



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 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 D 1319 (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 precautionary statements, see Sections 5, 6 and 7.*

2. Referenced Documents

2.1 ASTM Standards:

- D 1319 Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption³
- D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products⁴
- D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products⁴

D 6299 Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance⁵

D 6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants⁵

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.

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. (**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,

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 *Annual Book of ASTM Standards*, Vol 05.01.

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

⁵ *Annual Book of ASTM Standards*, Vol 05.03.

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

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 cyclohexane. (**Warning**—In addition to other precautions, bromine can cause 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.)

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**—Methyl isobutyl ketone-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 D 4057 or D 4177 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.

NOTE 1—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. Rotation of the burner head to decrease the absorbance may aid in achieving linearity.

NOTE 2—Three working standards may be used to cover the expected concentration range of the samples. Fuel specification limits should be considered. For example, the use of the high 40 mg/L standard may not be necessary.

9. Procedure

9.1 Deliver 100 μ L of bromine solution into a vial.

9.2 Add 1.0 mL of the gasoline sample. Mix well.

9.3 Add 9.0 mL of methyl isobutyl ketone. Mix well.

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

NOTE 3—Measure absorbances of the working standards and the samples promptly as the sample absorbances may change with time.

10. Calculations

10.1 The direct concentration read out of the instrument is the preferred mode of quantification. Alternatively, 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 0.1 mg/L Mn.

11. Quality Control

11.1 Confirm the performance of the test procedure by analyzing a quality control (QC) sample that is stable and representative of the sample of interest.

11.2 When the quality control/quality assurance protocols are already established in the testing facility, these may be used to confirm the reliability of the test result.

11.3 When there is no quality control/quality assurance protocol established in the testing facility, Appendix X1 can be used to perform this function.

12. Precision and Bias

12.1 *Precision*⁷—The precision of this test method as obtained by statistical examination of interlaboratory test results from eleven samples of motor gasoline, covering concentration range of 0.25 to 40 mg/L manganese, run in duplicate by eleven laboratories is as follows:

12.1.1 *Repeatability*— The difference between successive test results, obtained by the same operator with the same

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.

⁷ Supporting data are available from ASTM Headquarters. Request RR: D02-1500.

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:

$$0.3308\sqrt{(x + 0.1062)} \text{ mg Mn/L} \quad (1)$$

where x = average of the two results.

12.1.2 *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:

$$1.650\sqrt{(x + 0.1062)} \text{ mg Mn/L} \quad (2)$$

where x = average of the two results.

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

13. Keywords

13.1 AAS; atomic absorption spectroscopy; gasoline; manganese; methylcyclopentadienyl manganese tricarbonyl; MMT

APPENDIX

(Nonmandatory Information)

X1. QUALITY CONTROL

X1.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample that is, if possible, representative of the samples typically analyzed.

X1.2 Prior to monitoring the measurement process, the user of the method needs to determine the average value and control limits of the QC sample. See Practices D 6299, D 6300, and MNL 7.⁸

X1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process. See Practices D 6299, D 6300, and MNL 7.⁸ Any out-of-control data should trigger investigation for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

X1.4 In the absence of explicit requirements given in the test method, the frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample is analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample precision should be periodically checked against the ASTM method precision to ensure data quality. See Practice D 6300.

X1.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the samples routinely analyzed. An ample supply of QC material should be available for the intended period of use, and must be homogeneous and stable under the anticipated storage conditions.

X1.6 See Practices D 6299, D 6300 or MNL 7⁸ for further guidance on QC and Control Charting techniques.

⁸ ASTM MNL 7 "Manual on Presentation of Data Control Chart Analysis," 6th ed., Section 3: Control Chart for Individuals, available from ASTM Headquarters.

SUMMARY OF CHANGES

Committee D02.03 has identified the location of selected changes to this standard since the last issue (D 3831–98) that may impact the use of this standard.

- (1) Cyclohexane replaced the use of carbon tetrachloride as a bromine reagent solvent.
- (2) The scope's upper range of quantitation was extended from 30 mg/L to 40 mg/L.
- (3) The test method was modernized with regards to current ASTM Blue Book guidelines, preferred units (SI units only),

and Subcommittee D02.03 Quality Control requirements.

- (4) A round robin study using cyclohexane as the replacement bromine reagent solvent for carbon tetrachloride was conducted and found to have similar precision to the previous revision.

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