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BSI Standards Publication

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

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National foreword

This British Standard is the UK implementation of EN 16270:2015. It supersedes BS EN 16270:2012/BS 2000-606:2012 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee PTI/13, Petroleum Testing and Terminology.

A list of organizations represented on this committee can be obtained on request to its secretary.

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EN 16270

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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 chromatographic method

Carburants pour automobiles - Détermination des composés à haut point d'ébullition dont les esters méthyliques d'acides gras dans l'essence et dans le carburant éthanol pour automobiles (E85) - Méthode par chromatographie en phase gazeuse

Kraftstoffe für Kraftfahrzeuge - Bestimmung von hochsiedenden Komponenten inklusive Fettsäure-Methylester in Ottokraftstoff und Ethanol (E85)-Kraftstoff für Fahrzeuge - Gaschromatographisches Verfahren

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Foreword

This document (EN 16270:2015) 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of an identical text or by endorsement, at the latest by December 2015, and conflicting national standards shall be withdrawn at the latest by December 2015.

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 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.

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

1 Scope

This European Standard specifies a determination method of high boiling components in petrol according to EN 228 [1] and ethanol (E85) automotive fuels according to CEN/TS 15293 [2] by capillary gas chromatography using flame ionization 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.

This European Standard is applicable to materials having a vapour pressure low enough to permit sampling at ambient temperature and covers 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 (E85) automotive fuel the measurement range for the high boiling fraction 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 FAME compounds 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 documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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)*

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

3 Terms and definitions

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

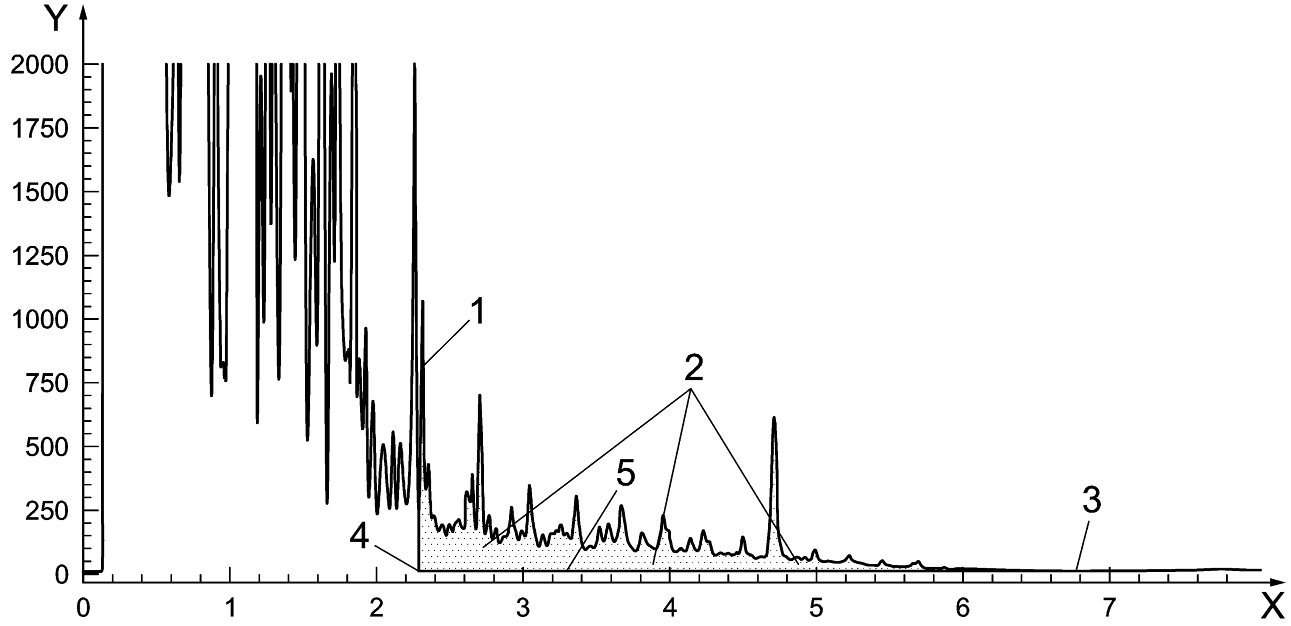
NOTE Figure 1a, 1b and 2 give some visual explanation of the definitions on the basis of an exemplary chromatogram.

3.1
high boiling fraction
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

3.2
start of high boiling fraction
1-methyl-naphthalene is the first peak to be included in the high boiling fraction

3.3
end of high boiling fraction

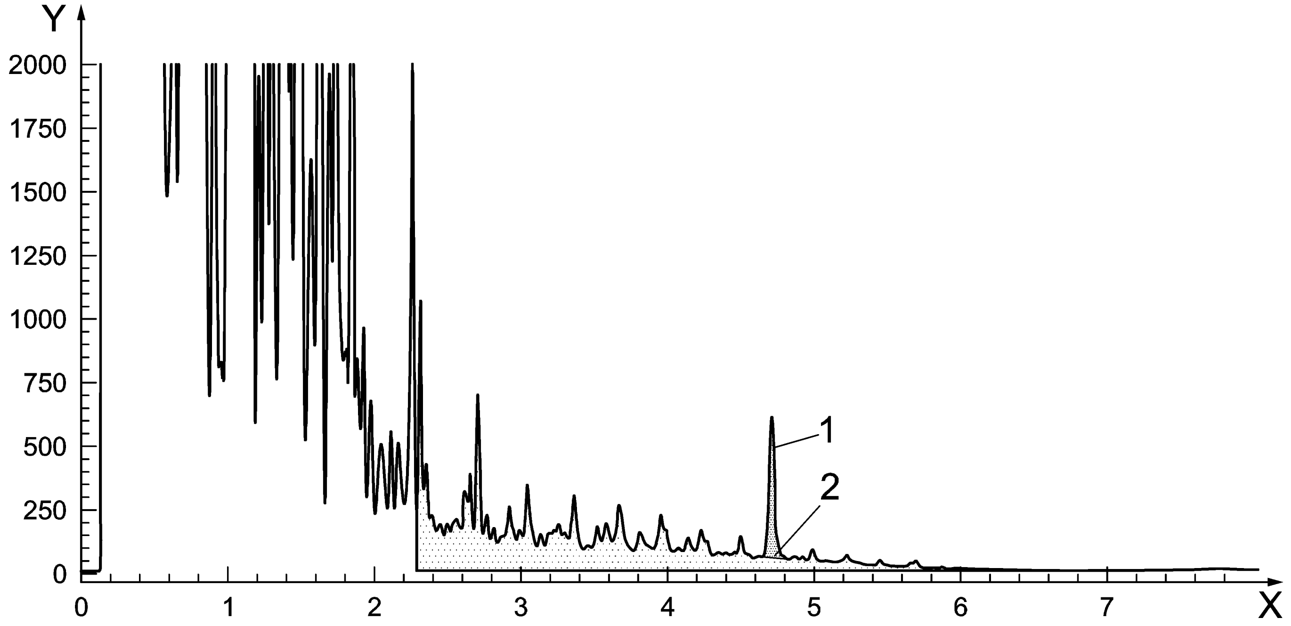
dotriacontane (n-C32) is the last peak to be included in the high boiling fraction



Key

1	1-Methyl-naphthalene	4	Start of high boiling fraction
2	Total high boiling area	5	Baseline for high boiling fraction
3	End of high boiling fraction		
X	time (min)	Y	FID signal

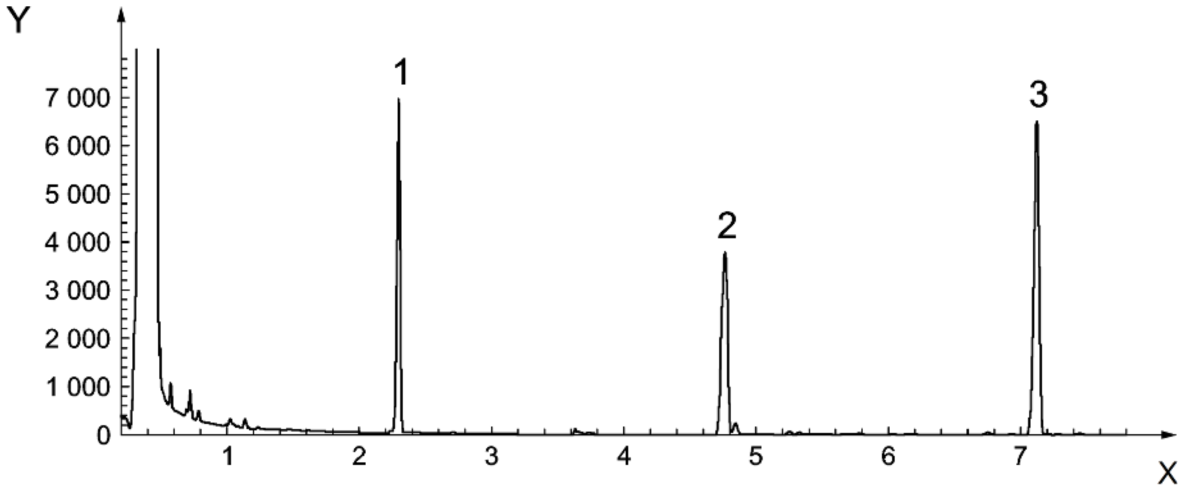
Figure 1a — Chromatogram explaining high boiling fraction



Key

1	C18 FAME peak area	2	Manual baseline for FAME fraction calculation
X	time (min)	Y	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	time (min)	Y	FID signal

Figure 2 — Example of a calibration mixture chromatogram

3.4

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 FAME compounds into account as other compounds 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.

3.5

total high boiling area for a calibration mixture
A_{tc}
sum of the areas of 1-methylnaphthalene and dotriacontane

Note 1 to entry: See Figure 2.

3.6

total FAME area for a calibration mixture
A_{fc}
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.

3.7

total high boiling area for a sample
A_{s}
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.

3.8

total FAME fraction area for a sample
A_{f}
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.

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 ionization detectors.

5.3 Compressed air, regulated for flame ionization detectors.

5.4 Calibration components, 1-methyl-naphthalene (≥98 % (m/m)), a fatty acid methyl ester (as specified in EN 14214) and dotriacontane ($C_{32}H_{66}$, ≥ 97 % (m/m)).

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

5.5 Solvent, for preparing calibration mixture. A typical solvent to be used is n-heptane (≥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 1-methylnaphthalene peak.

5.6 Calibration mixture

Prepare about 100 g 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 The calibration mixture 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 ionization detector, the detector shall be capable of operating at a temperature at least equivalent to the maximum column temperature employed in the method.

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 focusing at the front of the column. Table 1 contains the typical operating conditions.

6.2 Column

A 10 m capillary column with 0,53 mm internal diameter and coated with dimethyl polysiloxane is used. See Table 1 for further recommended conditions. Commercially available columns with film thickness (df) = 0,88 µm 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, µm	0,88
Carrier gas	Helium
Carrier gas flow rate, ml/min	26
Initial column temperature, °C	40
Final column temperature, °C	350
Oven programming rate, °C /min	35
Detector	FID
Detector temperature, °C	360
Injector temperature initial, °C	100
Injector programming rate, °C /min.	35
Injector temperature final, °C	360
Sample volume, 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.

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

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.

IMPORTANT — The following side effects are observed 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 (5.6) using the specified procedure described in Clause 10.

CAUTION — Take care to ensure the test portion volume chosen does not allow any peak to exceed the linear range of the detector, or overload the column. A skew of > 3 indicates the sample is too concentrated and a skew of < 1 indicates an old column or dirty liner. As a guide, 1 µl of the calibration mixture (5.6) has been found to be suitable.

9.3 Determine the Total high boiling fraction calibration area by summing the areas of 1-methylnaphthalene and dotriacontane, A_{tc} (3.5).

9.4 Determine the Total FAME fraction calibration area, A_{fc} (3.6).

10 Procedure

IMPORTANT — Automatic baseline compensation is available on several instruments but it is not allowed by this test method. Using electronically corrected data from the Gas chromatograph (GC) supplies a corrected FID output, which is unwanted from a point of view of original and traceable data.

10.1 Run a blank baseline analysis (analysis without injection) before the first sample analysis, and then after every five samples. Subtract blank baselines from subsequent analyses.

The identification of a constant baseline at the end of the run is critical to the analysis. Continuous attention shall be given to all factors that influence baseline stability, e.g. column bleed, septum bleed, detector temperature control, constancy of carrier gas flow, leaks and instrument drift. The baseline at the end of each analysis shall merge with the baseline of the blank run associated with it. Both signals shall merge to confirm integrity; if they do not, the analysis shall be repeated (see also Clause 11).

10.2 Cool the column to the starting temperature, and inject the selected sample volume.

10.3 Start programming the column temperature.

10.4 Continue the run until-the last component in the calibration mixture (dotriacontane) has fully eluted.

10.5 Determine the Total High Boiling fraction area for the sample, A_{s} (3.7), as shown in Figure 1a.

10.6 Determine the Total FAME fraction area for the sample, A_{f} (3.8), as shown in Figure 1b.

11 Visual inspection of the chromatograms

Using the data system, expand the chromatogram of the reference or sample, by 5 times. See Figure 3a and 3b for an example of a typical chromatogram.

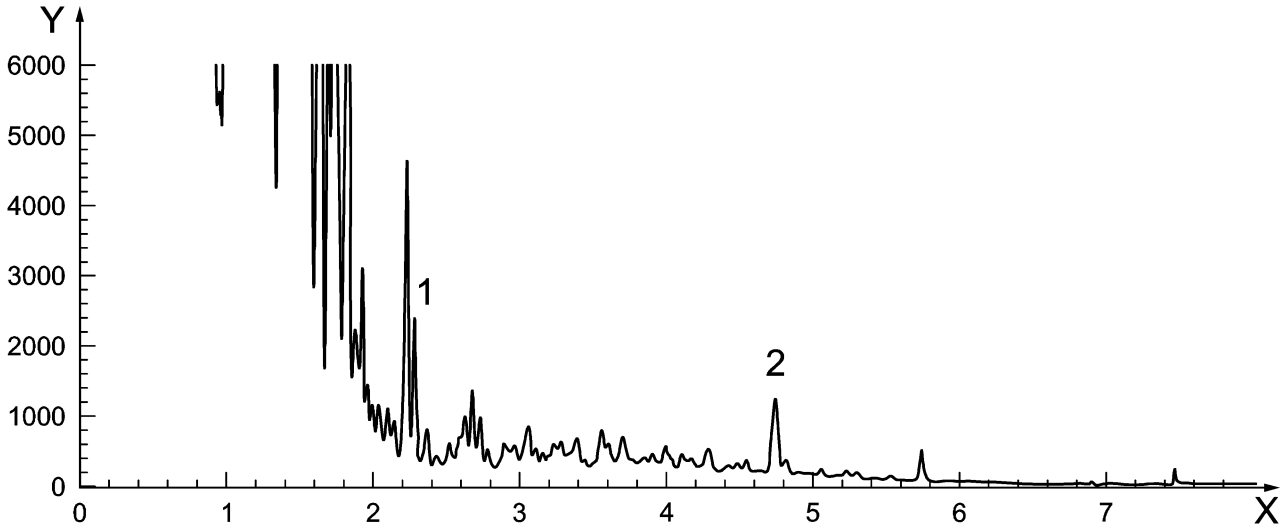


Figure 3a — Example chromatogram of a petrol sample

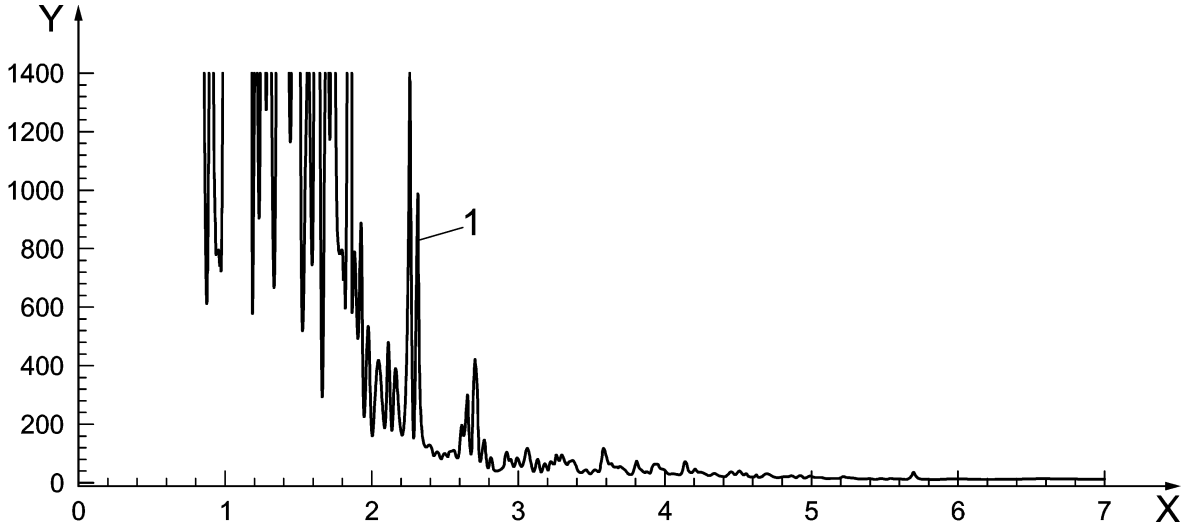


Figure 3b — Example chromatogram of an E85 ethanol fuel sample

Key

1	1-methyl-naphthalene	2	C18-FAME
X	time (min)	Y	FID signal

Figure 3 — Example chromatogram of a sample

Merge the blank baseline and the sample baseline, and observe the following points (see Figure 4):

- The start of the area of interest is taken at a point on the baseline where the blank and the sample baselines are merged. This is taken before the start of the sample (see Figure 4a).
- The end of the area of interest is taken at a point on the baseline where the blank and the sample baselines are merged. This is taken after the end of the sample and at or before the end of run (see Figure 4b).

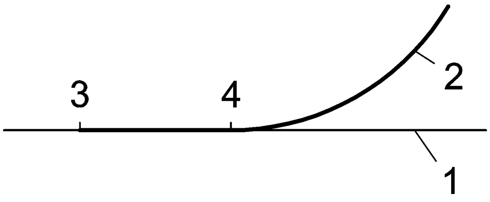


Figure 4 a) — Start of run

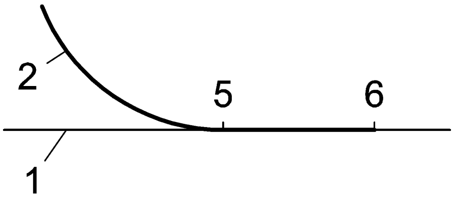


Figure 4 b) — End of run

Key

1	baseline	4	start of sample area
2	sample	5	end of sample area
3	start of area as interest	6	end of area of interest

Figure 4 — Baselines

12 Calculation

12.1 General

The cumulative area of the high boiling fraction in the sample includes the area of the FAME peaks.

The concentration of the fractions is calculated using the Formulae (1) and (2).

12.2 Total high boiling fraction

$$\Phi_s = \frac{A_s}{A_{tc}} \cdot \Phi_{tc} \tag{1}$$

where

Φ_s is total % (m/m) of high boiling fraction in sample;

A_s is total high boiling area for a sample (3.7) in sample;

A_tc is total high boiling area for a calibration (3.5);

Φ_tc is total % (m/m) of high boiling fraction in calibration mixture.

12.3 FAME fraction

$$\Phi_f = \frac{A_f}{A_{fc}} \cdot \Phi_{fc} \tag{2}$$

where

Φ_f is % (m/m) of FAME fraction in sample;

A_f is FAME area in sample (3.8);

A_{fc} is FAME area in calibration mixture (3.6);

Φ_{fc} is total % (*m/m*) of FAME fraction in calibration mixture.

13 Expression of results

Report the results as follows:

- Total high boiling fraction, Φ_s, in 0,01 % (*m/m)*
- FAME fraction, Φ_f, in 0,01 % (*m/m*)

14 Precision

14.1 General

An interlaboratory test programme on E85 samples has been carried out and the precision was determined by statistical examination of inter-laboratory test results using EN ISO 4259 [3].

14.2 Repeatability

The difference between two 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 the test method, exceed the values given in Table 2 or 3 only in one case in 20.

14.3 Reproducibility

The difference between two single and independent test 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 the test method, exceed the values given in Table 2 or 3 only in one case in 20.

Table 2 — Precision values for petrol

Petrol	**Repeatability *r*** % (*m/m*)	**Reproducibility *R*** % (*m/m*)
Total high boiling fraction	0,039 3 + 0,072 7 *X*	0,288 4 + 0,063 5 *X*
FAME fraction	0,022 2 + 0,044 2 *X*	0,073 1 + 0,118 3 *X*
where *X* is the average of the two results being compared		

Table 3 — Precision values for ethanol (E85) automotive fuel

E85	**Repeatability *r*** % (*m/m*)	**Reproducibility *R*** % (*m/m*)
Total high boiling fraction	$- 0{,}007\,5 + 0{,}083\,9\,X$	$0{,}059\,3 + 0{,}111\,5\,X$
FAME fraction	$- 0{,}004 + 0{,}065\,9\,X$	$- 0{,}013\,6 + 0{,}282\,6\,X$
where X is the average of the two results being compared		

15 Test report

The test report shall specify:

a) a reference to this European Standard, i.e. EN 16270;

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

c) the result of the test (see Clause 13);

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

e) the date of the test.

Bibliography

[1] EN 228, *Automotive fuels - Unleaded petrol - Requirements and test methods*

[2] CEN/TS 15293, *Automotive fuels - Ethanol (E85) automotive fuel - Requirements and test methods*

[3] EN ISO 4259, *Petroleum products - Determination and application of precision data in relation to methods of test (ISO 4259)*

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