Designation: D 858 – 02

An American National Standard

Standard Test Methods for Manganese in Water[1]

This standard is issued under the fixed designation D 858; 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 Department of Defense.

1. Scope

1.1 These test methods cover the atomic absorption determination of dissolved and total recoverable manganese in water and certain wastewaters. Three test methods are given as follows:

	Concentration Range	Sections
Test Method A—Atomic Absorption, Direct [2]	0.1 to 5 mg/L	7 to 15
Test Method B—Atomic Absorption, Chelation-Extraction [2]	10 to 500 µg/L	16 to 24
Test Method C—Atomic Absorption, Graphite Furnace	5 to 50 µg/L	25 to 33

1.2 Test Methods A, B, and C were used successfully on reagent grade and natural waters. Other matrices used in the study were brine (Test Method B), effluent from a wood treatment plant, and condensate from a medium Btu coal gasification process (Test Method C). It is the user's responsibility to ensure the validity of a test method for waters of untested matrices.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see 11.7.1, 20.2, 20.9, and 22.10.

1.4 Former Test Method A (Colorimetric) was discontinued. For historical information, see Appendix X1.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1066 Practice for Sampling Steam[3]
D 1068 Test Methods for Iron in Water[3]
D 1129 Terminology Relating to Water[3]
D1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits[3]
D 1193 Specification for Reagent Water[3]
D 1687 Test Methods for Chromium in Water[3]
D 1688 Test Methods for Copper in Water[3]
D 1691 Test Methods for Zinc in Water[3]
D 1886 Test Methods for Nickel in Water[3]
D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D19 on Water[3]
D 3370 Practices for Sampling Water from Closed Conduits[3]
D 3557 Test Methods for Cadmium in Water[3]
D 3558 Test Methods for Cobalt in Water[3]
D 3559 Test Method for Lead in Water[3]
D 3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry[3]
D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents[3]
D 5810 Guide for Spiking into Aqueous Samples[3]
D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis[4]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *total recoverable manganese*—an arbitrary analytical term relating to the recoverable forms of manganese that are determinable by the digestion method which is included in the procedure.

3.2 *Definitions:*

3.2.1 For definitions of terms used in these test methods, refer to Terminology D 1129.

4. Significance and Use

4.1 Elemental constituents in potable water, receiving water, and wastewater need to be identified for support of effective pollution control programs. Test Methods A, B, and C provide the techniques necessary to make such measurements.

4.2 Although inhaled manganese dusts have been reported to be toxic to humans, manganese normally is ingested as a trace nutrient in both food and water. Because it is considered to be relatively nontoxic to man, as well as aquatic life, a limit

[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, Chapter A1, 1970, p. 115.

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

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

of 50 µg/L has been established in the EPA National Secondary Drinking Water Regulations. This limit is based primarily on its ability to stain laundry and produce objectionable tastes in beverages.

4.3 Manganese does not occur naturally as a metal but is found in various salts and minerals, frequently in association with iron compounds. Manganese is not mined in the United States except when manganese is contained in iron ores that are deliberately used to form ferro-manganese alloys. Manganese salts are used as fertilizer additives and are commonly found in surface and ground waters.

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, where such specifications are available.[5] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 *Purity of Water*—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 lessening the bias and precision of the determination. Type II water was specified at the time of round-robin testing of this test method.

6. Sampling

6.1 Collect the sample in accordance with Practice D 1066, Specification D 1192, or Practices D 3370 as applicable.

6.2 Samples shall be preserved with HNO_3 (sp gr 1.42), normally about 2 mL/L, to a pH of 2 or less immediately at the time of collection. If only dissolved manganese is to be determined, the sample shall be filtered through a 0.45-µm (No. 325) membrane filter before acidification. The holding time for samples may be calculated in accordance with Practice D 4841.

TEST METHOD A—ATOMIC ABSORPTION, DIRECT

7. Scope

7.1 This test method covers the determination of dissolved and total recoverable manganese and has been used successfully with reagent and natural water. It is the analyst's responsibility to ensure the validity of the method in a particular matrix.

7.2 This test method is applicable in the range from 0.1 to 5 mg/L of manganese. The range may be extended to concentrations greater than 5 mg/L by dilution of the sample.

8. Summary of Test Method

8.1 Manganese is determined by atomic absorption spectrophotometry. Dissolved manganese is determined by atomizing a filtered sample directly with no pretreatment. Total recoverable manganese in the sample is determined in a portion of the filtrate obtained after a hydrochloric-nitric acid digestion of the sample. The same digestion procedure is 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), lead (Test Methods D 3559), nickel (Test Methods D 1886), and zinc (Test Methods D 1691).

9. Interferences

9.1 Magnesium in concentrations greater than 100 mg/L may interfere.

9.2 No interference from SiO_2 in concentrations up to 100 mg/L has been observed.

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

NOTE 1—Instrument manufacturers' instructions for use of the specific correction technique should be followed.

10. Apparatus

10.1 *Atomic Absorption Spectrophotometer*, for use at 279.5 nm.

NOTE 2—The manufacturer's instructions should be followed for all instrumental parameters. A wavelength other than 279.5 nm may be used if it has been determined to be equally suitable.

10.1.1 *Manganese Light Source*—Multielement lamps, electrodeless discharge lamps, or hollow-cathode lamps have been found satisfactory.

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

NOTE 3—If a high reagent blank is obtained, distill the HCl or use spectrograde acid. (**Warning**—When HCl is distilled, an azeotropic mixture is obtained (approximately 6 *N*HCl). Therefore, whenever concentrated HCl is specified in the preparation of a reagent or in the procedure, use double the amount specified if distilled acid is used.)

11.2 *Manganese Solution, Stock* (1.0 mL = 1.0 mg Mn)—Dissolve 3.076 g of manganous sulfate monohydrate ($MnSO_4 \cdot H_2O$) 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 stock solution of appropriate purity is also acceptable.

11.3 *Manganese Solution, Standard* (1.0 mL = 0.1 mg Mn)—Dilute 100.0 mL of manganese stock solution to 1 L with water.

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

NOTE 4—If a high reagent blank is obtained, distill the HNO_3 or use spectrograde acid.

[5] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States 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.

11.6 *Oxidant*:

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

11.7 *Fuel*:

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

12. Standardization

12.1 Prepare 100 mL each of a blank and at least four standard solutions to bracket the expected manganese concentration range of the samples to be analyzed by diluting the manganese standard solution with HNO_3(1 + 499). Prepare the standards each time the test is to be performed, and select so as to give zero, middle, and maximum points for an analytical curve.

NOTE 5—It is recommended that the blank (zero standard) be compared with reagent grade water to avoid the possibility of using a high blank.

12.2 When determining total recoverable manganese add 0.5 mL of HNO_3(sp gr 1.42) and proceed as directed in 13.2. When determining dissolved manganese proceed with 13.5.

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

12.4 Prepare an analytical curve by plotting the absorbance of each standard versus its concentration on linear graph paper. Alternatively read directly in concentration from the instrument.

13. Procedure

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

NOTE 6—If only dissolved manganese 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 or 20 mL, making certain that the samples do not boil.

NOTE 7—For brines and samples with high levels of suspended 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 paper, 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 Set the instrument to zero using reagent blank (zero standard). Aspirate each filtered acidified sample and standard; record its absorbance or concentration. Aspirate HNO_3(1 + 499) between each sample or standard.

TABLE 1 Precision and Concentration, Direct Aspiration

Reagent water:			
Concentration ($\bar{X}$), mg/L	0.424	2.034	4.053
S_T	0.045	0.177	0.317
S_O	0.021	0.070	0.151
Natural water:			
Concentration ($\bar{X}$), mg/L	0.417	2.033	4.076
S_T	0.045	0.179	0.305
S_O	0.037	0.074	0.149

14. Calculation

14.1 Determine the concentration of manganese in each sample, in milligrams per litre, using an analytical curve or, alternatively, read directly in concentration (see 12.4).

15. Precision and Bias [6]

15.1 The supporting data on this collaborative study includes reagent and natural water matrices. It is the responsibility of the analyst to ensure the validity of the test method in a particular matrix.

15.2 The precision of this test method was tested by eleven laboratories. Five laboratories reported data for two operators. The precision of this test method is shown in Table 1; the bias is shown in Table 2.

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

TEST METHOD B—ATOMIC ABSORPTION, CHELATION-EXTRACTION

16. Scope

16.1 This test method covers the determination of dissolved and total recoverable manganese and has been used successfully with reagent water, tap water, river water, artificial seawater and a synthetic (NaCl) brine. It is the user's responsibility to ensure the validity of this test method for waters of other matrices.

16.2 This test method is applicable in the range from 10 to 500 µg/L of manganese. The range may be extended to concentrations greater than 500 µg/L by dilution of the sample.

17. Summary of Test Method

17.1 Manganese 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 HNO_3 to destroy organic matter, dissolved in HCl, and diluted to a specified volume with water. A portion of the resulting solution is then atomized into the air-acetylene flame of the spectrophotometer. The digestion procedure summarized in 8.1 is used to determine total recoverable manganese.

[6] Supporting data for Test Methods A and B are available from ASTM International Headquarters. Request RR: D19-1034.

TABLE 2 Determination of Bias, Direct Aspiration

Amount Added, mg/L	Amount Found, mg/L	Bias, mg/L	% Bias	Statistically Significant (95% Confidence Level)
Reagent water:				
0.4	0.424	+ 0.024	+ 6	yes
2.0	2.034	+ 0.034	+ 1.7	no
4.0	4.053	+ 0.053	+ 1.3	no
Natural water:				
0.4	0.417	+ 0.017	+ 4.2	yes
2.0	2.033	+ 0.033	+ 1.7	no
4.0	4.076	+ 0.076	+ 1.9	yes

18. Interferences

18.1 See Section 9.

19. Apparatus

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

20. Reagents and Materials

20.1 *Bromcresol Green Indicator Solution* (1 g/L)—Dissolve 0.1 g of bromcresol green in 100 mL of 20 % ethanol.

20.2 *Chloroform* ($CHCl_3$) (**Warning**—Use in well-ventilated hood.)

20.3 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl) (see Note 3).

20.4 *Hydrochloric Acid* (1 + 2)—Add 1 volume of HCl (sp gr 1.19) to 2 volumes of water (see Note 3).

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

20.6 *Manganese Solution, Stock* (1.0 mL = 100 µg Mn)—Dissolve 0.3076 g of manganous sulfate monohydrate ($MnSO_4 \cdot H_2O$) in water containing 1 mL of HNO_3(sp gr 1.42) and dilute to 1 L with water.

20.7 *Manganese Solution, Standard* (1.0 mL = 1.0 µg Mn)—Dilute 10.0 mL of manganese stock solution and 1 mL of HNO_3(sp gr 1.42) to 1 L with water. This standard is used to prepare working standards at the time of analysis.

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

20.9 *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. Prepare and use in a well-ventilated hood. Avoid inhalation and direct contact.)

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

20.11 *Oxidant*—See 11.6.

20.12 *Fuel*—See 11.7.

21. Standardization

21.1 Prepare a blank and sufficient standards containing from 0.0 to 50.0 µg of manganese by diluting 0 to 50.0-mL portions of manganese standard solution (20.7) to 100 mL with water.

21.2 To determine total recoverable manganese use 125-mL beakers or flasks, add 0.5 mL of HNO_3(sp gr 1.42) and proceed as directed in 22.2. To determine dissolved manganese use 250-mL separatory funnels and proceed as directed in 22.5.

21.3 Construct an analytical curve by plotting the absorbances of standards versus micrograms of manganese.

22. Procedure

22.1 Measure a volume of a well-mixed acidified sample containing less than 50.0 µg of manganese (100-mL maximum) into a 125-mL beaker or flask and adjust the volume to 100 mL with water.

NOTE 8—If only dissolved manganese is to be determined, measure a volume of sample filtered through a 0.45-µm (No. 325) membrane filter and acidified (6.2) containing less than 50.0 µg of manganese (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 until the volume has been reduced to 15 to 20 mL, making certain that the samples do not boil.

NOTE 9—For brines and samples with high levels 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 adjust the volume to approximately 100 mL.

22.5 Add 2 drops of bromcresol green indicator solution and mix.

22.6 Adjust the pH by addition of NaOH solution (100 g/L) until a blue color persists. Add HCl (1 + 49) by drops until a light olive-green color is obtained. The pH at this point should be 4.0.

NOTE 10—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 2 min.

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 beakers.

NOTE 11—If color still remains in the chloroform extract, reextract the aqueous phase until the chloroform layer is colorless.

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

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

NOTE 12—If acid is added to the beaker in a vertical position, a violent reaction will occur accompanied by high heat and spattering.

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

TABLE 3 Precision and Concentration, Chelation–Extraction

Reagent water:			
Concentration ($\bar{X}$), µg/L	21.47	121.47	292.83
S_T	2.4	10.50	27.36
S_O	2.2	7.37	9.10
Natural water:			
Concentration ($\bar{X}$), µg/L	22.17	120.87	268.02
S_T	3.50	9.00	14.99
S_O	3.74	7.21	12.08

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

NOTE 13—If a precipitate appears when the hydrochloric acid (1 + 2) is added to the dried residue, obtain a fresh supply of pyrrolidine that 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 adjust to volume with water.

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

23. Calculation

23.1 Determine the weight of manganese in each sample by referring to 21.3. Calculate the concentration of manganese in micrograms per litre using Eq 1:

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

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

24. Precision and Bias [6]

24.1 The precision of this test method was tested by six laboratories in reagent water, natural waters, and in synthetic brines. One laboratory reported data from two operators. The precision of this test method for reagent and natural water matrices is shown in Table 3; the bias is shown in Table 4.

24.2 It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

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

TEST METHOD C—ATOMIC ABSORPTION, GRAPHITE FURNACE

25. Scope

25.1 This test method covers the determination of dissolved and total recoverable manganese and has been used successfully with reagent water, river water, well and filtered tap water, an effluent from a wood treatment plant, and a condensate from a medium Btu coal gasification process. It is the user's responsibility to ensure the validity of the test method to waters of other matrices.

TABLE 4 Determination of Bias, Chelation–Extraction

Amount Added, µg/L	Amount Found, µg/L	Bias, µg/L	% Bias	Statistically Significant (95 % Confidence Level)
Reagent water:				
20	21.47	+ 1.47	+ 7.4	yes
120	121.47	+ 1.47	+ 1.2	no
300	292.83	−7.13	−2.4	no
Natural water:				
20	22.17	+ 2.17	+ 10.9	yes
120	120.87	+ 0.87	+ 0.7	no
300	268.02	−31.98	−10.6	yes

25.2 This test method is applicable in the range from approximately 5 to 50 µg/L of manganese using a 20-µL injection. The range can be increased or decreased by varying the volume of sample injected or the instrumental settings. Samples containing high concentrations may be diluted but preferably should be analyzed by direct aspiration atomic absorption spectrophotometry (Test Method A).

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

26. Summary of Test Method

26.1 Manganese 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 D 3919.

26.2 Dissolved manganese is determined on a filtered sample with no pretreatment.

26.3 Total recoverable manganese 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.

27. Interferences

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

28. Apparatus

28.1 *Atomic Absorption Spectrophotometer*, for use at 279.5 nm with background correction (see Note 14 and Note 15).

NOTE 14—A wavelength other than 279.5 nm may be used if it has been determined to be suitable.

NOTE 15—The manufacturer's instructions should be followed for all instrumental parameters.

28.2 *Manganese Hollow-Cathode Lamp*—A single-element lamp is preferred, but multielement lamps may be used.

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

28.4 *Graphite Tubes*, compatible with furnace device. Pyrolytically coated tubes are preferred.

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

28.6 *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.).

28.7 Automatic sampling is recommended.

29. Reagents and Materials

29.1 *Manganese Solution, Stock* (1.0 mL = 100 µg Mn)—See 20.6.

29.2 *Manganese Solution, Standard* (1.0 mL = 1.0 µg Mn)—See 20.7.

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

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

30. Standardization

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

31. Procedure

31.1 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) and then with water.

31.2 Measure 100.0 mL of each standard and well-mixed sample into 125-mL beakers or flasks. For total recoverable manganese add HNO_3(sp gr 1.42) to each standard and sample at a rate of 5 mL/L and proceed as directed in 31.4-31.6.

31.3 If only dissolved manganese is to be determined, filter the sample through a 0.45-µm membrane filter prior to acidification, and proceed to 31.6.

31.4 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 (Note 8).

31.5 Cool and filter the sample through a suitable filter (such as fine-textured, acid-washed, ashless paper) into a 100-mL volumetric flask. Wash the filter paper two or three times with water, and bring to volume (Note 16). The acid concentration at this point should be 0.5 % HNO_3.

NOTE 16—If suspended material is not present, this filtration may be omitted but the sample must still be diluted to 100 mL.

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

32. Calculation

32.1 Determine the concentration of manganese in each sample in accordance with the Samples Analysis Procedure in Practice D 3919.

TABLE 5 Determination of Bias and Overall Precision in Reagent Water, Atomic Absorption Graphite Furnace

Amount Added, µg/L	Amount Found, µg/L	S_T	Bias, µg/L	% Bias	Statistically Significant
7.5	7.37	0.74	−0.13	−1.7	no
15	14.9	1.78	−0.1	−0.7	no
44	42.9	7.44	−1.1	−2.5	no

33. Precision and Bias [7]

33.1 The precision of this test method was tested by 13 laboratories in reagent water, river water, well water, filtered tap water, an effluent from a wood treatment plant, and condensate from a medium Btu coal gas process. Two laboratories 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 5 and Table 6.

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

33.3 3 Precision and bias for this test method conform to Practice D 2777-77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D 2777-98, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

34. Quality Control

34.1 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 manganese.

34.2 *Calibration and Calibration Verification*:

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

34.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The absorbance shall fall within 4 % of the absorbance from the calibration. Alternately, the concentration of a mid-range standard should fall within ± 10 % of the known concentration.

34.2.3 If calibration cannot be verified, recalibrate the instrument.

34.3 *Initial Demonstration of Laboratory Capability*:

34.3.1 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.

[7] Supporting data are available from ASTM International Headquarters. Request RR: D19-1106.

TABLE 6 Determination of Bias and Overall Precision in Water of Choice, Atomic Absorption Graphite Furnace

Amount Added, µg/L	Amount Found, µg/L	S_T	Bias, µg/L	% Bias	Statistically Significant
7.5	7.66	1.13	+ 0.16	+ 2.1	no
15	15.8	2.86	+ 0.8	+ 5.3	no
44	42.6	8.13	−1.4	−3.2	no

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

34.3.3 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 Test Method D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

34.4 *Laboratory Control Sample (LCS)* :

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

34.4.2 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.

34.5 *Method Blank*:

34.5.1 Analyze a reagent water test blank with each batch. The concentration of manganese found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of manganese 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.

34.6 *Matrix Spike (MS)*:

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

34.6.2 The spike concentration plus the background concentration of mananese 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.

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

$$P = \frac{100\,[A(V_s + V) - B\,V_s]}{C\,V} \quad (2)$$

where:

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

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

34.7 *Duplicate*:

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

34.7.2 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 Test Method D 5847 for information on applying the F test.

34.7.3 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.

34.8 *Independent Reference Material (IRM)*:

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

35. Keywords

35.1 atomic absorption; chelation; flame; graphite furnace; manganese; water

APPENDIX

(Nonmandatory Information)

X1. RATIONALE FOR DISCONTINUATION OF TEST METHODS

X1.1 Test Method A, Colorimetric (for concentrations of manganese ranging from 0.025 to 15 mg/L):

X1.1.1 This test method was discontinued in 1988. It was published in its entirety in the 1988 *Annual Book of ASTM Standards*, Vol 11.01.

X1.1.2 This test method covers the determination of manganese in water and includes both dissolved and particulate material. It is applicable for manganese present as Mn in the range from 0.025 to 15 mg/L.

X1.1.3 Particulate manganese is solubilized by acid digestion and the dissolved manganese is oxidized to permanganate with ammonium persulfate in the presence of silver nitrate. The color is compared with standards either visually or instrumentally.

X1.1.4 This test method was discontinued because there were insufficient laboratories interested in participating in a collaborative study to obtain the necessary precision and bias as required by Practice D 2777.