



Standard Test Method for Alkyl Nitrate in Diesel Fuels by Spectrophotometry¹

This standard is issued under the fixed designation D 4046; 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.

^{ε1} NOTE—Warning notes were placed in the text in April 2000.

1. Scope

1.1 This test method describes a procedure for the determination of 0.03 to 0.30 volume % of alkyl nitrate in diesel fuels.

1.2 This test method can be used for the determination of any alkyl nitrate in diesel fuel provided that standards used for calibration contain the same alkyl nitrate ester as the test specimens to be analyzed.

1.3 The preferred units are acceptable SI units.

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 Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water²

3. Summary of Test Method

3.1 The determination is based on the simultaneous hydrolysis of the ester in 65 % sulfuric acid solution and nitration of *m*-xylenol by the nitric acid liberated. The nitroxylenol is extracted from the reaction mixture and reacted with sodium hydroxide to form the yellow salt. The color is measured spectrophotometrically at 452 nm, and the concentration of alkyl nitrate is determined by reference to the slope of the calibration curve.

4. Significance and Use

4.1 This test method can be used to determine the amount of alkyl nitrate that has been added to diesel fuel to improve Cetane Number. The test method is applicable as a basis for judging compliance with specifications covering any alkyl nitrate.

5. Interferences

5.1 Other nitrate esters, inorganic nitrate ions, and nitrogen oxides will interfere.

6. Apparatus

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

6.2 *Separatory Funnel*, Squibb-type glass stoppered with TFE-fluorocarbon stopcock, 125-mL capacity.

6.3 *Shaking Machine*, automatic, capable of multiple samples and 250 oscillations/min.

6.4 *Spectrophotometer*, capable of measuring absorption in the region of 452 ± 5 nm.

6.5 *Volumetric Flask*, 10- and 100-mL capacity.

6.6 *Measuring Pipet*, 1-mL, 3-mL, 4-mL, and 10-mL.

6.7 *Buret*, 10-mL 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.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.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type II of Specification D 1193.

7.3 *Acetic Acid*, reagent grade.

7.4 *Alkyl Nitrate*.

7.5 *Alkyl Nitrate, Standard Solution*—Pipet 3.0 mL of the alkyl nitrate to be determined into a 100-mL volumetric flask and dilute to volume with diesel fuel.

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 *Annual Book of ASTM Standards*, Vol 11.01.

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.

7.6 Diesel Fuel, additive-free (**Warning**—Flammable.).

7.7 Isooctane (2,2,4-trimethylpentane). (**Warning**—Flammable.).

7.8 Isopropyl Alcohol, reagent grade. (**Warning**—Flammable.).

7.9 *m*-Xylenol Solutions—Dilute 4 mL of *m*-xylenol (2,4-dimethylphenol) to 100 mL in acetic acid.

7.10 Sodium Hydroxide Solution—Dissolve 50 g of sodium hydroxide (NaOH) pellets in 1000 mL of distilled water.

7.11 Sulfuric Acid—Add slowly with stirring, 500 mL of nitrate-free sulfuric acid (H₂SO₄) (rel dens 1.84) to 269 mL of cold distilled water.

8. Calibration and Standardization

8.1 Carefully measure 1.0, 3.0, 5.0, 8.0, and 10 mL of alkyl nitrate standard solution (7.5) from a buret into each of five separate 100-mL volumetric flasks and dilute to the mark with diesel fuel.

8.2 Measure 1.0-mL portions of each standard into each of five 10-mL volumetric flasks. To another 10-mL flask add 1.0 mL of blank diesel fuel. Dilute all flasks to volume with isopropyl alcohol.

8.3 Pipet 1.0 mL of each standard solution (8.2) into each of five separate 125-mL separatory funnels. To another funnel add 1.0 mL of the blank solution. This covers concentrations from 0.03 to 0.30 volume % alkyl nitrate.

8.4 Add 1.0 mL of *m*-xylenol solution (7.9) to each separatory funnel and swirl to mix thoroughly.

8.5 Add 40 mL of H₂SO₄ (7.11). The *m*-xylenol must be added before the sulfuric acid. Otherwise low or negative results will be obtained.

8.6 Secure the stopper with springs or rubber bands and shake the separatory funnel and its content for 30 min on the automatic shaking machine set at fast speed.

NOTE 1—The amount of contact the sample has with the H₂SO₄ determines the extent of hydrolysis. Therefore, the speed and time of shaking should be the same for both the samples and the calibration standards.

8.7 To each separatory funnel add 25 mL of isooctane.

8.8 Shake the separatory funnel for 1 min by hand. Allow the layers to separate and discard the acid (bottom) layer. Add 25 mL of distilled water and again shake for 1 min to wash out residual acid. Discard the water (bottom) layer.

8.9 Pipet 10.0 mL of NaOH solution into the separatory funnel, shake for 1 min and allow the phases to separate for at least 10 min or when phases separate cleanly (Note 2). Drain a few drops of the lower phase to rinse the stem and discard. Fill a 1-cm absorption cell and read the absorbance at 452 ± 5 nm with respect to water.

NOTE 2—If no color forms, check the pH. When the solution is not alkaline, add an additional 10.0 mL of NaOH solution and correct calculations for the increased solution volume.

8.10 Subtract the absorbance of the blank from that of each standard to obtain corrected absorbance values. Calculate the slope of the curve as follows:

$$\text{Slope, } C = A/B \quad (1)$$

where:

A = sum of the volume percent alkyl nitrate standards and
 B = sum of corrected absorbances.

9. Procedure

9.1 Pipet 1.0 mL of test specimen into a 10-mL volumetric flask and dilute to volume with isopropyl alcohol.

9.2 Pipet 1.0 mL of the sample test specimen prepared in 9.1 into a 125-mL separatory funnel. To another funnel add 1.0 mL of blank isopropyl alcohol.

NOTE 3—A more accurate blank would be obtained if the same base stock as the samples diluted with isopropyl alcohol, were used.

9.3 Follow steps 8.4-8.9.

NOTE 4—If an absorbance is too high, dilute an aliquot of the solution five-fold with blank solution and correct calculations accordingly.

9.4 Subtract the absorbance of the blank from the absorbance of the samples and calculate the result using the slope of the calibration curve.

$$\text{Alkyl nitrate, volume \%} = CD \quad (2)$$

where:

C = slope of the calibration curve and
 D = absorbance of the sample.

10. Precision and Bias ⁴

10.1 The precision of this test method as obtained by statistical examination of interlaboratory test results is as follows:

10.1.1 *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 this test method, exceed the following values only in one case in twenty:

0.017 vol %

10.1.2 *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 this test method, exceed the following values only in one case in twenty:

0.036 vol %

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

11. Keywords

11.1 alkyl nitrate; diesel fuel; nitroxylanol; spectrophotometry

⁴ The results of the cooperative test program, from which these values have been derived are available from ASTM Headquarters. Request RR:D02-1139.

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