![SIST logo]

SLOVENSKI STANDARD
oSIST prEN 14078:2024

01-junij-2024

Tekoči naftni proizvodi - Določanje metilnih estrov maščobnih kislin (FAME) v srednjih destilatih - Metoda infrardeče spektroskopije

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

Flüssige Mineralölerzeugnisse - Bestimmung des Gehaltes an Fettsäuremethylester (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

Ta slovenski standard je istoveten z: prEN 14078

ICS:

75.160.20	Tekoča goriva	Liquid fuels

oSIST prEN 14078:2024   **en**

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

DRAFT
prEN 14078

May 2024

ICS 75.160.20

Will supersede EN 14078:2014

English Version

Liquid petroleum products - Determination of fatty acid 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

This draft European Standard is submitted to CEN members for enquiry. It has been drawn up by the Technical Committee CEN/TC 19.

If this draft becomes a European Standard, CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

This draft European Standard was established by CEN in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN-CENELEC Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Republic of North Macedonia, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Türkiye and United Kingdom.

Recipients of this draft are invited to submit, with their comments, notification of any relevant patent rights of which they are aware and to provide supporting documentation.

Warning : This document is not a European Standard. It is distributed for review and comments. It is subject to change without notice and shall not be referred to as a European Standard.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

CEN-CENELEC Management Centre: Rue de la Science 23, B-1040 Brussels

Ref. No. prEN 14078:2024 E

prEN 14078:2024 (E)

Contents

Page

European foreword

This document (prEN 14078:2024) 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 document is currently submitted to the CEN Enquiry.

This document will supersede EN 14078:2014.

prEN 14078:2024 includes the following significant technical changes with respect to EN 14078:2014:

— possibility to use a cell with windows consisting of ZnSe added;

— gravimetric dilution described in 7.5 corrected to volumetric dilution.

Any feedback and questions on this document should be directed to the users' national standards body. A complete listing of these bodies can be found on the CEN website.

iTeh Standards
(https://standards.iteh.ai)
Document Preview

1 Scope

This document 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 three 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);

— range C: for FAME contents ranging from approx. 20 % (V/V) to approx. 50 % (V/V).

Principally, higher FAME contents can also be analysed 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. 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 document, 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 document can involve hazardous materials, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this document to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 14103:2020, *Fat and oil derivatives — Fatty Acid Methyl Esters (FAME) — Determination of ester and linolenic acid methyl ester contents*

EN 14214, *Liquid petroleum products — Fatty acid methyl esters (FAME) for use in diesel engines and heating applications — Requirements and test methods*

EN 14331, *Liquid petroleum products — Separation and characterisation of fatty acid methyl esters (FAME) from middle distillates — Liquid chromatography (LC)/gas chromatography (GC) method*

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

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

3 Principle

The mid infrared absorption spectrum of a test portion of a sample which is diluted as appropriate if necessary 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

4

evaluation of the data will be carried out as grams FAME per litre. For conversion of grams FAME per litre (g/l) to the reporting unit "% (V/V)", a fixed density of FAME of 883,0 kg/m^3 (at 15 °C) is adopted.

Three measurement ranges (A, B or C) have been chosen for which specific adjustments for the calibration and dilution need to be followed. Measurement should be conducted preferably without dilution for range A and a shorter path length of the measurement cell as well as an appropriate dilution for range B and C. 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.

The accuracy of the measured results depends on the best match of molecular masses (proportional to chain length) between the FAME material used for calibration and the FAME material in the analysed sample. For a correct result it is recommended to use FAMEs for calibration (4.1) that have a similar average molecular mass to the product being tested. If this is not possible, a correction has to be carried out.

4 Reagents and materials

4.1 FAME for calibration, FAME as specified in EN 14214.

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 Cell (classical version which consists of holder and window material) or any other liquid transmission accessory (as alternative for the classical liquid cell) with windows consisting of KBr, or NaCl, or ZnSe, or KRS-5, or CaF$_2$ or BaF$_2$, with accurately 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/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, B or C:

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

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

— range C: shorter path length and a dilution higher than for range B, adapted to the anticipated FAME content.

The path length shall be known. 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 sample measurement.

If cells sensitive to water are used the path length shall be checked more frequently. In case the path length has changed, 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 neighbourhood of 1 745 cm^{-1}.

7.3 Selection of the path length

7.3.1 Range A

For from approx. 0,05 % (V/V) to approx. 3 % (V/V) 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 FAME contents from approx. 3 % (*V/V*) to approx. 20 % (*V/V*) 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.

7.3.3 Range C

For FAME contents above 20 % (*V/V*), the following measurement parameters are recommended:

— path length of approx. 0,05 mm, known to the nearest 0,01 mm, with a dilution rate of 1 : 5;

— path length of approx. 0,1 mm, known to the nearest 0,01 mm, with a dilution rate of 1 : 10.

For detailed information refer to data given in Table A.1.

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*);

— range C from approx. 20 % (*V/V*) to approx. 50 % (*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.

WARNING — This method detects all FAME components by measurement of the C = O IR absorption at approximately 1 745 cm^{-1} and C6 to C24 molecules, as specified in EN 14214. The accuracy of the measured results depends on the best match of molecular masses (proportional to chain length) between the FAME material used for calibration and the FAME material in the analysed sample. This means that presence of FAME with lower average chain length, determined with a calibration using FAME of longer average chain length, will result in considerable overestimation, and vice versa. For a correct result it is recommended to use FAMEs for calibration (4.1) that have a similar average molecular mass to the product being tested. If this is not possible, a correction has to be carried out as described at (8.3).

FAME free middle distillate should be used as an additional calibration sample (nominal FAME content "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.

prEN 14078:2024 (E)

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 normalized extinction coefficients E_{corr} (Y), for all calibration solutions the straight calibration line is calculated by linear regression using the model according to Formula (2):

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

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 not permitted. The inversion of the calibration function necessary for the evaluation of measurements is described in 8.1.

7.5 Sample preparation

Depending on the FAME concentration the samples may need to be diluted with FAME Diesel fuel free of FAME. The dilution ratio shall be chosen according to Annex A in order to find the optimal absorbance.

The samples are diluted by pipetting a sample amount corresponding to the dilution ratio into a suitable volumetric flask, which is then filled up to the mark with FAME-free middle distillate.

It is recommended to use the same Diesel fuel free of FAME for sample dilution as used for preparation of the calibration samples.

7.6 Recording of infrared spectra

7.6.1 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.