SLOVENSKI STANDARD
SIST EN 14078:2010

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Nadomeġļa:
SIST EN 14078:2004

Tekoļ i naftni proizvodi - Doloļ evanje metilnih estrov maġļ obnih kislin (FAME) v srednjih destilatih - Metoda infrardeļ e spektroskopije

Liquid petroleum products - Determination of fatty methyl ester (FAME) content in middle distillates - Infrared spectrometrymethod

Flüssige Mineralölprodukte - Bestimmung von Fettsäure Methylester (FAME) in Mitteldestillaten - Infrarotspektrometrisches Verfahren

Produits pétroliers liquides - Détermination de la teneur en esters méthyliques d'acides gras (EMAG) des distillats moyens - Méthode par spectrométrie infrarouge

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EUROPEAN STANDARD

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Liquid petroleum products - Determination of fatty methyl ester (FAME) content in middle distillates - Infrared spectrometry method

Produits pétroliers liquides - Détermination de la teneur en esters méthyliques d'acides gras (EMAG) des distillats moyens - Méthode par spectrométrie infrarouge

Flüssige Mineralölerzeugnisse - Bestimmung des Gehaltes an Fettsäuremethylester (FAME) in Mitteldestillaten - Infrarotspektrometrisches Verfahren

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COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Contents

Foreword

This document (EN 14078:2009) has been prepared by Technical Committee CEN/TC 19 “Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin”, the secretariat of which is held by NEN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by June 2010, and conflicting national standards shall be withdrawn at the latest by June 2010.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document supersedes EN 14078:2003.

The revision was pursued with the aim to extend the measurement range to lower FAME contents and to improve the precision of the test method. Therefore, the infrared (IR) determination was analytically revised, i.e. by splitting the calibration, measurement into two separate measurement ranges. The significantly improved precision data was backed up by extensive round robin tests. Thus the application range for this test method could be lowered significantly down to a FAME content of approximately 0,05 % (*V/V*).

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and the United Kingdom.

1 Scope

This European Standard specifies a test method for the determination of Fatty Acid Methyl Ester (FAME) content in diesel fuel or domestic heating fuel by mid infrared spectrometry, which applies to FAME contents of the two measurement ranges as follows:

— range A: for FAME contents ranging from approx. 0,05 % (*V/V*) to approx. 3 % (*V/V*);

— range B: for FAME contents ranging from approx. 3 % (*V/V*) to approx. 20 % (*V/V*).

Principally, higher FAME contents can also be analyzed if diluted; however, no precision data for results outside the specified range is available at present.

This test method was verified to be applicable to samples which contain FAME conforming to EN 14214 or EN 14213. Reliable quantitative results are obtained only if the samples do not contain any significant amounts of other interfering components, especially esters and other carbonyl compounds which possess absorption bands in the spectral region used for quantification of FAME. If such interfering components are present, this test method is expected to produce higher values.

NOTE 1 For the purposes of this European Standard, the term "% (*V/V*)" is used to represent the volume fraction (φ) of a material.

NOTE 2 For conversion of grams FAME per litre (g FAME/l) to volume fraction, a fixed density for FAME of 883,0 kg/m^3 is adopted.

WARNING — The use of this 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.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 14213, *Heating fuels — Fatty acid methyl esters (FAME) — Requirements and test methods*

EN 14214, *Automotive fuels — Fatty acid methyl esters (FAME) for diesel engines — Requirements and test methods*

EN ISO 3170, *Petroleum liquids — Manual sampling (ISO 3170:2004)*

EN ISO 3171, *Petroleum liquids — Automatic pipeline sampling (ISO 3171:1988)*

3 Principle

The mid infrared absorption spectrum of a test portion of a sample which has been diluted as appropriate with FAME-free solvent is recorded. The absorbance at the peak maximum of the typical absorption band for esters at about (1 745 ± 5) cm^{-1} is measured. Initially, calibration as well as evaluation of the data will be carried out as grams FAME per litre. For conversion of grams per litre (g/l) to the reporting unit "% (*V/V*)", a fixed density of FAME of 883,0 kg/m^3 (15 °C) is adopted.

Two measurement ranges (A or B) have been chosen for which specific adjustments for the calibration and dilution need to be followed. Measurement preferably without dilution for range A and a shorter path length of the measurement cell for range B. In particular, the lower determination range A is a challenging one; all ensuing

details shall be kept as a package without any omissions or additions of individual details. That is the only way to adhere to the improved precision data of range A determined by round robin tests.

Based on the absorbance measured at the maximum of the peak of the absorption band the FAME content is calculated by means of a calibration function which was determined by measuring calibration solutions for which the FAME content is known.

4 Reagents and materials

4.1 FAME for calibration, FAME as specified in EN 14214 (automotive diesel fuel) or EN 14213 (domestic heating oil).

4.2 FAME free middle distillate as solvent for dilution and as reference material for the measurement of the background spectrum. In particular, a middle distillate suitable for the type of sample (diesel fuel or domestic heating oil) shall be used for range A in order to avoid spectral decompensation as far as possible. In this context, the property "FAME free" means middle distillates without any absorption bands in the IR signal range typical for FAME.

4.3 Solvents for cleaning, such as ethanol, n-pentane or cyclohexane.

5 Apparatus

5.1 Infrared spectrometer, dispersive or interferometer type, capable of operating in the wave number range from approx. 400 cm^{-1} to approx. 4 000 cm^{-1}, with a linear absorption in the absorbance range from (0,1 to 1,1) absorbance units, and having a resolution of minimum 4 cm^{-1}.

5.2 Cells, made of KBr, NaCl, or CaF_2, with known path length, where the additional instructions for the selection and treatment of cells dependent on the applied measurement range as given in 7.1 are followed.

EXAMPLE A standard solution with a FAME concentration of 3 g FAME/l (0,34 % (*V/V*)) should give an absorbance of about 0,4 at the maximum peak at about 1 745 cm^{-1} if a cell with a path length of 0,5 mm is used.

6 Sampling and sample handling

Samples shall be taken according to EN ISO 3170 or EN ISO 3171 as well as in accordance with the requirements of national standards or regulations for the sampling of the product under test. If samples are not tested immediately, they shall be stored tightly sealed and in a cool and dark place.

7 Procedure

7.1 Selection and treatment of the cell

The path length of the cell (5.2) shall be selected so that adequate net signal intensities can be obtained (in at least two decimal places, see marked cells in Table A.1). Signal intensities shall still be within the linear detector range.

Specific adjustments shall be followed (see recommendations given in Table A.1) depending on measurement range A or B:

— range A: path length as long as possible and measurement preferably without dilution; and

— range B: shorter path length and dilution adapted to the anticipated FAME content.

The path length shall be known or determined exactly. If in use for a longer period of time it should be checked more frequently. A specific and individual calibration shall be made for every cell in use, retaining all other

measurement parameters for every applied measurement range. The use of several or different cells during the same calibration is not permissible.

The very same cell shall be used for calibration and for measurement. Only the exactly determined path length applies for the cell in use; nominal data (nominal path length, labelling, nominal spacer data or the like) shall not be used without any adequate control or correction measures.

If cells sensitive to water are used the path length shall be checked more frequently. In case the path length has changed, path length determination and calibration shall be carried out anew.

7.2 Cleaning of the cells

After every measurement the cell shall be carefully cleaned with a solvent (4.3). This is particularly important after measuring samples with high FAME content and extremely important when the measurement of samples with low FAME contents is prepared. The cell may also be cleaned by rinsing repeatedly with FAME free middle distillate (4.2).

In persistent cases cyclohexane may also be used for cleaning (yet not for calibration or dilution purposes) as well as the following alternative cleaning procedure:

a) rinse twice with 5 ml n-pentane each time; then

b) rinse once with 5 ml ethanol (absolute); then

c) rinse once again with 5 ml n-pentane and finally dry with suitable equipment.

In case the cleanliness of the cell is in doubt, a reference spectrum of a FAME free sample shall be recorded and checked for control reasons. The spectrum shall not show signals in the range of 1 750 cm^{-1}.

7.3 Selection of the path length

7.3.1 Range A

For low FAME contents cells with a long path length (e.g. KBr of approx. 0,5 mm, known to the nearest 0,01 mm) have proven to be well suited. Other materials and path lengths are also permissible, though on no account should the path length be chosen less than about 0,2 mm to enable a signal and signal-to-noise ratio as favourable as possible.

7.3.2 Range B

For high FAME contents a path length of approx. 0,1 mm, known to the nearest 0,01 mm, is recommended in combination with a dilution rate of 1:5 (refer to data given in Table A.1). Other cells and path lengths are also possible; however, dilution should be arranged within a comparable dimension in order to avoid any major dilution errors.

7.4 Calibration

7.4.1 General instructions

Calibration and ensuing measurement shall be carried out retaining all other measurement parameters.

The lower the FAME content, the smaller is the carbonyl band (even if the absorption intensity is still high) and thus the more critical the background correction. Especially for range A (low FAME contents) the background correction with the calibration samples and (possibly also with spectra of blank samples) should be practiced thoroughly.

7.4.2 Preparation of calibration solutions

The following ranges should be followed as general guidance:

— range A from approx. 0,05 % (*V/V*) to approx. 3 % (*V/V*);

— range B from approx. 3 % (*V/V*) to approx. 20 % (*V/V*).

A set of at least five calibration solutions (preferably more) with precisely known concentrations of FAME (4.1) in FAME free middle distillate (4.2) shall be prepared for the measurement range of interest by weighing FAME into appropriate graduated flasks and filling to the mark with FAME free middle distillate.

FAME free middle distillate should be used as an additional calibration sample (nominal FAME contents "zero"). Additional calibration samples should not be made by means of dilution due to possible error propagation.

Each calibration solution shall be produced separately by weighing.

7.4.3 Calculation of the calibration function

In every case and without exception the form of the calibration function is

$$Y = F(X) \tag{1}$$

where

Y is the signal (dependent variable), i.e. corrected Extinction E_{corr};

X is the content (independent variable), i.e. FAME content in grams FAME per litre (g FAME/l).

Based on the FAME content (X) and the relevant normalised extinction coefficients E_{corr} (Y), for all calibration solutions the straight calibration line is calculated by linear regression using the model according to Equation (2):

$$Y(\mathrm{i}) = a \times X(\mathrm{i}) + b \tag{2}$$

where

Y(i) is the determined corrected extinction E_{corr} for calibration sample (i);

X(i) is the adjusted FAME content, in grams FAME per litre (g FAME/l), of calibration sample (i);

a,b are the regression coefficients (slope and intercept) obtained from the linear regression.

The regression coefficient b ("Y-axis intercept") should ideally be zero in case of accurate work. However, it shall not be set to zero at random. Deviation from zero results from the regular statistical spread of the measuring points around the line of best fit and from the leverage of calibration samples with higher FAME contents. In case of high or striking values for the Y-axis intercept the calibration should be rechecked carefully.

Other calibration models are unacceptable. The inversion of the calibration function necessary for the evaluation of measurements is described in 8.1.

7.5 Recording of infrared spectra

7.5.1 General instructions

If multiple scans are possible, at least 16 scans (identical for all records, see also 7.4.1) shall be used. All further steps apply to both the calibration samples and for the samples to be tested. It is important that all other settings of the IR spectrometer are also retained.

7.5.2 Background and reference spectrum

At every calibration a background spectrum shall be taken and recorded as a reference spectrum for the compensation which is carried out with every measurement. For that the appropriate base fuel for the relevant type of sample (refer to 7.4.1 and 4.2) shall be used.