Designation: ~~D3559 – 08~~ 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~~ 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. ~~No other units of measurement are included in this~~ 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 ~~10.4.1~~, ~~Note 2~~3, ~~11.2~~11.3, ~~11.3~~11.4, 11.8.1, ~~21.7~~21.8, ~~21.8~~21.9, ~~21.11~~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

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

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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~~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**

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 *total recoverable lead*—an arbitrary analytical term relating to the recoverable forms of lead that are determined by the digestion method which are included in the procedure.~~

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.

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~~ 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.

[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.

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 ,~~ 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 *Oxidant:*~~

~~10.3.1 *Air,* which has been passed through a suitable filter to remove oil, water, and other foreign substances, is the usual oxidant.~~

~~10.4 *Fuel:*~~

~~10.4.1 *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 50 psig (345 kPa).~~

~~10.4.1.1 **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.~~

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.~~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. ~~Warning:~~A ~~Lead salts are toxic. Handle with care and avoid personal contamination.~~purchased lead stock solution of appropriate known purity is also acceptable. (**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:~~(**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.~~ 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 (~~11.3~~11.4) with HNO_3 ~~(1 + 499).~~ (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.~~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.

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. 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.

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 ~~– 06,~~ – 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.~~ instrument (12.1). The calibration correlation coefficient shall be equal to or greater than 0.990. ~~In addition to the initial calibration blank, a calibration blank shall be analyzed at the end of the batch run to ensure contamination was not a problem during the batch analysis.~~

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 ~~or 10 samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every 10 samples.~~ (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.

[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.

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~~ 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. ~~Warning:~~A ~~Lead salts are toxic. Handle with care and avoid personal contamination.~~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:~~(**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. ~~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:~~(**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. ~~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:~~(**Warning—**This is a very exothermic reaction. ~~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 (~~21.9~~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.~~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~~23.2 – 23.15 ~~thru 23.15~~. When determining dissolved lead use 250-mL separatory funnels and proceed as directed in ~~23.5~~23.5 – 23.15 ~~thru 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. ~~Warning:) See 21.11).~~

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:~~(**Warning—**Perform in a well-ventilated hood. ~~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),~~ 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:

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

where:

~~*1000* = 1000 mL / Liter~~
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.

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

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 ~~– 06,~~ – 13, these 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.~~ instrument (see 22.1). The calibration correlation coefficient shall be equal to or greater than 0.990. ~~In addition to the initial calibration blank, a calibration blank shall be analyzed at the end of the batch run to ensure contamination was not a problem during the batch analysis.~~

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 ~~or 10 samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every 10 samples.~~ (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:

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

where:

~~*A* = analyte concentration (mg/L) in spiked sample,~~

A = analyte known concentration (µg/L) in spiked sample,
~~B = analyte concentration (mg/L) in unspiked sample,~~
B = analyte known concentration (µg/L) in unspiked sample,
~~C = concentration (mg/L) of analyte in spiking solution,~~
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~~ 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—~~solution, n—*the standard solution added to the polarographic cell that is used to quantitate the sample.

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

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

28.2.3 *stripping peak ~~signal—~~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.