



Standard Test Method for Amyl Nitrate in Diesel Fuels¹

This standard is issued under the fixed designation D1839; 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 the determination of 0.1 to 0.5 volume % amyl nitrate in diesel fuels.

NOTE 1—This test method has been used for the determination of hexyl nitrate in diesel fuels, but has not been cooperatively tested for such samples. For the determination of hexyl nitrate, use standards containing nitrate esters of primary hexanol. Use a density of 0.97 in calculating results.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*²

D1193 Specification for Reagent Water

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

3. Summary of Test Method

3.1 This test method is based on the simultaneous hydrolysis of the ester in 62.5 % sulfuric acid and nitration of *m*-xylenol by the nitric acid liberated. The nitroxylenol is distilled from the reaction mixture and reacted with sodium hydroxide to form the yellow sodium salt. Residual diesel fuel is removed by ether extraction. The color is measured spectrophotometrically at 452 nm, and the concentration of amyl nitrate is determined by reference to a standard curve.

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 June 1, 2014. Published July 2014. Originally approved in 1961. Last previous edition approved in 2011 as D1839 – 11. DOI: 10.1520/D1839-14.

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.

4. Significance and Use

4.1 In diesel fuel, the presence of alkyl nitrates such as amyl nitrate, hexyl nitrate, or octyl nitrate causes a higher residue value than observed in untreated fuel, which can lead to erroneous conclusions as to the coke forming propensity of the fuel. The presence of such alkyl nitrate in the fuel can be determined using this test method. This test method can be used to determine the amount of amyl nitrate that has been added to diesel fuels to improve cetane number. This test method is applicable as a basis for judging compliance with specifications covering amyl nitrate.

5. Interferences

5.1 Nitrate esters, inorganic nitrate ions, and nitrogen oxides will interfere to give high results.

6. Apparatus

6.1 *Absorption Cells*, matched, having a 1.000- ± 0.002-cm light path.

6.2 *Distillate Collector*,³borosilicate glass with standard taper joints and sealed-in funnel (Fig. 1).

6.3 *Electric Heating Mantle*, to fit a 300-mL round-bottom flask, and having a variable transformer.

6.4 *Lunge-type Pipet*, 2-mL capacity.

NOTE 2—A 2.5-mL hypodermic syringe, with scabbard, can be used instead of the Lunge pipet.

6.5 *Reflux Condenser* (Allihn-type), borosilicate glass, 300 mm long, with standard-taper joints.

6.6 *Round-Bottom Flask*, of borosilicate glass and having a 300-mL capacity.

6.7 *Separatory Funnel*, Squibb-type, 125-mL capacity.

6.8 *Shaking Machine*, automatic, capable of 250 oscillations/min.

6.9 *Spectrophotometer*, capable of measuring absorption in the region of 452 nm.

³ The sole source of supply of the apparatus known to the committee at this time is obtainable from Corning Glass Co., Corning, NY, Catalog No. 3320. 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

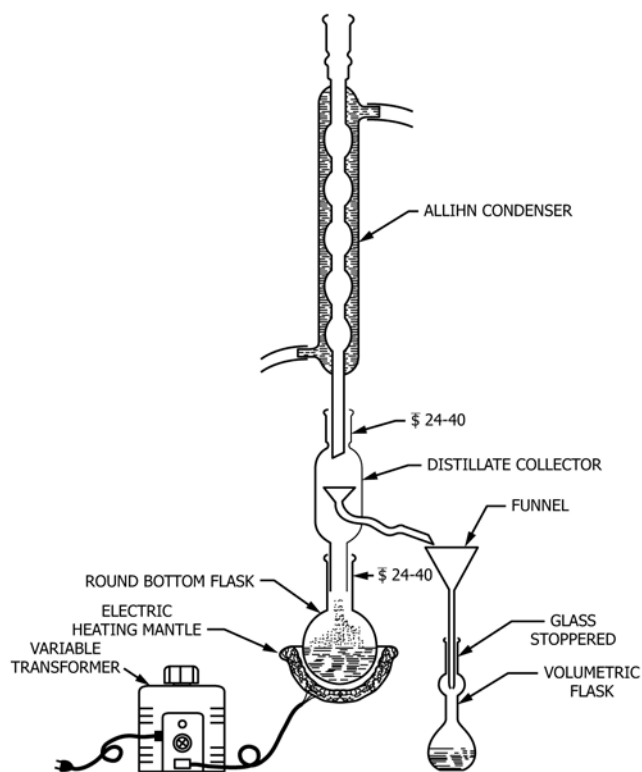


FIG. 1 Distillation Apparatus

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 shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁴ 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 specified, references to water shall be understood to mean reagent water as defined as Type II or III in Specification D1193.

7.3 *Acetone* (**Warning**—Extremely flammable. Vapors can cause flash fire. Harmful if inhaled.)

7.4 *Amyl Nitrate*—Any mixture of nitrate esters of primary amyl alcohol.

7.5 *Diethyl Ether* (**Warning**—Extremely flammable. Vapors can cause flash fire. Harmful if inhaled.)

7.6 *Sodium Hydroxide Solution* (20 g/L)—Dissolve 20 g of sodium hydroxide (NaOH) pellets in water and dilute to 1 L.

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.

7.7 *Sulfuric Acid* (5 + 3) —Slowly add, with stirring, 500 mL of nitrate-free concentrated sulfuric acid (H_2SO_4 , rel dens 1.84) to 300 mL of water. The *m*-xylenol solution must be added before the H_2SO_4 , otherwise low or negative results will be obtained. Cool before use.

7.8 *m-Xylenol Solution*—Dilute 4 mL of *m*-xylenol (2,4-dimethylphenol⁵) to 100 mL with acetone. Prepare fresh each day.

8. Sampling

8.1 Samples shall be taken in accordance with the appropriate instructions in Practice D4057.

9. Preparation of Calibration Curve

9.1 Prepare a series of standard samples containing a known amount of amyl nitrate in diesel fuel, covering the range of 0.2 to 2.0 mg of amyl nitrate per gram (Note 3). Weigh 0.5-g portions of these standards, to the nearest 0.1 mg, into the Squibb-type separatory funnels and treat as described in Section 10. Calculate the milligrams of amyl nitrate in each standard by multiplying the weight of the standard taken by the corresponding concentration of amyl nitrate. Construct a calibration curve by plotting absorbance values as the ordinate and corresponding milligrams of amyl nitrate per 50 mL as the abscissa.

NOTE 3—Experience with the method indicates that different base stocks of diesel fuels do not cause variations in the results. If low results are obtained for a particular fuel, prepare standards using the fuel in question to check the reaction and recoveries.

10. Procedure

10.1 Weigh into a separatory funnel a sample of diesel fuel to the nearest 0.1 mg, not exceeding 2 mL (Note 4), and not containing more than 1.0 mg of amyl nitrate. Add 2 mL of the *m*-xylenol solution and shake thoroughly. Add 50 mL of H_2SO_4 . Shake for 30 min on the automatic shaking machine. Transfer the contents of the separatory funnel to the round-bottom flask and wash the funnel with 100 mL of water, combining this rinse with the solution in the flask.

NOTE 4—Incomplete reaction will take place if more than 2 mL of sample is used.

10.2 With the apparatus assembled as shown in Fig. 1, distill the sample into a 50-mL volumetric flask containing 5 mL of NaOH solution. Collect 40 mL of distillate. Cool, and dilute to volume with water, allowing any floating diesel fuel to be above the mark.

NOTE 5—When the solution is not yellow, check the pH. When it is not alkaline, add additional NaOH solution.

10.3 Transfer the solution to a separatory funnel and extract with several portions of ether to remove the diesel fuel that otherwise would cause a turbid water layer.

⁵ The sole source of supply of the apparatus known to the committee at this time is obtainable from Eastman Kodak Co., Rochester, NY, Reagent No. 1150. 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.

10.4 Filter the water layer through a coarse-texture paper into an absorption cell and measure its absorbance at 452 nm with respect to water (Note 6). Subtract a blank (Note 7) from the reading and read the milligrams of amyl nitrate from the calibration curve (Section 8).

NOTE 6—The color developed is stable for several hours. It obeys Beer's law over the range from 0.2 to 2.0 mg of amyl nitrate.

NOTE 7—Obtain a blank by performing the analysis on the samples of diesel fuel and the reagents without the amyl nitrate present. A blank of 0.019 absorbance can be used since it is the average obtained on a number of representative diesel fuels.

11. Calculation

11.1 Calculate the amyl nitrate present in the sample as follows:

$$\text{Amyl nitrate, mass \%} = 100A/1000W = A/10W \quad (1)$$

$$\text{Amyl nitrate, vol \%} = BD/C \quad (2)$$

where:

- A = milligrams of amyl nitrate obtained from the calibration curve,
- B = mass % of amyl nitrate obtained from Eq 1,
- C = density of amyl nitrate (0.998 at 20°C),
- D = density of diesel fuel sampled at 20°C, and
- W = grams of sample used.

12. Reporting

12.1 Report the results to the nearest 0.1 m or v%, and indicate that they were obtained using Test Method D1839.

13. Precision and Bias⁶

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

13.1.1 *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 value only in one case in twenty:

$$0.10 \text{ volume \%} \quad (3)$$

13.1.2 *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:

$$0.10 \text{ volume \%} \quad (4)$$

13.2 *Bias*—The bias of this test method cannot be determined since an appropriate standard reference material containing a known level of amyl nitrate in diesel fuel is not available.

14. Keywords

14.1 amyl nitrate; diesel fuel; nitroxyleneol; spectrophotometric

⁶ There is no existing research report for this test method.

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D1839–91(2005)) that may impact the use of this standard. (Approved June 1, 2014.)

(1) Revised subsection 4.1 to add more information to Significance and Use.

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