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Petroleum products — Determination of alkyl nitrate in diesel fuels — Spectrometric method

Produits pétroliers — Détermination du nitrate d'alkyle dans les carburants diesels — Méthode spectrométrique

Reference number
ISO 13759:1996(E)

Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 13759 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

Annex A of this International Standard is for information only.

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Petroleum products — Determination of alkyl nitrate in diesel fuels — Spectrometric method

WARNING — The use of this International Standard may involve hazardous materials, operations and equipment. This standard does not purport to address all of the safety problems 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.

1 Scope

This International Standard specifies a procedure for the determination of alkyl nitrate in diesel fuel in the concentration range 0,03 % (*V/V*) to 0,30 % (*V/V*) (volume fraction 0,03 % to 0,30 %).

A knowledge of the specific alkyl nitrate present in the diesel fuel is required for accurate determinations, as the calibration of instrumentation is reliant on reference solutions containing the nitrate to be analysed. When the specific alkyl nitrate is not known, a result comparative to a reference alkyl nitrate (4.2) gives indicative information.

NOTE — The addition of certain alkyl nitrates to diesel fuel enhances the cetane number as measured by the engine test described in ISO 5165. It has no effect on the cetane index value as described in ISO 4264. See annex A.

The presence of nitrate esters, inorganic nitrate ions and nitrogen oxides will interfere with this determination.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 835-1:1981, *Laboratory glassware — Graduated pipettes — Part 1: General requirements.*

ISO 1042:1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

3 Principle

The alkyl nitrate is hydrolysed in strong sulfuric acid solution and the nitric acid released is reacted with 2,4-dimethylphenol. The nitroxylenol is extracted from the reaction mixture and treated with sodium hydroxide to form a solution of the yellow salt. The colour intensity is measured spectrometrically at 452 nm, and the concentration of alkyl nitrate is determined by reference to the calibration curve.

4 Reagents

For the analysis described in this International Standard, use only reagents of recognized analytical grade, and water complying with the requirements of Grade 3 of ISO 3696.

4.1 Acetic acid (CH_3COOH), glacial.

4.2 Alkyl nitrate standard solution.

Pipette 3,0 ml of alkyl nitrate of composition identical to that to be analysed into a 100 ml flask (5.5) and dilute to the mark with diesel fuel (4.6).

In the absence of knowledge of the specific alkyl nitrate to be analysed, use 2-ethylhexyl nitrate of minimum purity 97 % to construct the calibration curve.

4.3 Sulfuric acid solution.

Add slowly with stirring, 500 ml of concentrated sulfuric acid, 98 % (*m/m*) (mass fraction 98 %) minimum purity, to 270 ml of cold water.

4.4 Sodium hydroxide solution.

Dissolve 50 g of sodium hydroxide pellets in water, and dilute to 1 000 ml with water.

4.5 2,4-dimethylphenol (xylenol) solution.

Dilute 4 ml of 2,4-dimethylphenol $[(CH_3)_2C_6H_3OH]$ with acetic acid (4.1), making up to the mark in a 100 ml flask (5.5).

4.6 Diesel fuel or component, clean, stable, containing no additives (blank fuel).

NOTE — Where practicable, the composition of the blank fuel should be similar to that of the sample under test.

4.7 2,2,4-trimethylpentane $[CH_3C(CH_3)_2CH_2CH(CH_3)CH_3]$, 99,75 % minimum purity.

4.8 Propan-2-ol $[CH_3CH(CH_3)OH]$.

5 Apparatus

5.1 Absorption cells, matched, having a 10,00 mm ± 0,02 mm path length.

5.2 Spectrometer, capable of measuring absorption in the wavelength range of 452 nm ± 5 nm.

5.3 Separating funnels, Squibb-type, glass-stoppered, with polytetrafluoroethylene stopcock, 125 ml capacity.

5.4 Shaking machine, automatic, capable of accommodating multiple samples, to shake at a minimum of 250 oscillations/min.

5.5 Volumetric flasks, 10 ml and 100 ml capacity, Class A in accordance with ISO 1042.

5.6 Pipettes, 1 ml and 10 ml capacity, Class A in accordance with ISO 835-1.

5.7 Burette, 10 ml capacity, Class A in accordance with ISO 385-1.

5.8 Graduated cylinders, of 50 ml or 100 ml capacity.

6 Preparation of calibration curve

6.1 Not more than 24 h before each determination, prepare calibration curves in accordance with the procedure described in 6.2 to 6.11.

6.2 Carefully measure 1,0 ml, 3,0 ml, 5,0 ml, 8,0 ml and 10,0 ml of alkyl nitrate solution (4.2) from the burette (5.7) into individual 100-ml volumetric flasks (5.5), and dilute to the mark with diesel fuel (4.6).

6.3 Pipette 1,0 ml portions of each of the solutions prepared in 6.2 into five 10-ml volumetric flasks (5.5). Pipette 1,0 ml of diesel fuel into a separate 10-ml volumetric flask. Dilute the contents of all flasks to the mark with propan-2-ol (4.8).

6.4 Pipette into individual separating funnels (5.3) 1,0 ml of each of the solutions prepared in 6.3 including the blank diesel fuel.

6.5 Pipette 1,0 ml of 2,4-dimethylphenol solution (4.5) into each separating funnel and swirl to mix thoroughly.

6.6 Add 40 ml of sulfuric acid solution (4.3) from a graduated cylinder (5.8) to each separating funnel.

NOTE — If the 2,4-dimethylphenol is not added before the sulfuric acid, low or negative results will be obtained.

6.7 Secure the stoppers of the separating funnels and shake the funnels and contents for 30 min on the shaking machine (5.4).

NOTE — The amount of contact that the sample has with the sulfuric acid determines the extent of hydrolysis. Therefore, the speed and time of shaking should be identical for both test samples and calibration standards.

6.8 Add 25 ml of 2,2,4-trimethylpentane (4.7) to each separating funnel and shake for 1 min on the shaking machine. Allow the layers to separate and discard the acid (bottom) layer. Add 25 ml water to each funnel and again shake for 1 min on the shaking machine, allow to separate and discard the water (bottom) layer.

6.9 Pipette 10,0 ml of sodium hydroxide solution (4.4) into each separating funnel, shake by hand for 1 min, and allow the phases to separate for at least 10 min or until they separate cleanly (see note in 6.7). Drain a few drops of the lower (water) phase to rinse the stem, check that the solution is alkaline, and discard.

When the solution is not alkaline, add an additional 10,0 ml of sodium hydroxide solution and correct calculations (see 6.11) for the increased solution volume.

Fill an absorption cell (5.1) with solution from each separating funnel and read the absorbance on the spectrometer (5.2) with respect to water, cleaning the cell between each change of solution.

6.10 Subtract the absorbance of the blank from that of the standard solutions to obtain corrected absorbance values.

6.11 Plot the corrected absorbance values against concentration, and if the response is smooth and rectilinear, calculate the slope, C, of the calibration curve using the following equation:

$$C = A/B \quad \ldots (1)$$

where

A is the sum of the concentrations of alkyl nitrate standard, expressed as a percentage by volume;

B is the sum of the corrected absorbances.

7 Test procedure

7.1 Pipette 1,0 ml of the test diesel fuel into a 10-ml volumetric flask (5.5) and dilute to the mark with propan-2-ol (4.8).

7.2 Pipette 1,0 ml of the test specimen prepared in 7.1 into a separating funnel (5.3). Add 1,0 ml of propan-2-ol to another funnel as a blank test.

NOTE — A more accurate test would be obtained if the same base fuel as that of the test specimen, diluted with propan-2-ol, were used as the blank solution.

7.3 Carry out the procedure described in 6.5 to 6.10.

NOTE — If an absorbance is too intense to remain on-scale, dilute an aliquot of the test specimen (7.1) five-fold with blank fuel (4.6), repeat the procedure, and correct the calculations accordingly.

8 Calculation

8.1 Subtract the absorbance of the blank from the absorbance of the sample, and calculate the concentration of the alkyl nitrate, N, as a percentage by volume, by inserting the value for the slope of the calibration curve, as calculated in 6.11, in the following equation (see also 8.2):

$$N = CD \quad \ldots (2)$$

where

C is the slope of the calibration curve;

D is the absorbance of the test sample.

8.2 For some additive/fuel combinations, the response is not linear. If, after checking, this is confirmed, the calculation in equation (1) is not carried out, and the calculation in equation (2) is replaced by locating the measured corrected absorbance obtained in 6.10 on the best-fit curve and reading off the alkyl nitrate concentration.

9 Expression of results

Report the concentration of alkyl nitrate by name, or, if the specific alkyl nitrate is not known, as calculated based on 2-ethylhexyl nitrate as a percentage volume fraction [% (V/V)], to the nearest 0,001 %.

10 Precision

The precision of the method, as obtained by statistical examination of interlaboratory test results, is as follows:

10.1 Repeatability, *r*

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 normal and correct operation of the test method, exceed the value of 0,017 % (*V/V*) (volume fraction of 0,017 %) only in one case in twenty.

10.2 Reproducibility, *R*

The difference between two single and independent results, obtained by different operators working in different laboratories on nominally identical test material would, in the normal and correct operation of the test method, exceed the value of 0,036 % (*V/V*) (volume fraction of 0,036 %) only in one case in twenty.

11 Test report

The test report shall contain at least the following information:

a) a reference to this International Standard;

b) the type and complete identification of the product tested;

c) the result of the test (see clause 9);

d) any deviation, by agreement or otherwise, from the standard procedures specified;

e) the date of the test.

Annex A
(informative)

Bibliography

[1] ISO 4264:1995, *Petroleum products — Calculation of cetane index of middle-distillate fuels by the four-variable equation.*

[2] ISO 5165:— 1), *Diesel fuels — Determination of ignition quality — Cetane engine method.*

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1) To be published. (Revision of ISO 5165:1992)

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