Designation: D3348 – 07

StandardTest Method for Rapid Field Test for Trace Lead in Unleaded Gasoline (Colorimetric Method)[1]

This standard is issued under the fixed designation D3348; 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 and is intended for use in the field by nontechnical people for the quantitative measurement of lead in unleaded gasoline in the range from 0.01 to 0.10 g Pb/U.S. gal (2.64 to 26.4 mg Pb/L). This method applies to all commercial gasolines and responds to all types of lead alkyls as well as to other organic and inorganic forms of lead.

NOTE 1—This test method is based on the use of the Mobil Lead Test Kit (Fig. 1).

NOTE 2—This test method is a screening test and is not to be used as a replacement for withdrawn Test Method D3116, withdrawn Test Method D3229, or Test Method D3237.

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

1.3 *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 warning statements, see Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D3116 Test Method for Trace Amounts of Lead in Gasoline (Withdrawn 1994)[3]

D3229 Test Method for Low Levels of Lead in Gasoline by X-Ray Spectrometry (Withdrawn 1992)[3]

D3237 Test Method for Lead in Gasoline by Atomic Absorption Spectroscopy

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D6792 Practice for Quality System in Petroleum Products and Lubricants Testing Laboratories

3. Summary of Test Method

3.1 The gasoline is treated with iodine and tetraethyl ammonium chloride in chloroform and subjected to ultraviolet light. The lead alkyls form water-soluble lead alkyl iodides, which are removed from the gasoline by shaking it with an aqueous ammonium nitrate solution. The aqueous extract is filtered into a solution of 4-(2-pyridylazo)-resorcinol disodium salt (PAR) and ammonium hydroxide. The lead is determined by measuring its PAR complex colorimetrically at 490 nm using a previously prepared calibration curve.

4. Significance and Use

4.1 This test is used to determine trace quantities of lead in unleaded gasoline. Unwarranted amounts of lead may cause deposits in automotive pollution control equipment and poisoning of catalytic mufflers.

5. Interferences

5.1 PAR also reacts with many other metals forming highly colored complexes. However, none of these are normally found present in a soluble form in gasoline. The following metals were found to form colors with PAR and if present may interfere to give high results: Fe II, Fe III, Co II, Ni II, Cu II, Zn II, Cd II, Mn II, Sn II, V IV, Pb II, U VI, Ti IV, and the rare earths.

6. Apparatus

6.1 *Ultraviolet Lamp,* long wavelength, 3660 Å, placed in a standard 4-W fluorescent fixture.

NOTE 3—A 3-min electric timer[4,5] is connected to the fixture in the prototype kit.

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

[4] The sole source of supply of the 3–min timer known to the committee at this time is H. M. Rhodes, Avon, CT 06001, Catalog No. 90021.

[5] If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

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

FIG. 1 Mobil Lead Test Kit

6.2 *Measuring Block,* aluminum, drilled to hold an 18 by 150-mm test tube, with a mark at a level equal to 5.0 mL of liquid in the test tube.

6.3 *Colorimeter, Portable,* capable of operating at 490 mm. Any equivalent instrument capable of measurement near 514 nm (the optimum Pb-PAR complex wavelength) may be used.

6.4 *Test Tubes,*[5,6] borosilicate, 18 by 150 mm.

6.5 *Pipets,* glass, dropping, capable of delivering 2.0 mL with a 2-mL bulb. (**Warning—**Gasoline or any of the reagents must not come in contact with rubber. If this happens, discard the bulb and pipet and start again.)

6.6 *Funnel,* plastic, 2 in. in inside diameter.

6.7 *Filter Paper,* ashless, hardened, smooth, very fast, 11.0 cm in diameter.

NOTE 4—Certain filter papers that would allow the organic layer (gasoline/chloroform) to filter through are not acceptable.

6.8 *Graduated Cylinder,* plastic, 10-mL.

6.9 *Glass Vials,*[5,7] with caps, disposable, 1-oz capacity.

7. Reagents

7.1 *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.[8] 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.

7.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean distilled water or water of equal purity.

[6] The sole source of supply of the disposable culture tubes known to the committee at this time is Sargent Welch Co., 35 Stern Ave., Springfield, NJ 07081, Catalog No. S-79523K.

[7] The sole source of supply of the glass vials known to the committee at this time is J. W. Wilson Glass Co., 501 S. Park Ave., Linden, NJ 07036, Catalog No. 60957.

[8] *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.

7.3 *Ammonium Hydroxide (sp gr 0.90)*—Concentrated ammonium hydroxide (NH_4OH).

7.4 *Ammonium Nitrate Solution (Reagent B)*—Dissolve 15.0 ± 0.1 g of ammonium nitrate (NH_4NO_3) in 750 mL of water in a 1-L volumetric flask. Dilute to the mark with water.

7.5 *Chloroform ($CHCl_3$)*—(**Warning—**May be fatal if swallowed. Harmful if inhaled. May produce toxic vapors if burned. Chronic or repeated exposure can cause liver or kidney damage. Harmful if inhaled or swallowed. Carcinogen (animal positive). Skin and eye irritant. May produce toxic vapors if burned. See A1.1.)

7.6 *Disodium Salt of 4-(2-pyridylazo)-Resorcinol Dihydrate (PAR·$2H_2O$) (Reagent C)*—Dissolve 25.0 ± 0.1 mg of PAR in 750 mL of water in a 1-L volumetric flask. Add 10.0 ± 0.1 mL of concentrated NH_4OH. Dilute to the mark with water. Store this in brown bottles out of direct sunlight or in the dark. (**Warning—**Low results are obtained if the monosodium or unsalted PAR is used in this test. Field experience has shown that the PAR reagent can deteriorate within two to six months. The PAR reagent should be tested by adding the reagent to a test tube and determining the percent transmittance. If the percent transmittance is less than 80 %, the reagent should be discarded.)

7.7 *Gasoline, Lead-Free*—Gasoline containing less than 0.05 g Pb/gal (13.0 mg Pb/L). (**Warning—**Extremely flammable. Harmful if inhaled. Vapors may cause flash fire. See A1.2.)

7.8 *Iodine.*

7.9 *Iodine/TEAC/$CHCl_3$ Solution (Reagent A)*—Dissolve 1.000 g ± 1 mg of iodine in 75 mL of chloroform ($CHCl_3$) in a 100-mL volumetric flask. Add 1.000 g ± 1 mg of tetraethylammonium chloride (TEAC) and mix until dissolved. Dilute to the mark with $CHCl_3$.

NOTE 5—Solutions described in 7.4, 7.6, and 7.9 have been found to be stable for at least 2 months.

7.10 *Lead Standards*—This method was developed using lead standards prepared by addition of known amounts of various lead alkyls to blended unleaded gasoline to cover the range of this method.

7.11 *Tetraethylammonium Chloride Monohydrate (TEAC).*

7.12 *Quality Control (QC) Sample(s),*— preferably are portions of one or more gasoline materials or product standards of known lead content that were not used in the generation of the instrument calibration curve. These (QC) samples are to be used to check the validity of the testing process as described in Section 10. An ample supply of QC sample material shall be available for the intended period of use, and must be homogeneous and stable under the anticipated storage conditions.

8. Calibration

8.1 Prepare a calibration curve as follows, using at least four gasoline standards of known lead content that cover the range from 0.01 to 0.10 g Pb/gal (2.64 to 26.4 mg Pb/L).

8.1.1 Rinse the 2-mL graduated pipet three times with the gasoline sample. Add 2.0 mL of the sample to a 1-oz glass vial. Add 2.0 mL of iodine/TEAC/$CHCl_3$ solution (Reagent A) from another pipet, to the vial containing the gasoline. Tightly cap the vial.

8.1.2 Place the vial on the ultraviolet light and set the timer to give the sample a 3-min exposure.

8.1.2.1 (**Warning—**Ultraviolet light can be harmful to the eyes. A protective shield has been provided in the prototype kit. DO NOT remove it or otherwise defeat its purpose. DO NOT stare at the light.)

8.1.3 After exposure, remove and uncap the vial. Measure 10.0 mL of ammonium nitrate solution (Reagent B) into the 10-mL graduated cylinder. Add this to the vial containing the sample. Recap and shake the vial vigorously for 1 min. (The timer in the kit may be used.)

8.1.4 Place a clean 18-mm test tube in the aluminum measuring block. Add 5.0 mL of PAR solution (Reagent C) to the test tube using the mark on the block such that the upper level of liquid in the tube is equal to the mark on the block. Place the plastic funnel in the test tube. Fold a piece of filter paper and place in the funnel.

8.1.5 When the two layers of liquid in the vial have separated (8.1.3), pour the entire contents of the vial inside the filter paper. The aqueous layer will filter into the test tube; the gasoline/$CHCl_3$ layer will remain in the filter paper. Tap the funnel to add any remaining drops of aqueous solution to the test tube. Remove the funnel and discard its contents. Swirl the test tube gently using a wrist action to obtain a uniform color.

NOTE 6—The lead-PAR complex formed in 8.1.5 must be measured within 10 min after starting 8.1.5.

NOTE 7—A few drops of the organic layer may come through the filter paper. This will not alter the results and can therefore be tolerated. However, if more than 10 drops do come through, refilter the aqueous layer through a fresh filter paper into a clean empty test tube.

NOTE 8—Swirling may cause air bubbles to be trapped in the liquid. Wait for these to settle before continuing. Wipe the test tube off with a clean towel to remove any fingerprints that may be present on the surface of the tube.

8.2 Zero and standardize the colorimeter as follows:

8.2.1 Set the colorimeter at 490 nm. Set zero absorbance (100 % transmittance) with water in an 18-mm test tube. Read and record the absorbance (or percent transmittance) obtained for the standards.

8.2.2 Plot the absorbance values versus concentration on rectangular coordinate paper. (If percent transmittance values are used, plot them versus concentration using semilog paper, with the percent transmittance values on the log scale.) Draw a best fit line by eye. (See Fig. 2 and Fig. 3 for examples.) When plotting absorbance versus concentration note that the curve does not pass through the origin.

9. Procedure

9.1 Prepare the sample in accordance with the directions given in 8.1.1-8.1.5.

NOTE 9—Short form instructions are outlined in Appendix X1.

9.2 Place the test tube containing the water in the colorimeter and set the absorbance to zero, or to 100 % transmittance.

9.3 Place the sample in the colorimeter and read the absorbance or percent transmittance.