



Designation: D858 – 12

Standard Test Methods for Manganese in Water¹

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

1. Scope*

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

Test Method	Concentration Range	Sections
A—Atomic Absorption, Direct	0.1 to 5 mg/L	7 to 15
B—Atomic Absorption, Chelation-Extraction	10 to 500 μ g/L	16 to 24
C—Atomic Absorption, Graphite Furnace	5 to 50 μ 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 The values stated in either SI units or inch-pound units are to be regarded separately as standard. The values stated in each system are mathematical conversions and may not be exact equivalents; therefore, each system shall be used independently of the other.

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 hazard statements, see 11.7, 20.2, 20.9, and 22.10.

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

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. Referenced Documents

2.1 ASTM Standards:²

- D1066 Practice for Sampling Steam
- D1068 Test Methods for Iron in Water
- D1129 Terminology Relating to Water
- D1193 Specification for Reagent Water
- D1687 Test Methods for Chromium in Water
- D1688 Test Methods for Copper in Water
- D1691 Test Methods for Zinc in Water
- D1886 Test Methods for Nickel in Water
- D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
- D3370 Practices for Sampling Water from Closed Conduits
- D3557 Test Methods for Cadmium in Water
- D3558 Test Methods for Cobalt in Water
- D3559 Test Methods for Lead in Water
- D3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry
- D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
- D5810 Guide for Spiking into Aqueous Samples
- D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

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 that is included in the procedure.

3.2 Definitions:

3.2.1 For definitions of terms used in these test methods, refer to Terminology D1129.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

*A Summary of Changes section appears at the end of this standard

4. Significance and Use

4.1 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 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.³ 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 D1193, Type I. Other reagent water types may be used, provided it is first ascertained that the water is of sufficiently high purity to permit its use without 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 D1066, or Practices D3370 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-µm (No. 325) membrane filter before acidification. The holding time for samples may be calculated in accordance with Practice D4841.

NOTE 1—Alternatively, the pH may be adjusted in the laboratory if the sample is returned within 14 days. This could reduce hazards of working with acids in the field when appropriate.

³ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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 D3557), chromium (Test Methods D1687), cobalt (Test Methods D3558), copper (Test Methods D1688), iron (Test Methods D1068), lead (Test Methods D3559), nickel (Test Methods D1886), and zinc (Test Methods D1691).

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 2—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 3—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 4—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 *M*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 ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) 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 manganese stock solution of appropriate known 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 5—If a high reagent blank is obtained, distill the HNO_3 or use spectrograde acid.

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:* Acetylene—standard, commercially available acetylene is the usual fuel. Acetone, always present in acetylene cylinders, can affect analytical results. The cylinder should be replaced at 345 kPa (50 psi). (**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 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 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.

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

NOTE 7—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 8—For brines and samples with high levels of suspended matter, the amount of reduction in volume is left to the discretion of the analyst.

NOTE 9—Many laboratories have found block digestion systems a useful way to digest samples for trace metals analysis. Systems typically consist of either a metal or graphite block with wells to hold digestion tubes. The block temperature controller must be able to maintain uniformity of temperature across all positions of the block. For trace metals analysis, the digestion tubes should be constructed of polypropylene and have a volume accuracy of at least 0.5%. All lots of tubes should come with a certificate of analysis to demonstrate suitability for their intended purpose.

13.4 Cool and filter 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 and standard.

14. Calculation

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

15. Precision and Bias⁴

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 D2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of

⁴ Supporting data Test Methods A and B have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1034. Contact ASTM Customer Service at service@astm.org.

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

Practice **D2777** – 08, 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 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.

20.2 *Chloroform* (CHCl₃) (**Warning**—Use in well-ventilated hood.)

20.3 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl) (see **Note 4**).

20.4 *Hydrochloric Acid* (1 + 2)—Add 1 volume of HCl (sp gr 1.19) to 2 volumes of water (see **Note 4**).

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. A purchased stock solution of appropriate purity is also acceptable.

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 5**).

20.9 *Pyrrolidine Dithiocarbamic Acid-Chloroform Reagent*—Add 36 mL of pyrrolidine 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. (**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 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. Alternatively read directly in concentration from the instrument.

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 10—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.