SLOVENSKI STANDARD
SIST EN 16761-2:2016

01-februar-2016

Goriva za motorna vozila - Določevanje metanola v motornem gorivu etanol (E85) s plinsko kromatografijo - 2. del: Metoda z uporabo tehnike "heart cut"

Automotive fuels - Determination of methanol in automotive ethanol (E85) fuel by gas chromatography - Part 2: Method using heart cut technique

Kraftstoffe für Kraftfahrzeuge - Bestimmung von Methanol im automotive Ethanol (E85) als Kraftstoff durch Gaschromatographie - Teil 2: Methode mit Herz schnitt Technik

Carburants pour automobiles - Détermination de la teneur en méthanol dans l'automobile l'éthanol (E85) de carburant par chromatographie en phase gazeuse - Partie 2: Méthode utilisant coeur coupe technique

Ta slovenski standard je istoveten z: **EN 16761-2:2015**

ICS:

71.040.50	Fizikalnokemijske analitske metode	Physicochemical methods of analysis
75.160.20	Tekoča goriva	Liquid fuels

SIST EN 16761-2:2016 **en,fr,de**

EUROPEAN STANDARD
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EN 16761-2

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ICS 75.160.20

English Version

Automotive fuels - Determination of methanol in automotive ethanol (E85) fuel by gas chromatography - Part 2: Method using heart cut technique

Carburants pour automobiles - Détermination de la teneur en méthanol dans le carburant éthanol (E85) pour automobiles par chromatographie en phase gazeuse - Partie 2: Méthode "heart-cutting"

Kraftstoffe für Kraftfahrzeuge - Bestimmung des Methanolgehalts in Ethanolkraftstoff (E85) mittels Gaschromatographie - Teil 2: Verfahren mittels Heart-Cut-Technik

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

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European foreword

This document (EN 16761-2:2015) 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of an identical text or by endorsement, at the latest by June 2016, and conflicting national standards shall be withdrawn at the latest by June 2016.

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.

The determination of a significant amount of methanol in ethanol (E85) automotive fuels was deemed to be necessary to check the product for compliance against EU emission regulations. The CEN/TC 19 Ethanol Fuels Task Force requested the development of such a determination technique.

In EN 16761, *Automotive fuels — Determination of methanol in automotive ethanol (E85) fuel by gas chromatography*, two test methods were developed that comply with this scope:

— *Part 1: Method using single column technique*;

— *Part 2: Method using heart cut technique* [the present document].

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, 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 methanol in automotive ethanol (E85) fuel (also designated as ethanol (E85) automotive fuel or shortly "E85") by capillary gas chromatography using heart cutting technique. Fuel quality specifications for this product exist, see Bibliography Entry [1].

This standard is applicable to fuels having a methanol content from about 0,5 % (*V/V*) to about 1,5 % (*V/V*). Other methanol contents can also be determined, however no precision data for results outside the specified range is available.

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

WARNING — The use of this standard can 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 users of this standard to take appropriate measures to ensure the safety and health of personnel prior to application of the standard, and fulfil statutory and regulatory requirements for this purpose.

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 228, *Automotive fuels — Unleaded petrol — Requirements and test methods*

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

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

EN ISO 3675, *Crude petroleum and liquid petroleum products — Laboratory determination of density — Hydrometer method (ISO 3675)*

EN ISO 3838, *Crude petroleum and liquid or solid petroleum products — Determination of density or relative density — Capillary-stoppered pyknometer and graduated bicapillary pyknometer methods (ISO 3838)*

EN ISO 12185, *Crude petroleum and petroleum products — Determination of density — Oscillating U-tube method (ISO 12185)*

3 Terms and definitions

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

3.1
methanol calibration area
area of the methanol peak in the calibration chromatogram

Note 1 to entry: Figure 4 shows an example of a calibration chromatogram.

3.2
methanol sample area
A_s
area of methanol peak in the sample chromatogram

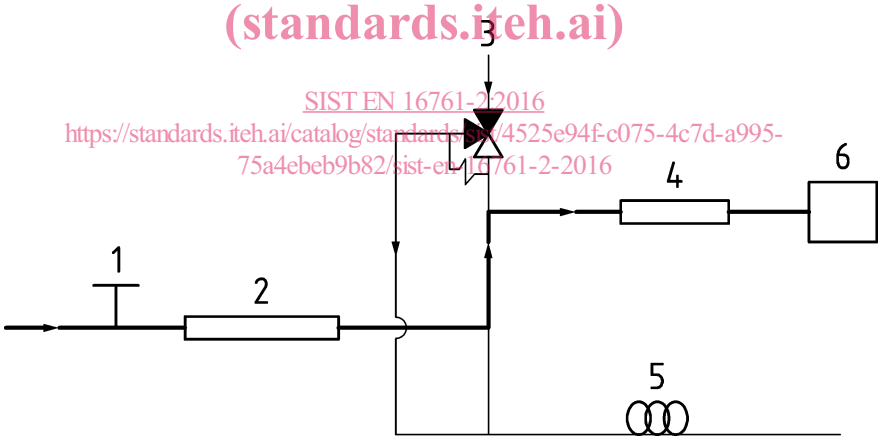
Note 1 to entry: Figure 6 shows an example of a sample chromatogram.

4 Principle

This standard describes the analysis of methanol content in automotive ethanol (E85) fuels using the heart cut technique. The analyser is based upon the principle described by D.R. Deans [3]. This technique controls the pressure between two columns and directs the effluent of a (pre) column to usually two columns, an analytical column and a monitor column. By using columns of a very different nature as pre column and analytical column (e.g. a non-polar and a polar column) separations can be achieved that are difficult to obtain using a single column.

This allows the analysis of methanol to be independent of any impurities or high boiling material that may be present in the sample. The method uses external standard calibration.

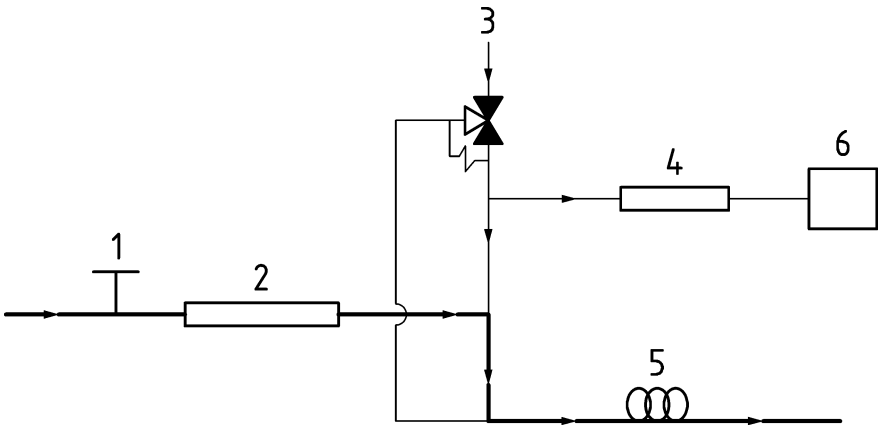
The sample is injected onto a methyl silicone pre column which elutes the methanol and part of the ethanol plus any light hydrocarbons to the analytical column (Figure 1). After methanol has fully eluted onto the analytical column, the valve and thus a Pressure Control Module (PCM) pressure is switched and the components coming from the pre column are directed to the monitor column (Figure 2). The methanol is now separated from the ethanol and hydrocarbons on the analysis column and detected by the Flame Ionization Detector. The detector response, which is proportional to the component concentration, is recorded. The peak areas are measured and the concentration of methanol is calculated using the response factor from the external standard calibration.



Key

1	split/splitless inlet	3	Pressure Control Module	5	monitor column
2	pre column	4	analytical column	6	Flame Ionization Detector

Figure 1 — Valve in ON-position



Key

1 split/splitless inlet
2 pre column
3 Pressure Control Module
4 analytical column
5 monitor column
6 Flame Ionization Detector

Figure 2 — Valve in OFF-position

5 Reagents and materials

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

5.1 Carrier gases, helium or nitrogen, of at least 99,995 % (*V/V*) purity, any oxygen present should be removed, e.g. by a chemical resin filter. 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, methanol (anhydrous, ≥ 99,8 % (*m/m*)) and ethanol (pro-analysis ≥ 99,8 % (*m/m*) by GC). It should be ensured that the ethanol contains no methanol detectable by this test method in a mixture (85/15 % (*V/V*)) of ethanol and petrol (5.5).

5.5 Oxygenate-free petrol (EN 228-compliant).

5.6 Calibration solution:

Prepare an E85 stock solution by (S1) by mixing 15 % (V/V) of an oxygenates free petrol (5.5) with 85 % (V/V) ethanol (5.4).

Prepare a calibration solution (C1) of methanol (5.4) in E85 by accurately weighing 0,1 g of methanol with 9,9 g of stock solution S1 with an accuracy of 0,1 mg.

6 Apparatus

6.1 Gas chromatograph, with the following performance characteristics:

6.1.1 Flame ionization detector, FID, capable of operating at a temperature at least equivalent to the maximum column temperature employed in the method.

6.1.2 Column temperature programmer, capable of linear programmed temperature operation over a range from ambient temperature to 250 °C.

6.1.3 Sample inlet system, consisting of an injector with variable split flow or similar device.

6.2 Columns, the following set of columns are recommended, other columns may be used as long as a similar separation efficiency is achieved:

— pre-column: 30 m (length) × 0,53 mm (diameter) × 0,88 µm (film thickness) Polydimethylsiloxane (PDMS);

— analytical column: Polar column, typically a 10 m x 0,53 mm x 10 µm OxyPlot or Lowox[1] column has been proven to work satisfactorily;

— monitor column: empty fused silica, typically 0,7 m x 0,25 mm. Length shall be tuned for each system.

6.3 Carrier gas control: the chromatograph shall be able to deliver a constant carrier gas pressure over the whole temperature range of the analysis.

6.4 Micro-syringe, of appropriate volume, e.g. 5 µl, for introduction of 0,5 µl of the calibration solution 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, 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 of parts of the sample 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 below:

—	Oven Temp Program:	100 °C for 5 min then 25 °C/min to 250 °C for 4 min
—	Run Time:	15 min
—	Injector temperature:	200 °C
—	Inlet pressure:	38 kPa
—	Injection volume:	0,5 µL
—	Split ratio:	100:1

1) Both column types are examples of suitable commercially available products. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of these products.