



Designation: D 858 – 02

## Standard Test Methods for Manganese in Water<sup>1</sup>

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 reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

*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 <sup>2</sup>	0.1 to 5 mg/L	7 to 15
Test Method B—Atomic Absorption, Chelation-Extraction <sup>2</sup>	10 to 500 $\mu$ g/L	16 to 24
Test Method C—Atomic Absorption, Graphite Furnace	5 to 50 $\mu$ 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 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<sup>3</sup>
- [D 1068](#) Test Methods for Iron in Water<sup>3</sup>
- [D 1129](#) Terminology Relating to Water<sup>3</sup>

<sup>1</sup> 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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<sup>2</sup> 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.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

[D1192](#) Specification for Equipment for Sampling Water and Steam in Closed Conduits<sup>3</sup>

[D 1193](#) Specification for Reagent Water<sup>3</sup>

[D 1687](#) Test Methods for Chromium in Water<sup>3</sup>

[D 1688](#) Test Methods for Copper in Water<sup>3</sup>

[D 1691](#) Test Methods for Zinc in Water<sup>3</sup>

[D 1886](#) Test Methods for Nickel in Water<sup>3</sup>

[D 2777](#) Practice for Determination of Precision and Bias of Applicable Methods of Committee D19 on Water<sup>3</sup>

[D 3370](#) Practices for Sampling Water from Closed Conduits<sup>3</sup>

[D 3557](#) Test Methods for Cadmium in Water<sup>3</sup>

[D 3558](#) Test Methods for Cobalt in Water<sup>3</sup>

[D 3559](#) Test Method for Lead in Water<sup>3</sup>

[D 3919](#) Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry<sup>3</sup>

[D 4841](#) Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents<sup>3</sup>

[D 5810](#) Guide for Spiking into Aqueous Samples<sup>3</sup>

[D 5847](#) Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis<sup>4</sup>

### 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

<sup>4</sup> *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.<sup>5</sup> 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<sub>3</sub> (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.

<sup>5</sup> *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.

## 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<sub>2</sub> 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 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 (MnSO<sub>4</sub>·H<sub>2</sub>O) in a mixture of 10 mL of HNO<sub>3</sub> (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<sub>3</sub>).

NOTE 4—If a high reagent blank is obtained, distill the HNO<sub>3</sub> or use spectrograde acid.

11.5 *Nitric Acid (1 + 499)*—Add 1 volume of HNO<sub>3</sub>(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<sub>3</sub>(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<sub>3</sub>(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<sub>3</sub>(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<sub>3</sub>(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 <sup>6</sup>

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<sub>3</sub> 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.

<sup>6</sup> 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<sub>3</sub>)* (**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<sub>4</sub>·H<sub>2</sub>O) in water containing 1 mL of HNO<sub>3</sub> (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<sub>3</sub> (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<sub>3</sub>) (see [Note 4](#)).

20.9 *Pyrrolidine Dithiocarbamic Acid-Chloroform Reagent*—Add 36 mL of pyrrolidine to 1 L of CHCl<sub>3</sub>. Cool the solution and add 30 mL of CS<sub>2</sub> in small portions, swirling between additions. Dilute to 2 L with CHCl<sub>3</sub>. 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<sub>3</sub> (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<sub>3</sub> (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.