrate solution (43.2) and diluting to 100 mL with water in a volumetric flask.

43.6 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3). (See Note 4).

43.7 *Nitric Acid* (1 + 1)—Cautiously dilute 50 mL of nitric acid (sp gr 1.42) to 100 mL with water by adding acid to water.

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

44. Standardization

44.1 Initially, set the instrument according to the manufacturer's specifications. Follow the general instructions as provided in Practice D3919. Analyze at least three working standards containing concentrations of lead that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument.

45. Procedure

45.1 Clean all glassware to be used for preparation of standard solutions or in the solubilization step, or both, by rinsing first with HNO_3 (1 + 1) (43.7) and then with water.

45.2 Measure 100.0 mL of a well-mixed sample into a 125-mL beaker or flask. For total recoverable lead add HNO_3 (sp gr 1.42) (43.6) to each sample at a rate of 5 mL/L and proceed as directed in 45.4 through 45.6.

45.3 If only dissolved lead is to be determined, filter the sample through a 0.45 µm membrane filter prior to acidification, add 10 mL of lanthanum nitrate solution (43.2) per 100 mL of sample and proceed to 45.6.

45.4 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 6.) (See Note 7.)

45.5 Cool and filter the sample through a suitable filter (such as fine texture, acid washed, ashless paper) into a 100-mL volumetric flask. Wash the filter paper 2 or 3 times with water, add 10 mL of lanthanum nitrate solution (43.2) and bring to volume.

NOTE 23—If suspended material is not present, this filtration may be omitted.

45.6 Inject a measured aliquot of sample into the furnace device following the directions as provided by the particular instrument manufacturer. Refer to Practice D3919.

46. Calculation

46.1 Determine the concentration of lead in each sample by referring to Practice D3919.

46.2 The dissolved lead results obtained from a graph or instrument readout must be multiplied by 1.1 to compensate for dilution made by the addition of lanthanum nitrate solution in 45.3.

47. Precision and Bias[13]

47.1 The precision of this test method was tested by 13 laboratories in reagent water, lake water, river water, well water, filtered tap water, condensate from a medium Btu coal gasification process, a waste treatment plant effluent and a production plant process water. One laboratory reported data from two operators. Although multiple injections may have been made, the report sheets provided allowed only for reporting single values. Thus, no single operator precision data can be calculated. Bias data and overall precision data are given in Table 4 and Table 5.

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

47.3 This section on precision and bias conforms to Practice D2777 – 77 which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D2777 – 13, these precision and bias data do meet existing requirements of interlaboratory studies of Committee D19 test methods.

48. Quality Control

48.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing lead.

48.2 *Calibration and Calibration Verification:*

48.2.1 Analyze at least three working standards containing concentrations of lead that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument (see 44.1). The calibration correlation coefficient shall be equal to or greater than 0.990.

48.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The concentration of a mid-range standard should fall within ±15 % of the known concentration. Analyze a calibration blank to verify system cleanliness.

48.2.3 If calibration cannot be verified, recalibrate the instrument.

48.2.4 It is recommended to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) at a 10 % frequency. The results should fall within the expected precision of the method or ±15 % of the known concentration.

48.3 *Initial Demonstration of Laboratory Capability:*

48.3.1 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.

48.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range concentration of lead. The matrix and chemistry of the solution should be equivalent to the solution used in the

[13] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1112. Contact ASTM Customer Service at service@astm.org.

collaborative study. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

48.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Tables 4 and 5. This study should be repeated until the recoveries are within the limits given in Tables 4 and 5. If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the *F* test and *t* test in evaluating the acceptability of the mean and standard deviation.

48.4 *Laboratory Control Sample (LCS):*

48.4.1 To ensure that the test method is in control, prepare analyze a LCS containing a known concentration of lead with each batch (laboratory defined or twenty samples). The laboratory control samples for a large batch should cover the analytical range when possible. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for a mid-range LCS shall fall within ±15 % of the known concentration.

48.4.2 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.

48.5 *Method Blank:*

48.5.1 Analyze a reagent water test blank with each laboratory-defined batch. The concentration of lead found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of lead 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.

48.6 *Matrix Spike (MS):*

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

48.6.2 The spike concentration plus the background concentration of lead must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is 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.

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

$$P = 100[A(V_s + V) - B\,V_s]/C\,V \quad (7)$$

where:

A = analyte known concentration (µg/L) in spiked sample,
B = analyte known concentration (µg/L) in unspiked sample,
C = known concentration (µg/L) of analyte in spiking solution,
V_s = volume (mL) of sample used, and
V = volume (mL) of spiking solution added.

48.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte concentration, listed in Guide D5810, Tables 4 and 5. 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 24—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

48.7 *Duplicate:*

48.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each laboratory-defined batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

48.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an *F* test. Refer to 6.4.4 of Practice D5847 for information on applying the *F* test.

48.7.3 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.

48.8 *Independent Reference Material (IRM):*

48.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

49. Keywords

49.1 atomic absorption; chelation-extraction; graphite furnace spectrophotometry; lead; voltammetry

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 [14] 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 [14] to cover any areas that might tend to accumulate dust.

A1.3 Remember when performing trace analyses that any solution or any equipment that 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. [14]

[14] Parafilm available from Fisher Scientific Co., Fairlawn, NJ, has been found satisfactory. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

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 $W_{Hg} = (W_T - W_B)/10$ = weight of a single mercury drop.

A2.6.2 Obtain the density of mercury at room temperature, $p H_g$, from the following table[15]. If the room temperature used is not listed here, find the density at the correct temperature from a suitable reference source.

Temperature,° C	ρH_g, g/mL[15]
20	13.5462
21	15.5438
22	13.5413
23	13.5389
24	13.5364
25	13.5340
26	13.5315
27	13.5291
28	12.5266
29	13.5242
30	13.5217

A2.6.3 Area of Hg drop = $4\ \pi\ (3W_{Hg}/4\pi p_{Hg})^{2/3}$

A2.7 *Sample Calculation:*

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

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

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

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

A2.8 Tabulated here are typical surface areas for each small vertical division on a manually operated hanging mercury drop electrode. [7]

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

[15] Reproduction from *Handbook of Chemistry and Physics*, 44th Edition, The Chemical Rubber Publishing Co., Cleveland, OH, 1963, p. 2199.

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 which 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 A2), but mercury droplets of eight divisions can be used.[7] 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,[6] 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 that particular 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 [16] with a 0.8 to 3.2.1-mm pore size [17] or be scrubbed with vanadous chloride, [16] 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 [18] or at high temperatures. [19]

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

[17] 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. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[18] One suitable system 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. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[19] 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. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

X3. CHEMICAL MATRIX MODIFIERS FOR LEAD DETERMINATIONS USING GRAPHITE FURNACE SPECTROPHOTOMETRY

X3.1 The determination of lead using graphite furnace spectrophotometry may require the use of a chemical matrix modifier. Numerous chemical modifiers have been reportedly used. Table X3.1 is a summary of the most commonly used modifiers.

TABLE X3.1 Lead Chemical Matrix Modifiers

Matrix Modifier	Concentration	Matrix
Lanthanum nitrate [A]	1 mL = 50 mg La	sulfate
Phosphoric acid [B]	1 %	any
Ammonium phosphate [C]	1 %	any
Reduced palladium [D]	50 to 1000 ppm	any

[A] Refer to *Methods for Chemical Analysis of Water and Wastes*, EPA-600/4-79-020, U.S. Environmental Protection Agency, Cincinnati, OH, 1979.

[B] Refer to *Test Methods for Evaluating Solid Waste*, SW-846, Third edition, U.S. Environmental Protection Agency, Washington, DC, 1986.

[C] Refer to Welz B., *Atomic Absorption Spectrometry*, Second edition, VCH Publishers, Deerfield Beach, FL, 1985, p. 209.

[D] Refer to Rettberg T. M., and Beach, L. M., "Peak Profile Characteristics in the Presence of Palladium for Graphite Furnace Atomic Absorption Spectroscopy," *Journal of Analytical Atomic Spectrometry*, Vol. 4, July 1989.

X4. VOLTAMMOGRAM

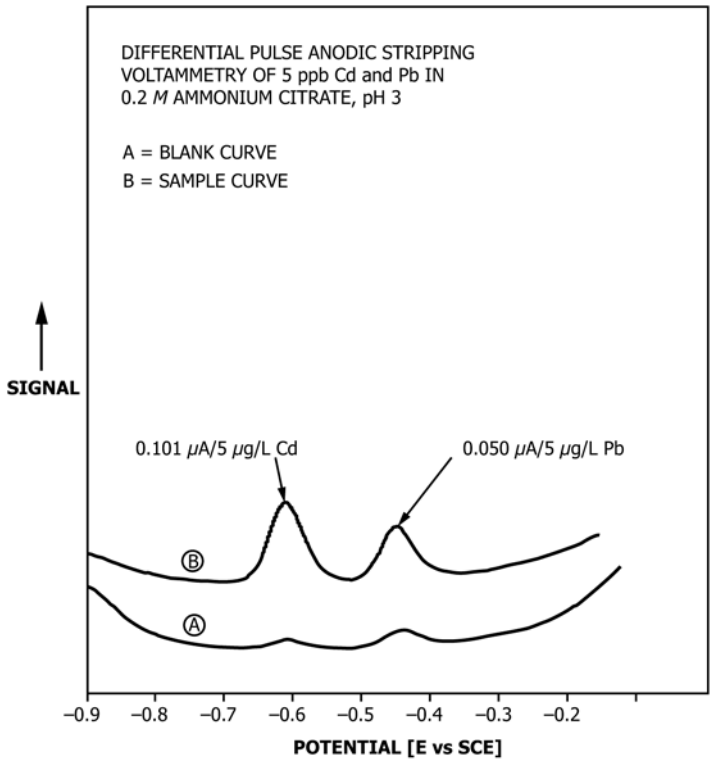

FIG. X4.1 Differential Pulse Anodic Stripping Voltammetry

X4.1 The voltammogram shown in Fig. X4.1 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-mm^2 area for 2 min with stirring plus 30 s without stirring.

SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D3559 – 08) that may impact the use of this standard. (Approved June 1, 2015.)

(1) Section 1 was updated with a new units of measurement statement.
(2) Section 2 was updated to include Test Method D5673.
(3) Sections 3 and 28 were updated.
(4) Section 6 was modified to allow for pH of the samples in the laboratory.
(5) Section 10 was modified to move the oxidant and fuel to Section 11.
(6) Sections 11, 21, 32, and 43 were modified to allow for commercial standards and filter paper information was added.
(7) Sections 12, 22, 34, and 44 were modified with calibration information.
(8) Sections 13 and 23 were modified to include note about the use of block digestion systems.
(9) Reagent references were added to Sections 12, 13, 23, and 45.
(10) 16.2.4, 26.2.4, 26.6.3, 38.2.4, 38.6.3, 48.2.4, and 48.6.3 were modified.
(11) 29.3 and Section 30 were modified or added to address the hazards with the mercury drop electrode.
(12) Section 39 was modified to inform the user of the possibility of using an ICP-MS.
(13) Section 42 was modified to move the argon to Section 43.