Designation: D3341 – 16

Standard Test Method for
Lead in Gasoline—Iodine Monochloride Method[1]

This standard is issued under the fixed designation D3341; 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 determines total lead in gasolines containing lead alkyls at concentrations between 0.026 g and 1.3 g Pb/L, and 0.12 g and 6.0 g Pb/UK gal, 0.1 g and 5.0 g Pb/US gal.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.2.1 The preferred units are grams per litre although both gram per US gallon and grams per UK gallon are acceptable due to their widespread use in the industry.

1.2.2 Temperature is given in degrees Fahrenheit and degrees Celsius in this test method.

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 Sections 6 and 8.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

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

3. Summary of Test Method

3.1 A known volume of the sample is diluted with heavy distillate and shaken with aqueous iodine monochloride reagent. Any tetraalkyl lead compounds present react with the iodine monochloride and are extracted into the aqueous phase as the dialkyl lead compounds. The aqueous extract is separated from the gasoline and evaporated to low bulk to decompose free iodine monochloride. Any organic matter present is removed by oxidation with nitric acid, which also serves to convert the dialkyl lead compounds into inorganic lead compounds. The residue is dissolved in distilled water and buffered to pH 5 using sodium acetate-acetic acid buffer. The lead content of the buffered solution is determined by titration with EDTA using xylenol orange as indicator.

4. Significance and Use

4.1 This test method determines the concentration of lead alkyl additives in gasoline. These additives improve the antiknock properties.

5. Apparatus

5.1 *Separatory Funnel,* borosilicate glass, capacity 250 mL, glass-stoppered with preferably an iodine flask type of neck.

5.2 *Erlenmeyer Flask,* borosilicate glass, capacity 500 mL.

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 shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] 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.

6.1.1 Commercially available reagents may be used in place of laboratory preparations when they conform to the specifications in 6.1.

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

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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.

Current edition approved July 1, 2016. Published July 2016. Originally approved in 1974. Last previous edition approved in 2011 as D3341 – 05 (2011). DOI: 10.1520/D3341-16.

[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] *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 Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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

6.3 *Ammonia Solution (1 + 1)*—Mix 1 volume of concentrated ammonia solution (rel dens 0.90) with 1 volume of distilled water.

6.4 *Bromthymol Blue Indicator Solution*— Dissolve 0.1 g of bromthymol blue in 50 mL of ethanol and dilute to 100 mL with distilled water.

6.5 *EDTA, Standard Solution (0.005 M)*—Dissolve approximately 3.75 g of diaminoethanetetra-acetic acid, disodium salt, in 2 L of distilled water. Determine the molarity of the solution by standardization with lead nitrate solution as follows:

6.5.1 Using a pipet, transfer 25.0 mL of the standard lead nitrate solution to a 250 mL Erlenmeyer flask. Dilute to about 75 mL with distilled water and add several drops of bromthymol blue indicator solution. Titrate with 1 + 1 ammonia solution until the color of the solution just changes to blue; then add 10 mL of sodium acetate-acetic acid buffer solution and 5 drops of xylenol orange indicator solution. In the presence of lead the solution will have a rose color. Titrate with the EDTA solution. The color changes near the end point, this being indicated by a sharp change from orange to a permanent bright lemon-yellow.

6.5.2 Record the titer and calculate the molarity of the EDTA solution. The addition of excess EDTA produces no further color change at the end point.

6.6 *Heavy Distillate*—A straight-run, lead-free, petroleum distillate of low bromine number, with approximately 10 % distilling at 400 °F (205 °C) and 90 % at 460 °F (240 °C) (**Warning—**Combustible).

6.7 *Iodine Monochloride Reagent* (1.0 M) (**Warning—**Iodine monochloride will react with ammonium ions under certain conditions to yield nitrogen triiodide, which is explosive. Take care, therefore, that this reagent does not come into contact with ammonia or ammonium salts.) Dissolve 111.0 g of potassium iodide (KI) in approximately 400 mL of distilled water. Add 445 mL of concentrated hydrochloric acid (sp gr 1.18) and cool to room temperature. Add 75.0 g of potassium iodate (KIO_3) slowly and with stirring, until all the free iodine initially formed has just redissolved to give a clear orange-red solution (the amounts of KI and KIO_3 are calculated to give a slight excess of iodate; if a greater excess is present, this will cause precipitation of lead and indifferent end points in the EDTA titration). Cool to room temperature and dilute to 1 L with distilled water. Store in a glass-stoppered bottle (**Warning—**Do not use rubber stoppers to stopper vessels containing iodine monochloride solutions.).

6.8 *Lead Nitrate, Standard Solution (0.005 M)*—Weigh with an accuracy of ±0.001 g about 1.7 g of lead nitrate ($Pb(NO_3)_2$) that has been dried at 105 °C and cooled in a desiccator. Dissolve it in distilled water and add 10 mL of concentrated nitric acid. Dilute to 1 L with distilled water in a volumetric flask and shake thoroughly to mix. Calculate the molarity of the solution according to the equation:

$$\text{Molarity} = \text{wt}\left(\text{g}\right) \text{ of lead nitrate}/331.23 \tag{1}$$

6.9 *Nitric Acid,* concentrated, relative density 1.42.

6.10 *Sodium Acetate, Acetic Acid Buffer Solution*—Dissolve 23.0 g of anhydrous sodium acetate in about 500 mL of distilled water. Using a buret, add 6.2 mL of glacial acetic acid. Dilute to 1 L with distilled water in a 1 L volumetric flask and shake to mix.

6.11 *Xylenol Orange Indicator Solution*— Dissolve 0.2 g of xylenol orange, sodium salt, in 100 mL of distilled water and add 1 drop of 1 + 1 hydrochloric acid. (Prepare freshly each week.)

7. Sampling

7.1 Samples shall be taken in accordance with the instructions in Practices D4057 or D4177.

8. Procedure

8.1 Transfer 50 mL of the iodine monochloride reagent and 25 mL of heavy distillate to the 250 mL separatory funnel. Measure the temperature of the sample to the nearest 0.5 °C (1 °F) (Note 1). Using a pipet **Warning—**(Never suck leaded gasoline or corrosive liquids into a pipet by the mouth), transfer 25 mL ± 0.05 mL of the sample of the gasoline to the separatory funnel. Immediately stopper the funnel and shake the contents for 60 s. Allow the funnel to stand for several minutes, until the two phases have separated and run the lower aqueous phase into a 500 mL Erlenmeyer flask made of borosilicate glass. Wash the gasoline phase by shaking with three separate 20 mL portions of distilled water and add the washings to the Erlenmeyer flask.

NOTE 1—For cool gasolines having a Reid vapor pressure above 7.0 lb cool the sealed sample container to approximately 60 °F (15 °C) before removing the sample for analysis.

8.2 Place several glass beads in the flask, cover the mouth of the flask with a small ribbed watch glass, and place on a hot plate. Heat the contents and allow to boil until the volume of the solution is 15 mL to 20 mL. Without removing the flask from the hot plate, add 5 mL of concentrated nitric acid down the side of the flask and evaporate the contents almost to dryness to oxidize any organic material present. Repeat the nitric acid treatment, evaporating almost to dryness until all the organic matter has been removed and a white residue remains. Finally remove the watch glass and evaporate the solution to dryness. Remove the flask from the hot plate and allow the contents to cool.

8.3 Add about 200 mL of distilled water to the flask and swirl to dissolve the residue. The residue may be quickly dissolved by heating the solution, but this must be cooled before titrating. Add 5 drops of bromthymol blue indicator and titrate with 1 + 1 ammonia solution until the color just changes to blue; then add 10 mL of sodium acetate-acetic acid buffer solution and 5 drops of xylenol orange indicator solution. In the presence of lead, the solution will now have a rose color.

8.4 Titrate with the 0.005 *M* standard EDTA solution. The color of the solution changes to orange near the end point, the end point being indicated by a sharp change from orange to a permanent bright lemon-yellow. Note the titer. The addition of excess EDTA solution produces no further color change at the end point.

8.5 Carry out a blank determination on the reagents, excluding the heavy distillate and omitting the extraction stage and, if necessary, correct the sample titer accordingly.

9. Calculation

9.1 Calculate the concentration of lead by means of one of the following equations (see also Note 2):

$$\text{Lead, g/US gal at } 60°\text{F } (15.5°\text{C}) = 31.37\, TM\, (1 + 0.00065\, (t - 60)) \tag{2}$$

$$\text{Lead, g/UK gal at } 60°\text{F } (15.5°\text{C}) = 37.68\, TM\, (1 + 0.00065\, (t - 60)) \tag{3}$$

$$\text{Lead, g/L at } 15°\text{C} = 8.288\, TM\, (1 + 0.0012\, (t_x - 15)) \tag{4}$$

where:

T = volume of EDTA solution used to titrate the sample, mL,
M = molarity of EDTA solution,
t = the temperature of gasoline when pipeting sample, °F, and
t_x = temperature of gasoline when pipeting sample, °C.

NOTE 2—The constant 31.37 is obtained from the expression $0.20721 \times 3785.3/25$, where 0.20721 is the number of grams of lead equivalent to 1 mL of M EDTA solution, 3785.3 is the number of millilitres in a US gal, and 25 represents the sample volume in millilitres. The constant 37.68 is obtained by multiplying 31.37 by 1.201 (the ratio of millilitres in 1 UK gal to millilitres in 1 US gal, 4546.0 and 3785.3 respectively). The constant 8.288 is obtained by dividing 31.37 by 3.7853.

NOTE 3—The coefficient of expansion of gasolines is taken as 0.00065/°C at 60 °F and 0.0012/°C at 15 °C.

NOTE 4—For gasoline containing only tetraethyl-lead (TEL) or tetramethyl-lead (TML), the grams of lead per unit volume can be converted to millilitres per unit volume by multiplying by the following factors:

$$\text{For tetraethyl lead (TEL)} = 0.946 \tag{5}$$

$$\text{For tetramethyl lead (TML)} = 0.648$$

10. Quality Control

10.1 Confirm the performance of the test procedure by analyzing a quality control sample that is stable and representative of the sample of interest.

10.1.1 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 reult.

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

11. Report

11.1 Report the result to the nearest 0.01 g Pb/US gal at 60 °F, 0.01 g Pb/UK gal at 60 °F, or 0.002 g Pb/L at 15 °C, as appropriate.

12. Precision and Bias

12.1 *Precision*—The precision of the method as determined 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:

$$\text{Litre:} 0.00365 + 0.0073 A_2 \tag{6}$$

where:

A_2 = the average of the results in grams of lead per litre at 15.5 °C.

$$\text{US gallon:} 0.0138 + 0.0073 A \tag{7}$$

where:

A = the average of the results in grams of lead per US gallon at 60 °F (15.5 °C).

$$\text{UK gallon:} 0.0166 + 0.0073 A_1 \tag{8}$$

where:

A_1 = the average of the results in grams of lead per UK gallon at 60 °F (15.5 °C).

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:

$$\text{Litre:} 0.0135 + 0.027 A_2 \tag{9}$$

where:

A_2 = the average of the results in grams of lead per litre at 15.5 °C.

$$\text{UK gallon:} 0.0613 + 0.027 A_1 \tag{10}$$

where:

A_1 = the average of the results in grams of lead per UK gallon at 60 °F (15.5 °C).

$$\text{US gallon:} 0.0511 + 0.027 A \tag{11}$$

where:

A = the average of the results in grams of lead per US gallon at 60 °F (15.5 °C).

NOTE 5—The above precision was obtained in an ISO cooperative test program on samples covering a range from 1.0 g to 3.3 g Pb/US gal. In a subsequent ASTM testing program the range was extended down to 0.1 g Pb/US gal with equal or better precision. Although no samples with lead concentrations, as high as the 5.0 g Pb/US gal specified in the Scope were tested, there is no obvious reason why the method should not be equally satisfactory at that concentration.

NOTE 6—In the cooperative test program from which the above precision was obtained, dimethyl yellow was used as the indicator.

12.1.3 *Bias*—It is not practicable to specify the bias of this test method for measuring lead because the responsible subcommittee, after diligent search, was unable to attract volunteers for an interlaboratory study.

13. Keywords

13.1 gasoline; iodine monochloride; lead

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.

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 and ASTM MNL 7).[4]

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 and ASTM MNL 7).[4] Any out-of-control data should trigger investigation for root cause(s).

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 checked against the ASTM method precision to ensure data quality.

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 homogenous and stable under the anticipated storage conditions. See Practice D6299 and ASTM MNL 7[4] for further guidance on QC and control charting techniques.

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

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D3341 – 05 (2011)) that may impact the use of this standard. (Approved July 1, 2016.)

(1) Added Practice D4177 to Referenced Documents and as an additional sampling procedure reference in subsection 7.1.