



Standard Test Methods for Manganese in Water¹

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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 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 $\mu\text{g/L}$	16 to 24
Test Method C—Atomic Absorption, Graphite Furnace	5 to 50 $\mu\text{g/L}$	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 Note 5, Note 10, Note 11, and Note 16.

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 Steam³
- D 1068 Test Methods for Iron in Water³
- D 1129 Terminology Relating to Water³

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 A1, 1970, p. 115.

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

- D1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits³
- D 1193 Specification for Reagent Water³
- D 1687 Test Methods for Chromium in Water³
- D 1688 Test Methods for Copper in Water³
- D 1691 Test Methods for Zinc in Water³
- D 1886 Test Methods for Nickel in Water³
- D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water³
- D 3370 Practices for Sampling Water from Closed Conduits³
- D 3557 Test Methods for Cadmium in Water³
- D 3558 Test Methods for Cobalt in Water³
- D 3559 Test Method for Lead in Water³
- D 3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry³
- D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents³

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 of 50 $\mu\text{g/L}$ 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.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 *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 HNO₃ (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- μ m (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 SiO₂ 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. **Caution**—When HCl is distilled, an azeotropic mixture is obtained (approximately 6 NHCl). 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 (MnSO₄·H₂O) in a mixture of 10 mL of HNO₃ (sp gr 1.42) and 100 mL of water. Dilute to 1 L with water.

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 (HNO₃).

NOTE 4—If a high reagent blank is obtained, distill the HNO₃ or use spectrograde acid.

11.5 *Nitric Acid* (1 + 499)—Add 1 volume of HNO₃ (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*:

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 *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.

11.7.1 *Acetylene*—Standard, commercially available acetylene is the usual fuel. Acetone, always present in acetylene cylinders, can affect analytical results (see Note 5). The cylinder should be replaced at 50 psig (345 kPa).

NOTE 5—**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 HNO₃(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 6—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 HNO₃(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 HNO₃(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 if this capability is provided with the instrument.

NOTE 7—Some instruments are equipped with an accessory that permits direct reading of concentration from the instrument readout. Alternatively, this method of standardization may be used.

13. Procedure

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

NOTE 8—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 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.

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 HNO₃(1 + 499) between each sample or standard.

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 Bias⁵

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.

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 HNO₃ 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.

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.

⁵ Supporting data for Test Methods A and B are available from ASTM Headquarters. Request RR: D19-1034.

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

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

20.2 Chloroform (CHCl₃)

NOTE 10—**Precaution:** 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 (MnSO₄·H₂O) in water containing 1 mL of HNO₃ (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 HNO₃ (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 (HNO₃) (see Note 4).

20.9 *Pyrrrolidine Dithiocarbamic Acid-Chloroform Reagent*—Add 36 mL of pyrrrolidine to 1 L of CHCl₃. Cool the solution and add 30 mL of CS₂ in small portions, swirling between additions. Dilute to 2 L with CHCl₃. The reagent can be used for several months if stored in a cool, dark place.

NOTE 11—**Warning:** All components of this reagent are highly toxic. **Precaution**—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 HNO₃ (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 or calculate a standard curve (see Note 7).

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 12—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 13—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 bromocresol 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 14—The pH adjustment in 22.6 may be made with a pH meter instead of using an indicator.

22.7 Add 10 mL of pyrrrolidine 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 15—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.

NOTE 16—**Precaution:** Perform in a well-ventilated hood.

22.11 Hold the beaker at a 45° angle, and slowly dropwise add 2 mL of HNO₃ (sp gr 1.42), rotating the beaker to effect thorough contact of the acid with the residue.

NOTE 17—If acid is added to the beaker in a vertical position, a violent reaction will occur accompanied by high heat and spattering.

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

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

NOTE 18—If a precipitate appears when the hydrochloric acid (1 + 2) is added to the dried residue, obtain a fresh supply of pyrrrolidine that has a different lot number or redistill the pyrrrolidine just before preparing the pyrrrolidine 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:

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

where:

A = volume of sample, mL, and

B = weight of manganese in sample, μg .

24. Precision and Bias ⁵

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.

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.

25.2 This test method is applicable in the range from approximately 5 to 50 $\mu\text{g/L}$ 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.

TABLE 3 Precision and Concentration, Chelation-Extraction

Reagent water:			
Concentration (\bar{X}), $\mu\text{g/L}$	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}), $\mu\text{g/L}$	22.17	120.87	268.02
S_T	3.50	9.00	14.99
S_O	3.74	7.21	12.08

TABLE 4 Determination of Bias, Chelation-Extraction

Amount Added, $\mu\text{g/L}$	Amount Found, $\mu\text{g/L}$	Bias, $\mu\text{g/L}$	% 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

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 19 and Note 20).

NOTE 19—A wavelength other than 279.5 nm may be used if it has been determined to be suitable.

NOTE 20—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.

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.). Strip chart recorders shall have a full scale deflection time of 0.2 s or less to ensure accuracy.

28.7 Automatic sampling is recommended if available.

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 (HNO₃) (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 HNO₃(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 HNO₃(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 12).

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 21). The acid concentration at this point should be 0.5 % HNO₃.

NOTE 21—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.

33. Precision and Bias ⁶

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.

34. Keywords

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

⁶ Supporting data are available from ASTM Headquarters. Request RR: D19-1106.

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

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

Amount Added, $\mu\text{g/L}$	Amount Found, $\mu\text{g/L}$	S_T	Bias, $\mu\text{g/L}$	% 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

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.

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