



Standard Test Method for Manganese In Gasoline By Atomic Absorption Spectroscopy¹

This standard is issued under the fixed designation D 3831; 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.

1. Scope

1.1 This test method covers the determination of the total manganese content, present as methylcyclopentadienyl manganese tricarbonyl (MMT)², of gasoline within the concentration range from 0.25 to 0.30 mg of manganese/L (0.001 to 0.120 g/U.S. gal).

1.2 This test method is not applicable to gasoline containing highly cracked materials (greater than 20 Bromine Numbers).

1.3 This test method has been developed and tested specifically for the determination of MMT in gasoline over the recommended concentration range. Application of the method to other concentration ranges, to the determination of MMT in other materials, or to the determination of other manganese compounds in gasoline have not been tested

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 precautionary statements, see Section 7.

1.5 The values stated in SI units are to be regarded as the standard. For reporting purposes, the values stated in grams per U.S. gallon are the preferred units in the United States.

2. Referenced Documents

2.1 ASTM Standards:

D 1159 Test Method for Bromine Number of Petroleum Distillates and Commercial Aliphatic Olefins by Electro-metric Titration³

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products⁴

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products⁴

3. Summary Test of Method

3.1 The gasoline sample is treated with bromine and diluted

with methyl isobutyl ketone. The manganese content of the sample is determined by atomic absorption spectrometry using an air-acetylene flame at 279.5 nm and standards prepared from an organo-manganese standard material.

4. Significance and Use

4.1 Certain organo-manganese compounds act as antiknock agents when added to gasoline. This test method provides a means for determining the concentration of such a material in a gasoline sample.

5. Apparatus

5.1 *Atomic Absorption Spectrometer*, capable of scale expansion and equipped with a manganese hollow-cathode lamp for monitoring manganese absorption at 279.5 nm, a premix slot-type burner with rotatable burner head, and an adjustable nebulizer.

5.2 *Glass Vials*, 40-mL size with polyethylene-lined screw caps.

5.3 *Pipet, Delivery*, 1-mL size.

5.4 *Micropipet*, 100-μL size, Eppendorf type or equivalent.

5.5 *Automatic Pipet*, capable of delivering 9.0-mL quantities.⁵

6. Reagents

6.1 *Purity of Reagents*—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.⁶ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Bromine Solution*—Add reagent grade bromine to an equal volume of carbon tetrachloride.

NOTE 1—**Warning:** In addition to other precautions, bromine can cause

¹ This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03.01 on Spectrometric Methods.

Current edition approved Nov. 10, 1998. Published January 1999. Originally published as D 3831 – 79. Last previous edition D 3831 – 90(1994)^{ε1}.

² MMT is a registered trademark of Ethyl Corp.

³ *Annual Book of ASTM Standards*, Vol 05.01.

⁴ *Annual Book of ASTM Standards*, Vol 05.02.

⁵ The standard repipet with 950-mL round amber bottle and 10-mL dispenser capacity, available from Fisher Scientific Co. 1600 Park View Dr., Pittsburgh, PA 15205, has been found satisfactory.

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

severe and painful burns when it contacts the skin. Wear protective gloves in preparing the solution and prepare, store, and use it in a well-ventilated hood.

NOTE 2—**Warning:** Carbon tetrachloride is a known carcinogen. Appropriate safety precautions apply. Prevent all contact.

6.3 *Manganese Standard Solution 0.05, 0.10, and 0.15 g Mn/gal (13.2, 26.42, 39.63 mg Mn/L)*—Dilute the 1.0 g Mn/gal (264.2 mg Mn/L) standard manganese solution with methyl isobutyl ketone using volumetric glassware to give the desired lower concentration manganese standard solutions.

6.4 *Manganese, Standard Solution 1.0 g Mn/gal (264.2 mg Mn/L)*—Dissolve the appropriate amount of manganese sulfonate in methyl isobutyl ketone to give a standard containing 1.0 g Mn/gal (264.2 mg Mn/L).

6.5 *Manganese Sulfonate*.⁷

6.6 *Methyl Isobutyl Ketone*, reagent grade.

NOTE 3—**Warning:** Methyl isobutyl ketone-Flammable. Vapor harmful.

NOTE 4—**Caution:** Solutions of MMT in gasoline are chemically unstable when exposed to light. Low and erratic results may be obtained if the gasoline sample is exposed to light prior to stabilization during analysis.

7. Sampling

7.1 Take samples of gasoline in compliance with the instructions in Practice D 4057.

7.2 Take gasoline samples directly into an all-metal can and analyze as soon as possible after sampling.

8. Calibration

8.1 *Preparation of Working Standards*—Prepare three working standards using the 0.05, 0.10, and 0.15 g Mn/gal (13.2, 26.42, 39.63 mg Mn/L) standard manganese solutions described in 6.3.

8.1.1 Using a micropipet, add 100 μ L of bromine solution to each of three separate 40-mL glass vials.

8.1.2 Pipet 1 mL of each of the three low-manganese standards into each of the glass vials. Mix with the bromine solution by swirling the vials.

8.1.3 Using the automatic pipet, deliver 9.0 mL of methyl isobutyl ketone to each of the vials. Mix well. This tenfold dilution of the low-manganese standards is the same as the final dilution of the sample.

8.2 *Preparation of Instrument*—Set the atomic absorption spectrometer operating conditions to those recommended by the manufacturer for monitoring manganese absorption at 279.5 nm using an air-acetylene flame.

8.2.1 Aspirate methyl isobutyl ketone into the flame. Adjust the nebulizer (sample flow rate), acetylene, and air flow rates to give a lean, nonluminous flame.

8.2.2 Aspirate the 0.15 g Mn/gal (39.63 mg Mn/L) working standard, and note the absorbance. If the absorbance exceeds a value of 0.1 unit, rotate the burner head to decrease the absorbance to approximately 0.1 unit. Zero the instrument with methyl isobutyl ketone. Using this low absorbance range aids in achieving linearity.

8.2.3 Scale expand the instrument so that the 0.15 g Mn/gal (39.63 mg Mn/L) working standard gives near full-scale recorder deflection.

8.2.4 With methyl isobutyl ketone as a blank, aspirate, in turn, the three working standards. Record the absorbances and check these data for linearity. If nonlinear, readjust the sample or acetylene flow rates, or both, slightly to leaner conditions and repeat the calibrations until absorbances are linear.

9. Procedure

9.1 Deliver 100 μ L of bromine solution into a glass vial with the micropipet.

9.2 Add 1.0 mL of the gasoline sample, using a 1-mL pipet. Mix well.

9.3 Add 9.0 mL of methyl isobutyl ketone using the automatic pipet. Mix well.

9.4 Aspirate the working standards and the sample into the flame and record the absorbances of each.

NOTE 5—Measure absorbances of the working standards and the samples promptly as absorbances may change with time.

10. Calculations

10.1 Plot the absorbance values that were obtained by aspirating the working standard solutions versus manganese concentration and draw the best straight line through the points. From the plot read the manganese concentration corresponding to the absorbance of the gasoline sample. Report the manganese content of the gasoline to the nearest 0.001 g Mn/U.S. gal (0.2 mg Mn/L). Other modes of readout, such as the concentration mode, may be used if available. The low absorbance range in 8.2.2 should be used to obtain calibration linearity.

11. Precision and Bias

11.1 *Precision*—The precision of this test method as obtained by statistical examination of interlaboratory test results is as follows:

11.1.1 *Repeatability*—The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

$$\begin{aligned} &0.026\sqrt{x} \text{ g Mn U.S. gal} \\ &(0.42 \sqrt{x} \text{ mg Mn/L}) \end{aligned} \quad (1)$$

where x = average of the two results.

11.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

$$\begin{aligned} &0.087\sqrt{x} \text{ g Mn/U.S. gal} \\ &(1.41 \sqrt{x} \text{ mg Mn/L}) \end{aligned} \quad (2)$$

where x = average of the two results.

11.2 *Bias*—The bias for the procedure in this test method cannot be determined, since a suitable reference material is not available.

⁷ Conostan manganese sulfonate, available from Conostan Division, Continental Oil Co., Ponca City, OK 74601, has been found satisfactory.