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**Goriva za motorna vozila - Določevanje komponent z visokim vreliščem, vključno z metilnimi estri maščobnih kislin, v gorivih za motorna vozila, motornem bencinu in etanolu (E85) - Metoda plinske kromatografije**

Automotive fuels - Determination of high-boiling components including fatty acid methyl esters in petrol and ethanol (E85) automotive fuel - Gas chromatography method

Kraftstoffe für Kraftfahrzeuge - Bestimmung von hochsiedenden Komponenten in Ottokraftstoff und Ethanol (E85)-Autokraftstoff - Gaschromatographisches Verfahren

Carburants pour automobiles - Détermination des composants haute-bouillantes dans l'essence et dans carburant automobile Ethanol (E85) - Méthode par chromatographie en phase gazeuse

**Ta slovenski standard je istoveten z: prEN 16270**

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**DRAFT**  
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English Version

**Automotive fuels - Determination of high-boiling components  
including fatty acid methyl esters in petrol and ethanol (E85)  
automotive fuel - Gas chromatography method**

Carburants pour automobiles - Détermination des  
composants haute-bouillantes dans l'essence et dans  
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chromatographie en phase gazeuse

Kraftstoffe für Kraftfahrzeuge - Bestimmung von  
hochsiedenden Komponenten in Ottokraftstoff und Ethanol  
(E85)-Autokraftstoff - Gaschromatographisches 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.

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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.

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

**CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels**

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## Foreword

This document (prEN 16270:2014) 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 16270:2012. Its scope has been extended to ethanol (E85) automotive fuel, the precision data have been updated and further technical improvements have been included.

## 1 Scope

This European Standard specifies a determination method of high boiling components in petrol according to EN 228 [1] and ethanol automotive fuels according to CEN/TS 15293 [2] by capillary gas chromatography using flame ionisation detection. This method is applicable to high boiling material, such as fatty acid methyl ester (FAME) or diesel fuel, having a boiling point greater than or equal to 1-methyl-naphthalene.

The standard is applicable to materials having a vapour pressure low enough to permit sampling at ambient temperature and a boiling range of at least 100 °C. This method pays special attention to fatty acid methyl esters.

In petrol the measurement range for the high boiling fraction is from about 0,7 % (m/m) to about 2,5 % (m/m). For the FAME fraction the range is from about 0,2 % (m/m) to about 2 % (m/m).

In ethanol automotive fuel the measurement range is from about 0,2 % (m/m) to about 2,2 % (m/m), for the FAME fraction the range is from about 0,05 % (m/m) to about 1,5 % (m/m)

NOTE 1 When calculating the FAME fraction, this method only takes the C18-isomers into account

NOTE 2 For the purposes of this European Standard, the terms "% (m/m)" and "% (V/V)" are used to represent respectively the mass fraction and the volume fraction.

**WARNING — The use of this European Standard may involve hazardous materials, operations and equipment. This European 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 to 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 14214, *Liquid petroleum products - Fatty acid methyl esters (FAME) for use in diesel engines and heating applications - 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 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

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NOTE Figure 1 gives some visual explanation of the definitions on the basis of an exemplary chromatogram.

## 3.1

**start of high boiling fraction**

1-methyl-naphthalene is the first peak to be included in the high boiling fraction

## 3.2

**end of high boiling fraction**

dotriacontane (n-C32) is the last peak to be included in the high boiling fraction

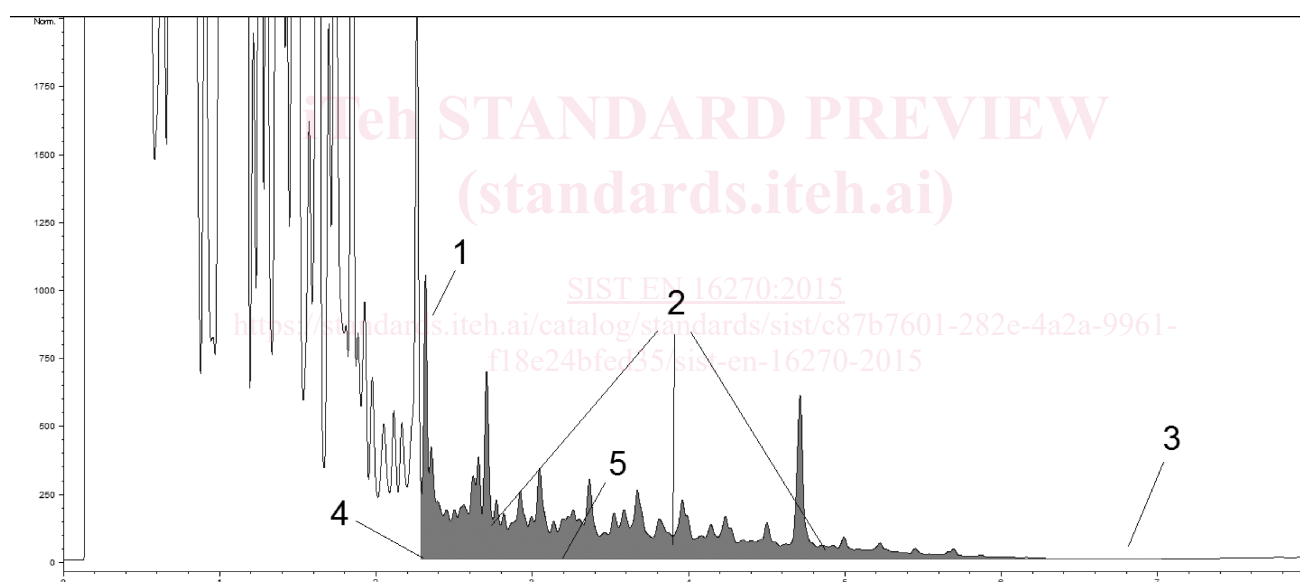
## 3.3

**Fatty acid methyl esters fraction****FAME fraction**

combined area of the C18:0, C18:1, C18:2 and C18:3-FAME peaks

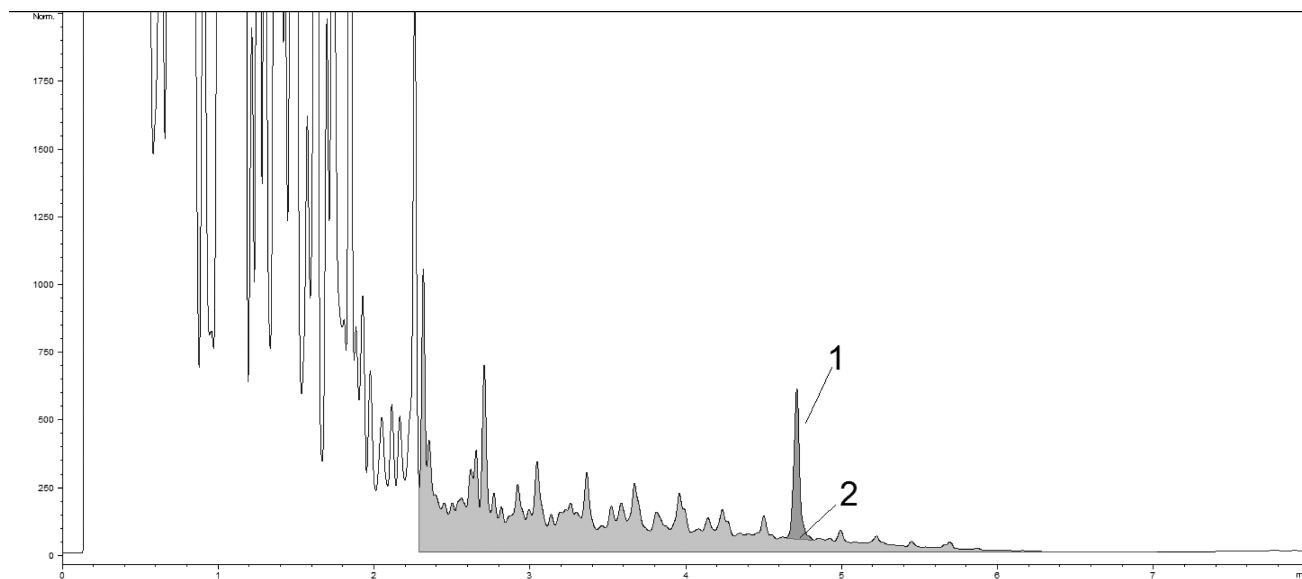
Note 1 to entry: The area is defined as shown in Figure 1b

Note 2 to entry: This method only takes the C18-isomers into account as other isomers such as C16:0 can only be present in very limited amounts. In addition, C16:0 co-elutes with an n-paraffin which affects the quantification.

**Key**

1	Methyl-naphthalene	4	Start high boiling fraction
2	Total high boiling area	5	Baseline for high boiling fraction
3	Dotriacontane		
x-axis	time (min)	y-axis	FID signal

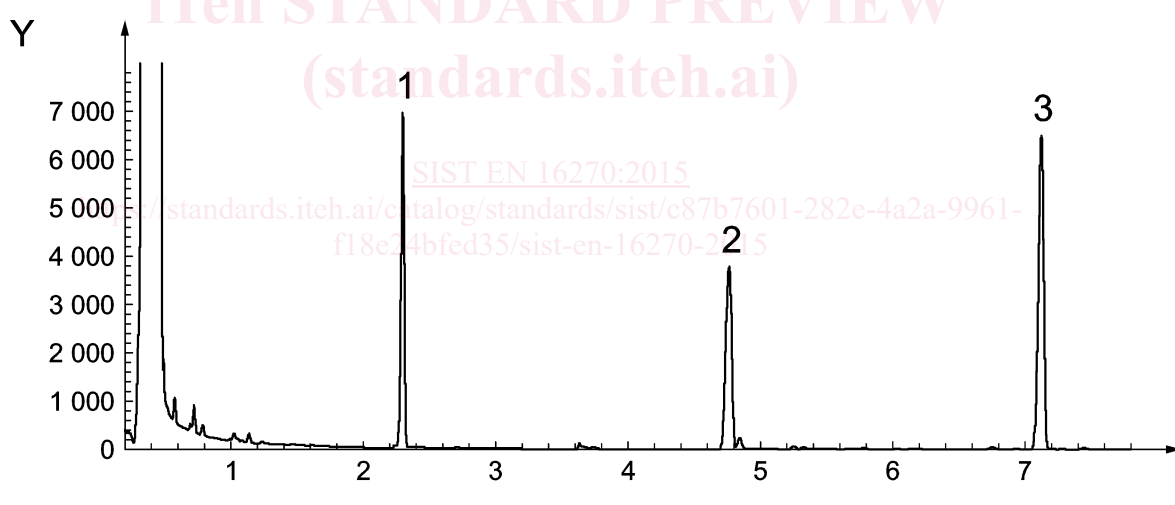
**Figure 1a – Chromatogram explaining high boiling fraction**



**Key**

1	C18 FAME peak area	2	Manual baseline for FAME calculation
x-axis	time (min)	y-axis	FID signal

**Figure 1b – Chromatogram explaining FAME fraction**



**Key**

1	1-Methyl-naphthalene – start of high boiling fraction	3	Dotriacontane – end of high boiling fraction
2	C18-FAME		
x-axis	time (min)	y-axis	FID signal

**Figure 2 — Example of a calibration mixture chromatogram**

**3.4**

**total high boiling area for a calibration mixture**

**Atc**

sum of the areas of 1-methylnaphthalene and dotriacontane

Note 1 to entry: See Figure 2.

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**3.5**  
**total FAME area for a calibration mixture**  
**A<sub>fc</sub>**  
 cumulative area from the start of the FAME C18-fraction until the end of the FAME C18-fraction for a calibration mixture

Note 1 to entry: See Figure 2.

**3.6**  
**total high boiling area for a sample**  
**A<sub>s</sub>**  
 cumulative area from the start of the high boiling fraction until the end of high boiling fraction for a sample

Note 1 to entry: See Figure 1a.

**3.7**  
**total FAME fraction area for a sample**  
**A<sub>f</sub>**  
 cumulative area from the start of the FAME C18-fraction until the end of the FAME C18-fraction for a sample

Note 1 to entry: See Figure 1b.

## 4 Principle

A test portion is introduced into a gas chromatographic column, which separates hydrocarbons in the order of increasing boiling point. The column temperature is raised at a linear reproducible rate and the area under the chromatogram is recorded throughout the analysis. The beginning and the end of the fractions are determined with a calibration mixture.

The high boiling fraction is the total fraction of high boiling material starting from 1-methylnaphthalene until and including dotriacontane and therefore includes all FAME peaks that may be present in this area.

## 5 Reagents and materials

Unless otherwise stated, only chemicals of recognized analytical quality shall be used.

**5.1 Carrier gases**, helium, nitrogen or hydrogen, of at least 99,999 % (V/V) purity, any oxygen present should be removed, e.g. by a chemical resin filter.

**WARNING — Follow the safety instructions from the filter supplier.**

**5.2 Hydrogen**, grade suitable for flame ionisation detectors.

**5.3 Compressed air**, regulated for flame ionisation detectors.

**5.4 Calibration components**, 1-methyl-naphthalene ( $\geq 98$  % (*m/m*)), a fatty acid methyl ester (as specified in EN 14214) and dotriacontane (C<sub>32</sub>H<sub>66</sub>,  $\geq 97$  % (*m/m*)).

NOTE Fatty acid methyl esters that are mainly consisting of C18 isomers such as rapeseed or soy are suitable components. Other methyl esters, such as palm oil, with higher amounts of C16 isomers, are not suitable

### 5.5 Calibration mixture

Prepare about 100g of a calibration mixture by gravimetrically blending the components mentioned in 5.4. Typically a blend of 0,1 % (*m/m*) 1-methyl-naphthalene, 0,2 % (*m/m*) dotriacontane and 0,2 % (*m/m*) FAME in n-heptane is used.



Record the masses to the nearest 0,1 mg when weighing the components. Calculate the % (*m/m*) of each calibration component in the mixture and round to the nearest 0,001 % (*m/m*). The boiling point range of the solvent shall not interfere with the calibration components.

NOTE 1 A typical solvent to be used is n-heptane ( $\geq 99$  % (*m/m*) purity). Other solvents or mixtures of hydrocarbons can be used provided their boiling point is in the range of about 80°C to about 160°C to limit possible evaporation when preparing the mixture and overcome interference with the boiling point of 1-methylnaphthalene.

NOTE 2 The calibration sample may contain mixtures of different origin of FAME's such as rapeseed or soy, as is most representative for a specific application.

## 6 Apparatus

**6.1 Gas chromatograph**, with the following performance characteristics:

**6.1.1 Flame ionisation detector**, the detector shall be capable of operating at a temperature at least equivalent to the maximum column temperature employed in the method.

NOTE The capillary column should sit just below the flame tip and it is recommended that the orifice of the jet should be 0,6 mm minimum to prevent frequent blocking with silicones.

**6.1.2 Column temperature programmer**, capable of linear programmed temperature operation over a range from ambient temperature to 350 °C.

**6.1.3 Sample inlet system**, consisting of a programmable temperature vaporizer (PTV) or temperature programmable cool on-column (COC) injection port. The maximum temperature of the injection device shall be higher than the final oven temperature. The minimum temperature shall be low enough to prevent sample or solvent flashback, but high enough to allow sample focussing at the front of the column. Table 1 contains the typical operating conditions.

## 6.2 Column

SIST EN 16270:2015

<https://standards.iteh.ai/catalog/standards/sist/c87b7601-282e-4a2a-9961->

A 10 m capillary column with 0,53 mm internal diameter and coated with dimethyl polysiloxane is used. See Table 1 for further advised conditions. Commercially available columns with film thickness ( $d_f$ ) = 0,88  $\mu\text{m}$  have been found to be satisfactory.

**Table 1 — Typical operating conditions for gas chromatograph**

Description	PTV or COC inlet
Column length, m	10
Column inner diameter, mm	0,53
Stationary phase	Dimethyl polysiloxane
Stationary phase thickness, $\mu\text{m}$	0,88
Carrier gas	Helium
Carrier gas flow rate, ml/min	26
Initial column temperature, °C	40
Final column temperature, °C	350
Programming rate, °C /min	35
Detector	FID
Detector temperature, °C	360

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Injector temperature initial, °C	100
Injector programming rate, °C /min.	35
Injector temperature final, °C	360
Sample size, µl	1

**6.3 Carrier gas control**

The chromatograph shall be able to deliver a constant carrier gas flow over the whole temperature range of the analysis.

**6.4 Micro-syringe**, of appropriate volume, e.g. 10 µl, for introduction of 1 µl of the calibration mixture and test portions

NOTE 1 The micro-syringe may be operated either manually or automatically.

NOTE 2 Plunger in needle syringes are not recommended due to excessive carry over of heavy ends to the following analysis.

**6.5 Refrigerator**

**SAFETY PRECAUTIONS** — It is recommended that the refrigerator be of an explosion-protected design.

**6.6 Analytical balance**, able to weigh with a precision of 0,1 mg

**7 Sampling**

Samples shall be taken as described in EN ISO 3170 or EN ISO 3171 and/or in accordance with the requirements of national standards or regulations for the sampling of petroleum products.

Store samples in either glass or metal containers. Plastic containers for sample storage shall not be used as evaporation can occur and prolonged contact with the sample can cause contamination of the sample due to possible leaching of the plasticizer.

**8 Preparation of the apparatus**

**8.1** Set up and operate the gas chromatograph in accordance with the manufacturer's instructions. Advised operating conditions are shown in Table 1.

**8.2** Deposits can form on the jet from combustion of decomposition products from the liquid stationary phase. These will affect the characteristics of the detector and should be removed.

NOTE The following parameters are affected by deposits on the jet: increase in inlet pressure, FID difficult to light and increase of baseline noise. To clean the jet, it is recommended that it is put in an ultrasonic cleaner with a suitable solvent, and a cleaning wire used.

**9 Calibration**

**9.1** Carry out the steps given in 9.2 to 9.4 before each sample sequence. The first run of the day shall not be a blank, a reference material or a sample, due to the possible elution of extraneous components, which have built up in the injector.

**9.2** Run the calibration mixture (5.5) using the specified procedure described in Clause 10.