



## Standard Test Methods for Lead in Gasoline by X-Ray Spectroscopy<sup>1</sup>

This standard is issued under the fixed designation D 5059; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

<sup>ε1</sup> NOTE—Warning notes were editorially moved into the standard text in August 2003.

### 1. Scope

1.1 These test methods cover the determination of the total lead content of a gasoline within the following concentration ranges:

0.010 to 5.0 g Pb/US gal  
0.012 to 6.0 g Pb/UK gal  
0.0026 to 1.32 g Pb/L

1.1.1 Test Methods A and B cover the range of 0.10 to 5.0 g Pb/US gal. Test Method C covers the range of 0.010 to 0.50 g Pb/US gal.

1.1.2 These test methods compensate for normal variation in gasoline composition and are independent of lead alkyl type.

1.2 *Test Method A* (formerly in Test Method D 2599)—Sections 5-9.

*Test Method B* (formerly in Test Method D 2599)—Sections 10-14.

*Test Method C* (formerly in Test Method D 3229)—Sections 15-19.

1.3 The values stated in SI 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. Note that in other countries, other units can be preferred.

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 hazard statements, see Sections 5, 6, 11, and 18.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

<sup>1</sup> These test methods are under the jurisdiction of Committee D02 on Petroleum Products and Lubricants and are the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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These test methods have been approved by the sponsoring committees and accepted by the cooperating organizations in accordance with established procedures.

D 2599 Test Method for Lead in Gasoline by X-Ray Spectrometry<sup>2</sup>

D 3229 Test Method for Low Levels of Lead in Gasoline by Wavelength Dispersive X-Ray Spectrometry<sup>3</sup>

D 3341 Test Method for Lead in Gasoline-Iodine Monochloride Method<sup>4</sup>

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products<sup>4</sup>

### 3. Summary of Test Method

3.1 There are three alternative test methods, as follows.

3.1.1 *Test Method A (Bismuth Internal Standard Method High Concentration)*—One volume of sample is mixed thoroughly with an equal volume of bismuth internal standard solution. The mixture is placed in the X-ray beam and the intensities of the lead  $L\text{-}\alpha_1$  radiation at 1.175 Å and the bismuth  $L\text{-}\alpha_1$  radiation at 1.144 Å are determined. The lead concentration of the sample is measured by comparing the ratio of gross counting rate at 1.175 Å with the gross counting rate at 1.144 Å to a previous prepared calibration curve of concentration versus the same ratios.

3.1.2 *Test Method B (Scattered Tungsten Radiation Method)*—The ratio of the net X-ray intensity of the lead  $L\text{-}\alpha_1$  radiation to the net intensity of the incoherently scattered tungsten  $L\text{-}\alpha_1$  radiation is obtained on a portion of the sample. The lead content is determined by multiplying this ratio by a calibration factor obtained with a standard lead solution of known concentration.

3.1.3 *Test Method C (Bismuth Internal Standard Method, Low Concentration)*—Twenty millilitres of sample is mixed thoroughly with two milliliters of bismuth internal standard solution. The mixture is placed in the X-ray beam of a spectrometer and the intensities of the lead  $L\text{-}\alpha_1$  radiation at 1.175 Å, the bismuth  $L\text{-}\alpha_1$  radiation at 1.144 Å, and a background at 1.194 Å are determined. A blank, made with *iso*-octane and bismuth internal standard, is run using the same

<sup>2</sup> Discontinued. See 1991 *Annual Book of ASTM Standards*, Vol 05.02.

<sup>3</sup> Discontinued. See 1991 *Annual Book of ASTM Standards*, Vol 05.03.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 05.02.

procedure. The lead concentration is measured by determining the ratio of the net counting rate at 1.175 Å to the gross counting rate at 1.144 Å for the sample, subtracting the comparable ratio found for the blank, and comparing to a previously prepared calibration curve of concentration versus the same ratios.

#### 4. Significance and Use

4.1 These test methods determine the concentration of lead (from alkyl addition) in gasoline. These alkyl additives improve the antiknock properties.

4.2 Test Method C is used to ensure compliance of trace lead as required by federal regulations for lead-free gasoline (40 CFR part 80).

### TEST METHOD A (BISMUTH INTERNAL STANDARD)

#### 5. Apparatus

5.1 *X-ray Spectrometer*, capable of measuring radiations mentioned in 3.1.1 and of being operated under the following instrumental conditions or other giving equivalent results:

Tube Voltage	50 kV
Tube Current	20 to 45 mA
Analyzing Crystal	Lithium Fluoride (LiF)
Optical Path	Air, Helium ( <b>Warning</b> —Compressed gas under pressure)
Detector	Proportional or Scintillation

NOTE 1—The X-ray spectrometer and manner of use should comply with the regulations governing the use of ionizing radiation or recommendations of the International Commission of Radiological Protection, or both.

#### 6. Reagents and Materials

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

##### 6.2 Hydrocarbon-Soluble Bismuth.

NOTE 2—Bismuth 2-Ethylhexoate has been found suitable to use. Other bismuth containing materials that are hydrocarbon-soluble may also be used when they are certified to conform to 6.1.

6.3 *Bismuth Internal Standard Solution*—Dilute the hydrocarbon-soluble bismuth with a suitable solvent. If bismuth 2-ethylhexoate is used, add 2-ethylhexanoic acid as a stabilizer (see Note 3) to obtain a solution containing the following:

3.00 g Bi/US gal at 15.5°C (60°F) or  
3.60 g Bi/UK gal at 15.5°C (60°F) or  
0.793 g Bi/L at 15°C

NOTE 3—Some stability difficulties have been experienced with bismuth 2-ethylhexoate internal standard solution. If the standard is blended to contain 5 % 2-ethylhexanoic acid, the standard has been found to last almost indefinitely. The 2-ethylhexanoic acid stabilizes *iso*-octane, toluene, and benzene solutions of the bismuth 2-ethylhexoate which are otherwise stable for only a day or two. Normal octanoic acid does *not* stabilize solution.

6.4 *Iso-octane*. (**Warning**—Extremely flammable.)

6.5 *Solvent*, capable of dissolving the bismuth internal standard. Mixed xylenes and dodecane have been found suitable to use.

6.6 *Hydrocarbon-Soluble Lead*—Either tetraethyllead (TEL) or a lead-containing compound (for example, lead naphthenate) with a certifiable lead concentration.

6.7 *Lead (Pb) Standard Solution*—Dissolve tetraethyllead (TEL) (**Warning**—TEL is toxic by ingestion), lead naphthenate (see Note 4), or other suitable lead containing compound in *iso*-octane (**Warning**—Extremely flammable), toluene, or a mixture of these two solvents. This standard solution shall contain an accurately known lead concentration of approximately the following magnitude:

5 g Pb/US gal at 15.5°C (60°F) or  
6 g Pb/UK gal at 15.5°C (60°F) or  
1.3 g Pb/L at 15.5°C

6.7.1 Keep the standard solution refrigerated when not in use.

NOTE 4—A lead naphthenate solution of same lead concentration has also proven satisfactory as a calibration material. Concentrated TEL is not used to make up standard solutions. The concentrated solution is too acutely toxic to be handled safely under normal laboratory conditions.

NOTE 5—When this lead standard solution is prepared with TEL, the lead concentration can be determined with Test Method D 3341.

6.8 *Toluene*. (**Warning**—Flammable. Vapor harmful.)

#### 7. Calibration

7.1 Make dilutions of the lead (Pb) standard solution to give 0.10, 1.00, 2.00, 3.00, 4.00 and 5.00 g Pb/US gal at 15.5°C (60°F) or 0.10, 1.00, 2.50, 3.50, 5.00, and 6.00 g Pb/UK gal at 15.5°C (60°F) or 0.025, 0.264, 0.529, 0.793, 1.057, 1.322 g Pb/L at 15°C in toluene, *iso*-octane, or a mixture of these solvents.

7.2 Allow the lead standards and bismuth internal standard solutions to come to room temperature.

7.3 Pipet accurately 10 mL of each standard into separate glass-stoppered bottles or flasks and add an equal, accurately measured volume of the bismuth internal standard solution to each one. Mix thoroughly.

7.4 Place one of these solutions in the sample cell using techniques consistent with good operating practice for the spectrometer employed. Place the cell in the instrument, allow the spectrometer atmosphere to reach equilibrium (if appropriate), and determine the counting rate at the lead  $L\text{-}\alpha_1$  line (1.175 Å) and at the bismuth  $L\text{-}\alpha_1$  line (1.144 Å).

NOTE 6—When possible, collect at least 100 000 counts at each line. When sensitivity or concentration, or both, makes it impractical to collect this many counts, the technique that allows the greatest statistical

<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 *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopoeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

precision in the time allotted for each analysis should be used. Sample stability should also be considered in determining counting rate. Variation in counting rates should be observed and if the counting rate tends to go in one direction only, the sample is probably decomposing. If this occurs, shorter counting times should be used consistent with acceptable statistical precision.

7.5 Determine the ratio,  $R$ , for each standard as follows:

$$R = A/B \quad (1)$$

where:

$A$  = counting rate at 1.175 Å, and

$B$  = counting rate at 1.144 Å.

7.6 Plot a calibration curve relating  $R$  to the grams of lead per gallon.

NOTE 7—Many modern X-ray spectrometer instruments will plot and store the calibration curve, slope, and related information in the instrument computer system, as an alternative to hand-plotting this information.

## 8. Quality Control Checks

8.1 Confirm the calibration of the instrument each day it is in use by analyzing a quality control (QC) sample containing a quantifiable concentration of lead, that is, independent of the calibration curve. It is advisable to analyze additional QC samples as appropriate, such as at the beginning and end of a batch of samples or after a fixed number of samples, to ensure the quality of the results. Analysis of result(s) from these QC samples can be carried out using control chart techniques.<sup>6</sup> When the QC sample result causes the laboratory to be in an out-of-control situation, such as exceeding the laboratory's control limits, instrument re-calibration may be required. An ample supply of QC sample material shall be available for the intended period of use, and shall be homogeneous and stable under the anticipated storage conditions. If possible, the QC sample shall be representative of samples typically analyzed and the average and control limits of the QC sample shall be determined prior to monitoring the measurement process. The QC sample precision shall be checked against the ASTM method precision to ensure data quality.

## 9. Procedure

9.1 Obtain sample in accordance with Practice D 4057.

9.2 Prepare the samples to be analyzed as described in 7.3 and 7.4 for the standard lead solutions and determine the ratio,  $R$ , as described in 7.5.

9.3 Determine the lead content of the samples by relating the  $R$  values obtained to the previously determined calibration curve.

## 10. Report

10.1 Report the lead content obtained as g Pb/US gal at 15.5°C (60°F) or g Pb/UK gal at 15.5°C (60°F) to the nearest 0.01 g, or g Pb/L at 15.5°C to the nearest 0.003 g, as appropriate.

NOTE 8—To convert grams per US gallon at 15.5°C (60°F) to: (a)

grams per UK gallon at 15.5°C (60°F) multiply by 1.200 and (b) grams per litre at 15.5°C, multiply by 0.2201.

## TEST METHOD B (SCATTERED TUNGSTEN RADIATION)

### 11. Apparatus

11.1 *X-ray Spectrometer*, capable of measuring radiations mentioned in 3.1.2 and of being operated under the following instrumental conditions or others giving equivalent results:

Tube Voltage	50 kV
Tube Current	20 to 45 mA
Tube Target	Tungsten
Analyzing Crystal	Lithium Fluoride (LiF)
Optical Path	Air, Helium (Warning—Compressed gas under pressure)
Collimation	Fine
Pulse Height Analyzer	Threshold discrimination set as low as possible consistent with the removal of noise with respect to the detector employed.
Detector	Proportional or Scintillation
Counting Technique	Fixed Time

11.1.1 Two restrictions are imposed upon the period of the fixed time: namely, that it is 30 s or greater, and that it is such that the count on the position of minimum intensity (background at  $A = 1.211$  Å) should exceed 200 000.

NOTE 9—The X-ray spectrometer and manner of use should comply with the regulations governing the use of ionizing radiation or recommendations of the International Commission of Radiological Protection, or both.

### 12. Reagents and Materials

12.1 *Iso-octane*. (Warning—Extremely flammable.)

12.2 *Lead (Pb) Standard Solution*—Dissolve tetraethyllead (TEL) (Warning—TEL is toxic by ingestion), lead naphthenate (see Note 4), or other suitable lead containing compound in *iso*-octane (Warning—Extremely flammable), toluene, or a mixture of these two solvents. When TEL is used, refer to Note 5. This standard solution shall contain an accurately known lead concentration of approximately the following magnitude:

5 g Pb/US gal at 15.5°C (60°F)
6 g Pb/UK gal at 15.5°C (60°F)
1.3 g Pb/L at 15.5°C

12.2.1 Keep the standard solution refrigerated when not in use.

### 13. Calibration

13.1 Place the standard lead solution in the sample cell using techniques consistent with good operating practice for the spectrometer employed. Insert the cell in the X-ray beam using the instrumental conditions described in Section 10 and allow the spectrometer atmosphere to reach equilibrium (when appropriate). Take one intensity reading at each of the following wavelength settings, then replace the standard solution with a fresh portion and repeat the readings. Repeat this procedure with *iso*-octane.

Analytical line, lead $L\text{-}\alpha_1$	$\lambda = 1.175$ Å
$WL\text{-}\alpha_1$ (incoherent)	$\lambda = 1.500$ Å, calculated for 90° instrument geometry (Note 7)
Background position	$\lambda = 1.211$ Å

NOTE 10—Calculated for the case where the angle between the incident radiation and take-off collimator is 90°, using the equation for:

<sup>6</sup> ASTM MNL 7, *Manual on Presentation of Data Control Chart Analysis*, "Section 3, Control Charts for Individuals," 6th ed., ASTM International, W. Conshohocken.

$$\text{Compton scatter } \lambda' - \lambda = 0.024 (1 - \cos \phi) \quad (2)$$

where:

$\lambda'$  = wavelength of incoherent scattered radiation,  
 $\lambda$  = wavelength of incident radiation ( $WL-\alpha_1$ ), and  
 $\phi$  = angle between incident and scattered radiation.

13.2 Determine the corrected background by multiplying the intensity of the background at  $\lambda = 1.211 \text{ \AA}$  by the following ratio obtained on the *iso*-octane blank:

$$\frac{\text{Background at } A = 1.175 \text{ \AA}}{\text{Background at } A = 1.211 \text{ \AA}} \quad (3)$$

13.3 Take the mean of the two intensity readings at each wavelength setting and calculate the ratio,  $R'$ , as follows:

$$R' = (\text{Lead } L-\alpha_1 - \text{corrected background}) / (\text{Incoherent } WL-\alpha_1 - \text{background}) \quad (4)$$

13.4 Divide the lead concentration of the standard solution by  $R'$  to obtain the calibration factor,  $F$ .

## 14. Quality Control Checks

14.1 Follow the requirements specified in 8.1 for samples analyzed by Test Method B.

## 15. Procedure

15.1 Obtain sample in accordance with Practice D 4057.

15.2 Remove the standard lead solution and the gasoline samples from the refrigerator and bring them to room temperature.

15.3 Establish the calibration factor,  $F$ , as described in 13.4. This must be done each day the method is in use.

15.4 Determine the ratio,  $R'$ , for the samples as shown in 13.1, 13.2, and 13.3 and obtain the lead content of the samples by multiplying  $R'$  by the calibration factor,  $F$ .

## 16. Report

16.1 Report the lead content obtained as g Pb/UK gal at 15.5°C (60°F), g Pb/US gal at 15.5°C (60°F) to the nearest 0.01 g or g Pb/L at 15.5°C to the nearest 0.003 g, as appropriate (see Note 4).

## TEST METHOD C (LOW-LEAD METHOD)

## 17. Apparatus

17.1 *X-ray Spectrometer*, as described in 5.1. See Note 9.

## 18. Reagents and Materials

18.1 Reagents are described in Section 6.

18.2 *Lead (Pb) Solution, Standard* (0.500 g Pb/gal)—Dilute an aliquot of the standard prepared in 6.6 appropriately so that it contains 0.500 g Pb/US gal at 60°F (15.6°C). Keep refrigerated when not in use. (**Warning**—TEL is toxic by ingestion.)

## 19. Calibration

19.1 Make exact dilutions of the 0.500 g Pb/gal standards to give 0.30, 0.10, 0.050, 0.010, 0.005 and 0.001 g Pb/US gal at 60°F in toluene, *iso*-octane, or a mixture of these two solvents. Retain a 0.000 g Pb/gal standard as a blank.

19.2 Allow all solutions to come to room temperature.

19.3 Pipet accurately 20.0 mL of each standard (including the 0.500 g Pb/gal standard) and the blank into separate glass-stoppered bottles or flasks and add accurately 2.0 mL of the bismuth internal standard to each one. Mix thoroughly.

19.4 Place one of these solutions in the sample cell using techniques consistent with good operating practice for the spectrometer employed. Place the cell in the instrument, allow the atmosphere to reach equilibrium (if appropriate), and determine counting rates at the Pb  $L-\alpha_1$  line (1.175 Å), the Bi  $L-\alpha_1$  line (1.144 Å), and the background (1.194 Å).

NOTE 11—If possible, collect at least 100 000 counts at each line. When sensitivity or concentration, or both, make it impractical to collect this many counts, the technique that allows the greatest statistical precision in the time allotted for each analysis should be used. Sample stability should also be considered in determining analysis time. Variation in counting rates should be observed and if the counting rate tends to go in one direction only, the sample is probably decomposing. If this occurs, shorter counting times should be used consistent with acceptable statistical precision.

19.5 Determine the ratio,  $R$ , for each standard and the blank as follows:

$$R = (A - C)/B \quad (5)$$

where:

$A$  = counting rate at 1.175 Å,  
 $B$  = counting rate at 1.144 Å, and  
 $C$  = counting rate at 1.194 Å.

19.6 Determine the corrected ratio,  $R_c$ , as follows:

$$R_c = R - R_b \quad (6)$$

where:  $R_b$  = ratio for blank.

19.7 Plot a calibration curve (see Note 7) relating  $R_c$  to the grams of lead per gallon. Determine the slope,  $S$ , of the resulting line if it is straight as follows:

$$S = (\text{g Pb/US gal})/R_c \quad (7)$$

## 20. Quality Control Checks

20.1 Follow the requirements specified in 8.1 for samples analyzed by Test Method C.

## 21. Procedure

21.1 Obtain sample in accordance with Practice D 4057.

21.2 Prepare the samples to be analyzed and a blank as described in 19.3 and 19.4 for the standard lead solutions and determine the ratio,  $R_c$ , as described in 19.5 and 19.6 using the blank determined at the time of analysis.

## 22. Calibration

22.1 Calculate the lead content of the samples by relating  $R_c$  to the previously determined calibration curve. If  $S$  was calculated in 19.7 determine lead content as follows:

$$\text{Pb, g Pb/US gal} = R_c \times S \quad (8)$$

## 23. Report

23.1 Report the lead content obtained in 10.2 as g Pb/US gal at 60°F (15.6°C) to the nearest 0.005 g.



## 24. Precision and Bias

24.1 The precision of these test methods as obtained by statistical examination of interlaboratory test results is as follows:

24.1.1 *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:

Test Method A (Bismuth Internal Standard)	Test Method B (Scattered Tungsten Radiation)	Test Method C (Low Lead Method)	Units of X
0.029 + 0.008X	0.014 + 0.015X	0.007 + 0.014X	g Pb/US gal at 15.5°C (60°F)
0.035 + 0.008X	0.017 + 0.015X	...	g Pb/UK gal at 15.5°C (60°F)
0.008 + 0.008X	0.004 + 0.015X	...	g Pb/L at 15°C

24.1.2 *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:

Test Method A (Bismuth Internal Standard)	Test Method B (Scattered Tungsten Radiation)	Test Method C (Low Lead Method)	Units of X
0.103 + 0.030X	0.037 + 0.039X	0.018 + 0.15X	g Pb/US gal at 15.5°C (60°F)
0.124 + 0.030X	0.044 + 0.039X	...	g Pb/UK gal at 15.5°C (60°F)
0.027 + 0.030X	0.010 + 0.039X	...	g Pb/L at 15°C

NOTE 12—The precision of the analyses are based on the use of tetraethyl lead standards only, and users of the test method are cautioned that the precision of the analyses using other lead containing standards may not apply.

24.2 *Bias*<sup>7</sup>—A result from these test methods does not differ from the actual value by more than the reproducibility of the test methods.

NOTE 13—The bias was determined from analysis of NIST reference materials by four laboratories.

## 25. Keywords

25.1 gasoline; lead; low lead; TEL, tetraethyllead; X-ray; X-ray fluorescence

<sup>7</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1283.

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