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Standard Test Methods for Lead in Water [1]

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This standard has been approved for use by agencies of the Department of Defense. Consult the DoD Index of Specifications and Standards for the specific year of issue which has been adopted by the 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 100µ g/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 *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, 11.2, 11.3, 20.7, 20.8, 20.11, 22.7, 22.10, 30.2.1, and 31.1.

2. Referenced Documents

2.1 *ASTM Standards:*

D 858 Test Methods for Manganese in Water [3]
D 1066 Practice for Sampling Steam [3]
D 1068 Test Methods for Iron in Water [3]
D 1129 Terminology Relating to Water [3]
D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits [3]
D 1193 Specification for Reagent Water [3]
D 1687 Test Methods for Chromium in Water [3]
D 1688 Test Methods for Copper in Water [3]
D 1691 Test Methods for Zinc in Water [3]
D 1886 Test Methods for Nickel in Water [3]
D 3370 Practices for Sampling Water from Closed Conduits [3]
D 3557 Test Methods for Cadmium in Water [3]
D 3558 Test Methods for Cobalt in Water [3]
D 3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry [3]
D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents [3]
E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals [4]
E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers [5]

3. Terminology

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

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.

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

[1] These test methods are under the jurisdiction of ASTM Committee D-19 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, Chapter , 1970, p. 115.

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

[4] *Annual Book of ASTM Standards*, Vol 03.05.

[5] *Annual Book of ASTM Standards*, Vol 03.06.

conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.[6] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type I. Other reagent water types may be used provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely affecting the bias and precision of the test method. Type II water was specified at the time of round-robin testing of this test method.

6. Sampling

6.1 Collect the samples in accordance with Practice D 1066, Specification D 1192, and Practices D 3370, 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.

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 D 3557), chromium (Test Methods D 1687), cobalt (Test Methods D 3558), copper (Test Methods D 1688), iron (Test Methods D 1068), manganese (Test Methods D 858), nickel (Test Methods D 1886), and zinc (Test Methods D 1691).

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 1—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.

10.5 *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

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

NOTE 2—If the reagent blank concentration is greater than the method detection limit, distill the HCl or use a spectrograde acid. **Caution**—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.

11.2 *Lead Solution, Stock* (1 mL = 1 mg lead)—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—**Lead salts are toxic. Handle with care and avoid personal contamination.

11.3 *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 pipet by mouth. Pipet with the end of a suction device or employ other conventional means of quantitative measurement.

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

NOTE 3—If the reagent blank concentration is greater than the method detection limit, distill the HNO_3 or use a trace metal grade acid.

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

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

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) with HNO_3(1 + 499). Prepare the standards each time the test is to be performed.

12.2 When determining total recoverable lead, add 0.5 mL of HNO_3(sp gr 1.42) to each blank and standard solution and proceed as directed in 13.2 through 13.4. After the digestion of the blank and standard solutions has been completed in 13.4, return to 12.3 to complete the standardization for total recoverable determinations. When determining dissolved 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 4—If only dissolved lead is to be determined, start with 13.5.

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

13.3 Heat the samples on a steam bath or 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 5—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.

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

13.5 Aspirate each filtered and acidified sample and determine its absorbance or concentration at 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 [7]

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.

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

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

TEST METHOD B—ATOMIC ABSORPTION, CHELATION-EXTRACTION

16. Scope

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

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

17. Summary of Test Method

17.1 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 D 3557), cobalt (Test Methods D 3558), copper (Test Methods D 1688), iron (Test Methods D 1068), nickel (Test Methods D 1886), and zinc (Test Methods D 1691).

18. Interferences

18.1 See Section 9.

19. Apparatus

19.1 All apparatus described in Section 10 are required.

20. Reagents

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

20.2 *Carbon Disulfide* (CS_2).

20.3 *Chloroform* ($CHCl_3$).

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

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

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

[7] Supporting data are available from ASTM Headquarters. Request RR:D 19-1030.

20.7 *Lead Solution, Stock* (1.0 mL = 200 µg lead)—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**—Lead salts are toxic. Handle with care and avoid personal contamination.

20.8 *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 pipet by mouth. Pipet with the end of a suction device or employ other convenient means of quantitative measurement.

20.9 *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.

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

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

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

21. Standardization

21.1 Prepare a blank and sufficient standards from 0.0 to 1000 µg/L lead from the lead standard solution (20.9) by making appropriate dilutions in water. Prepare standards immediately prior to use.

21.2 When determining total recoverable lead use 125-mL beakers or flasks, add 0.5 mL HNO_3(sp gr 1.42) and proceed as directed in 22.2 thru 22.15. When determining dissolved lead use 250-mL separatory funnels and proceed as directed in 22.5 thru 22.15.

21.3 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.

22. Procedure

22.1 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 6—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 22.5.

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

22.3 Heat the samples on a steam bath or 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 7—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.

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

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

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

NOTE 8—The pH adjustment in 22.6 may be made with a pH meter instead of using an indicator.

22.7 Add 10 mL of pyrrolidine dithiocarbamic acid-chloroform reagent and shake vigorously for 20 min (**Warning**—See 20.11).

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

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

NOTE 9—If color still remains in the $CHCl_3$ extract, reextract the aqueous phase until the chloroform layer is colorless.

22.10 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.

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

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

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

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

NOTE 10—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.

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

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

23. Calculation

23.1 Determine the weight of lead in each sample by referring to 21.3. Calculate the concentration of lead in micrograms per litre as follows:

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

where:
A = volume of original sample, mL, and
B = weight of lead in sample, µg.

24. Precision and Bias

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

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

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

TEST METHOD C—DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY

25. Scope

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

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

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

NOTE 11—The lower limit of detection for differential pulse anodic stripping voltammetry is not absolute and can easily be lowered by changing the experimental parameters as described in Appendix X1. However, these variations have not been interlaboratory tested.

26. Terminology

26.1 *Definitions*—See 3.1.

26.2 *Definitions of Terms Specific to This Standard:*

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

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

26.2.2.1 *SCE*—saturated calomel electrode.

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

27. Summary of Test Method

27.1 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 D 3557) simultaneously with lead.

27.2 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.

27.3 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.

27.4 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.

28. Interferences

28.1 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.

28.2 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.

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

29. Apparatus

29.1 *Polarographic Instrumentation*, capable of performing differential pulse work.[8]

29.2 *Hanging Mercury Drop Electrode.* [9]

29.3 *Reagent Purifier System.* [10]

29.4 *Counter Electrode*, platinum.

29.5 *Salt Bridge*, with slow leakage fritted glass tip, [11] to isolate saturated calomel electrode from the test solution.

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

29.7 *pH Meter*.

29.8 *Hot Plate*.

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

30. Reagents

30.1 *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

TABLE 2 Determination of Bias, Chelation-Extraction

Amount Added, µg/L	Amount Found, µg/L	S_T, µ g/L	S_O, 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

[8] Two suitable instrument 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.

[9] 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.

[10] 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.

[11] A Vycor (Corning Glass Works, Corning, NY) tip has been found suitable.

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

30.2 *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.

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

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

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

30.5 *Hydroxylamine Solution* (100 g/L)—Dissolve 5.00 g of hydroxylamine hydrochloride ($NH_2OH·HCl$) in reagent water and dilute to 50 mL.

30.6 *Nitric Acid* (sp gr 1.42) [12]—Redistilled concentrated nitric acid (HNO_3).

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

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

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

30.10 *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.

30.11 *Lead Solution, Stock* (1 mL = 0.1 mg Pb)—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.

31. Caution

31.1 The liquid mercury used for the hanging mercury drop electrode [9] forms a toxic vapor, and the liquid itself is toxic. Handle with gloves in a ventilated hood.

32. Calibration

32.1 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.

32.2 Prepare spiking solution as directed in 30.11. 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).

32.3 Add an appropriate aliquot of the lead spiking solution to the sample in the cell. Deaerate for 5 min at $10^5$$mm^3$/min to mix the solution and remove oxygen added with the spike.

32.4 Repeat the analysis procedure beginning with 33.8.

33. Procedure

33.1 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). See Annex A1 for a procedure to clean glassware.

NOTE 13—Soaking the cells (or digestion vessels) in aqua regia (1 + 1) for 1 h improves blank values.

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

NOTE 14—Concentrations greater than 100 µg/L of lead may be determined by dilution.

33.3 Add 2.0 mL of redistilled HNO_3 to each sample.

33.4 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 33.3 and 33.4 may be repeated if necessary for samples containing large amounts of organic matter.

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

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

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

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

33.8 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.

33.9 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.

33.9.1 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.

33.10 The following typical settings are for polarographic instrumentation capable of performing differential pulse work: [8] 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

[12] 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.