



Designation: **D3831—01 (Reapproved 2006) D3831 – 12**

Standard Test Method for Manganese in Gasoline By Atomic Absorption Spectroscopy¹

This standard is issued under the fixed designation D3831; 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 40 mg/L of manganese.

1.2 This test method is applicable to reformulated gasoline containing up to 12 % volume methyl tertiary butylether or up to 10 % volume ethanol. This test method may not be applicable to highly cracked materials containing greater than 18 volume % olefins as determined by Test Method **D1319** (nondepentanized).

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 The values stated in SI units are to be regarded as the standard. The preferred concentration units are mg/L manganese.

1.5 *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 warning statements, see Sections 5 and 6.

2. Referenced Documents

2.1 *ASTM Standards:*³

[D1319 Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption](#)

[D4057 Practice for Manual Sampling of Petroleum and Petroleum Products](#)

[D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products](#)

[D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance](#)

[D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants](#)

[D6792 Practice for Quality System in Petroleum Products and Lubricants Testing Laboratories](#)

[D7740 Practice for Optimization, Calibration, and Validation of Atomic Absorption Spectrometry for Metal Analysis of Petroleum Products and Lubricants](#)

3. Summary of Test Method

3.1 The gasoline sample is treated with bromine solution 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.

3.2 Protocols for using atomic absorption spectrometry are given in Practice **D7740**.

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.

¹ This test method is under the jurisdiction of ASTM Committee **D02** on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee **D02.03** on Elemental Analysis.

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² MMT is a registered trademark of Ethyl Corp.

³ 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

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. (**Warning**—Hazardous. Potentially toxic and explosive. Refer to the manufacturer’s instrument manual for associated safety hazards.)

5.2 *Vials*, up to 40-mL size with polyethylene or TFE-fluorocarbon-lined caps or glass stoppers.

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

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

5.5 *Automatic Pipet*, or equivalent delivery pipet, capable of delivering 9.0-mL quantities.

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.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.

6.2 *Bromine Solution*—Add reagent grade bromine to an equal volume of cyclohexane. (**Warning**—Bromine can cause severe and painful burns when it contacts the skin. In addition to other precautions, wear protective gloves in preparing the solution and prepare, store, and use it in a well-ventilated hood.)

6.3 *Manganese Standard Solution 400 mg Mn/L*—Dissolve the appropriate amount of organometallic manganese standard in methyl isobutyl ketone to give a standard solution of 400 mg Mn/L.

6.4 *Manganese, Standard Solution 4.0, 10.0, 20.0, and 40.0 mg Mn/L*—Dilute the 400 mg/L standard manganese solution with methyl isobutyl ketone using volumetric glassware to give the desired lower concentration manganese standard solutions.

6.5 *Organometallic Manganese Standard*—Pre-prepared commercially available organometallic stock solutions have been found to be satisfactory.

6.6 *Methyl Isobutyl Ketone*, reagent grade. (**Warning**—Flammable. Vapor harmful.) (**Warning**—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.)

6.7 *Quality Control (QC) Sample(s)*, preferably are a portion of one or more gasoline materials that are stable and representative of the samples of interest.

7. Sampling

7.1 Take samples of gasoline in compliance with the instructions in Practice **D4057** or **D4177** where appropriate. Analyze as soon as possible after sampling.

8. Calibration

8.1 *Preparation of Working Standards*—Prepare four working standards using the 4.0, 10.0, 20.0, and 40.0 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 four separate vials.

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

8.1.3 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. This test method assumes that good operating procedures are followed. Design differences between spectrometers make it impractical to exactly specify required instrument settings.

8.2.1 Nebulize 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 With methyl isobutyl ketone as a blank, nebulize, in turn, the four working standards.

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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.