Designation: D 3341 – 05

An American National Standard

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

This standard is issued under the fixed designation D 3341; 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 and 1.3 g Pb/L, and 0.12 and 6.0 g Pb/UK gal, 0.1 and 5.0 g Pb/US gal.

1.2 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.

1.3 *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]

D 1193 Specification for Reagent Water

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D 6299 Practice for Applying Statistical Quality Assurance 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 D 1193.

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:

[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] 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 *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.

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

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:

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

6.9 *Nitric Acid*, concentrated (rel dens 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 Practice D 4057.

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 ± 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 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):

Lead, g/US gal at 60°F (15.5°*C*)

$$= 31.37\ TM\ (1 + 0.00065\ (t - 60)) \quad (2)$$