This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

**Designation: D3237 – 17**

# Standard Test Method for Lead in Gasoline by Atomic Absorption Spectroscopy[1]

This standard is issued under the fixed designation D3237; 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.

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

## 1. Scope*

1.1 This test method covers the determination of the total lead content of gasoline within the concentration range of 0.010 g to 0.10 g of lead/U.S. gal (2.5 mg/L to 25 mg/L). This test method compensates for variations in gasoline composition and is independent of lead alkyl type.

1.2 The values given in grams per U.S. gallon are to be regarded as the standard in the United States. Note that in other countries, other units can be preferred.

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 6.6 and 6.8.

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D1368 Test Method for Trace Concentrations of Lead in Primary Reference Fuels (Withdrawn 1994)[3]

D2550 Method of Test for Water Separation Characteristics of Aviation Turbine Fuels (Withdrawn 1989)[3]

D3116 Test Method for Trace Amounts of Lead in Gasoline (Withdrawn 1994)[3]

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

D6792 Practice for Quality Management Systems in Petroleum Products, Liquid Fuels, 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 diluted with methyl isobutyl ketone and the alkyl lead components are stabilized by reaction with iodine and a quaternary ammonium salt. The lead content of the sample is determined by atomic absorption flame spectrometry at 283.3 nm, using standards prepared from reagent grade lead chloride. By the use of this treatment, all alkyl lead compounds give identical response.

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

## 4. Significance and Use

4.1 This test method is used to ensure compliance of trace lead as required by federal regulation for lead-free gasoline (40 CFR part 80).

## 5. Apparatus

5.1 *Atomic Absorption Spectrometer,* capable of scale expansion and nebulizer adjustment, and equipped with a slot burner and premix chamber for use with an air-acetylene flame.

5.2 *Volumetric Flasks,* 50 mL, 100 mL, 250 mL, and 1 L sizes.

5.3 *Pipets,* 2 mL, 5 mL, 10 mL, 20 mL, and 50 mL sizes.

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

## 6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that

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

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[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.

[3] The last approved version of this historical standard is referenced on www.astm.org.

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

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all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[4]

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Types II or III of Specification D1193.

6.3 *Aliquat 336* (tricapryl methyl ammonium chloride).

6.4 *Aliquat 336/MIBK Solution (10 % volume per volume)*—Dissolve and dilute 100 mL (88.0 g) of Aliquat 336 with MIBK to 1 L.

6.5 *Aliquat 336/MIBK Solution (1 % volume per volume)*—Dissolve and dilute 10 mL (8.8 g) of Aliquat 336 with MIBK to 1 L.

6.6 *Iodine Solution*—Dissolve and dilute 3.0 g of iodine crystals with toluene to 100 mL. (**Warning—**Flammable. Vapor harmful.)

6.7 *Lead Chloride* ($PbCl_2$).

6.8 *Lead-Sterile Gasoline*—Gasoline containing less than 0.005 g Pb/gal (1.32 mg Pb/L). (**Warning—**Extremely flammable. Harmful if inhaled. Vapors may cause flash fire.)

NOTE 1—One way to confirm lead concentrations of less than 0.005 g Pb/gal (1.32 mg Pb/L) is to refer to Test Methods D1368 and D3116. A procedure for the purification of gas turbine fuel appears in Appendix X4 of Test Method D2550 and can be used to decrease the lead concentration of low lead gasoline in lead-sterile gasoline.

6.9 *Lead, Standard Solution (5.0 g Pb/gal (1.32 g Pb/L))*—Dissolve 0.4433 g of lead chloride ($PbCl_2$) previously dried at 105 °C for 3 h in about 200 mL of 10 % Aliquat 336/MIBK solution in a 250 mL volumetric flask. Dilute to the mark with the 10 % Aliquat solution, mix, and store in a brown bottle having a polyethylene-lined cap. This solution contains 1321 µg Pb/mL, which is equivalent to 5.0 g Pb/gal.

6.10 *Lead, Standard Solution* (1.0 g Pb/gal (264 mg Pb/L))—By means of a pipet, accurately transfer 50.0 mL of the 5.0 g Pb/gal (1.32 g Pb/L) solution to a 250 mL volumetric flask, dilute to volume with 1 % Aliquat/MIBK solution. Store in a brown bottle having a polyethylene-lined cap.

6.11 *Lead, Standard Solutions* (0.02 g, 0.05 g, and 0.10 g Pb/gal (5. 3 mg, 13.2 mg, and 26.4 mg Pb/L))—Transfer accurately by means of pipets 2.0 mL, 5.0 mL, and 10.0 mL of the 1.0 g Pb/gal (264 mg Pb/L) solution to 100 mL volumetric flasks; add 5.0 mL of 1 % Aliquat 336 solution to each flask; dilute to the mark with MIBK. Mix well and store in bottles having polyethylene-lined caps.

6.12 *Methyl Isobutyl Ketone (MIBK),* (4-methyl-2-pentanone).

6.13 *Quality Control (QC) Samples,* preferably are portions of one or more liquid petroleum materials that are stable and representative of the samples of interest. These QC samples can be used to check the validity of the testing process as described in Section 11.

## 7. Sampling

7.1 Take samples of gasoline in compliance with the instructions in Practice D4057 or Practice D4177.

7.2 Collect sample in a metal container that can be sealed against leakage and store under temperature-consistent conditions prior to analysis.

## 8. Calibration

8.1 *Preparation of Working Standards*—Prepare three working standards and a blank using the 0.02 g, 0.05 g, and 0.10 g Pb/gal (5.3 mg, 13.2 mg, and 26.4 mg Pb/L) standard lead solutions described in 6.11.

8.1.1 To each of four 50 mL volumetric flasks containing 30 mL of MIBK, add 5.0 mL of low lead standard solution and 5.0 mL of lead-free gasoline. In the case of the blank, add only 5.0 mL of lead-free gasoline.

8.1.2 Add immediately 0.1 mL of iodine/toluene solution by means of the 100-µL Eppendorf pipet. Mix well and allow to react for 1 min.

8.1.3 Add 5 mL of 1 % Aliquat 336 solution. Dilute to volume with MIBK and mix well.

8.2 *Preparation of Instrument*—Optimize the atomic absorption equipment for lead at 283.3 nm. Using the reagent blank, adjust the gas mixture and the sample aspiration rate to obtain an oxidizing flame which is fuel lean and light blue in color.

8.2.1 Aspirate the 0.1 g Pb/gal (26.4 mg Pb/L) working standard and adjust the burner position to give maximum response. Some instruments require the use of scale expansion to produce an absorbance reading of 0.150 to 0.170 for this standard.

8.2.2 Aspirate the blank to zero the instrument and check the absorbances of the three working standards for linearity.

## 9. Procedure

9.1 To a 50 mL volumetric flask containing 30 mL MIBK, add 5.0 mL of gasoline sample and mix.

9.1.1 Add 0.10 mL (100 µL) of iodine/toluene solution and allow the mixture to react about 1 min.

9.1.2 Add 5.0 mL of 1 % Aliquat 336/MIBK solution and mix.

9.1.3 Dilute to volume with MIBK and mix.

9.2 Aspirate the samples and working standards and record the absorbance values with frequent checks of the zero.

## 10. Calculation

10.1 Plot the absorbance values versus the concentration represented by the working standards and read the concentrations of the samples from the graph.

10.2 If the AAS instrument has built-in computer software, it can be used to do the above calculations.

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[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.

## 11. Quality Control

11.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample (see 6.13).

11.1.1 When QC/Quality Assurance (QA) protocols are already established in the testing facility, these may be used when they confirm the reliability of the test result.

11.1.2 When there is no QC/QA protocol established in the testing facility, Appendix X1 can be used as the QC/QA system.

NOTE 2—Further guidance on QA/QC may be found in Practice D6792.

## 12. Precision and Bias

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

12.1.1 *Repeatability*—The difference between two 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:

0.005 g/U.S gal (1.3 mg/L)

12.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators 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:

0.01 g/U.S gal (2.6 mg/L)

12.2 *Bias*—The bias for this test method was determined by two individual laboratories analyzing standard reference materials.

| Sample | Certified Pb, g/U.S. gal. | Observed Results, g/U.S.gal | |
|---|---|---|---|
| | | Laboratory 1 | Laboratory 2 |
| SRM2712 | 0.031 | 0.032, 0.033 | 0.034, 0.033 |
| SRM2713 | 0.052 | 0.051, 0.054 | 0.050, 0.051 |
| SRM2714 | 0.075 | 0.077, 0.079 | |

The values obtained are within the repeatability of the test method and indicate no bias.[5]

## 13. Keywords

13.1 atomic absorption; gasoline; lead; lead-free

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1376. Contact ASTM Customer Service at service@astm.org.

## APPENDIX

### (Nonmandatory Information)

### X1. QUALITY CONTROL MONITORING

X1.1 Confirm the performance of the instrument or the test procedure by analyzing quality control (QC) sample(s).

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 Practice D6299).[6]

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 Practice D6299).[6,7] Investigate any out-of-control data for root cause(s). The results of this investigation may, but not necessarily, result in instrument re-calibration.

X1.4 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 should be 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 testing precision should be periodically checked against the ASTM test method precision to ensure data quality (see Practice D6299).[6]

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

X1.6 See Footnotes 6 and 7 for further guidance on QC and Control Charting techniques.

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[6] ASTM MNL 7, *Manual on Presentation of Data Control Chart Analysis*, 6th Ed., Section 3, ASTM International, W. Conshohocken, PA.

[7] In the absence of explicit requirements given in the test method, this clause provides guidance on QC testing frequency.

## SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D3237 – 12) that may impact the use of this standard. (Approved June 1, 2017.)

*(1)* Practice D4177 was added to subsections 2.1 and 7.1.

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