SLOVENSKI STANDARD
SIST EN 15721:2013

01-november-2013

Nadomešča:
SIST EN 15721:2009

Etanol kot komponenta za dodajanje motornemu bencinu - Določevanje višjih alkoholov, metanola ter hlapnih nečistoč - Metoda plinske kromatografije

Ethanol as a blending component for petrol - Determination of higher alcohols, methanol and volatile impurities - Gas chromatographic method

Ethanol zur Verwendung als Blendkomponente in Ottokraftstoff - Bestimmung von höheren Alkoholen, Methanol und flüchtigen Verunreinigungen - Gaschromatographisches Verfahren

Éthanol comme base de mélange à l'essence - Détermination de la teneur en alcools supérieurs, méthanol et impuretés volatiles - Méthode par chromatographie en phase gazeuse

Ta slovenski standard je istoveten z: **EN 15721:2013**

ICS:

71.080.60	Alkoholi. Etri	Alcohols. Ethers
75.160.20	Tekoča goriva	Liquid fuels

SIST EN 15721:2013 **en,fr,de**

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 15721

August 2013

ICS 75.160.20

Supersedes EN 15721:2009

English Version

Ethanol as a blending component for petrol - Determination of higher alcohols, methanol and other impurities - Gas chromatographic method

Éthanol comme base de mélange à l'essence - Détermination de la teneur en alcools supérieurs, méthanol et autres impuretés - Méthode par chromatographie en phase gazeuse

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Ref. No. EN 15721:2013: E

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Foreword

This document (EN 15721:2013) 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of an identical text or by endorsement, at the latest by February 2014, and conflicting national standards shall be withdrawn at the latest by February 2014.

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 15721:2009.

EN 15721:2013 includes the following significant technical changes with respect to EN 15721:2009: the method has been simplified and more tailored towards the determination of the higher alcohols as mentioned in EN 15376 (propan-1-ol, butan-1-ol, butan-2-ol, 2-methylpropan-1-ol (isobutanol), 2-methylbutan-1-ol, 3-methylbutan-1-ol, methanol). All other alcohol compounds are summed as impurities. The response factor check and the listed example response factors have been taken out.

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.

Introduction

This document specifies a gas chromatographic (GC) test method for the determination of a number of compounds present in ethanol for use as a blending component in petrol according to the CEN ethanol blending component specification EN 15376 [1]. The test method comprises of GC identification and analysis of a number of molecules, which are then attributed to several classes ("impurities", "methanol", "higher alcohols"), which are needed for calculation of the specified values as required in EN 15376.

The method described in this document was prepared by CEN/TC 19's Working Group 9 and is based on two methods ([2] and [3]) published from a European Regulation on wine and on other internationally published analytical methods on spirits [4]. The method is modified for determinations in ethanol for automotive applications.

1 Scope

This European Standard specifies a gas chromatographic method for ethanol, in which higher alcohols (propan-1-ol, butan-1-ol, butan-2-ol, 2-methylpropan-1-ol (isobutanol), 2-methylbutan-1-ol, and 3-methylbutan-1-ol) from 0,1 % up to 2,5 % (*m/m*), methanol from 0,1 % up to 3 % (*m/m*) and other impurities, in the range from 0,1 % up to 2 % (*m/m*) are determined.

Impurities are all the compounds not attributed to the groups of higher alcohols or methanol.

NOTE 1 The European ethanol blending component specification[1] sets a limit for the combined result of ethanol + higher alcohols, not the ethanol content itself.

Due to possible interferences, the method is not applicable to denatured ethanol samples.

Water, if present in the sample, is not included in this analysis, because a signal for water is not visible in the chromatogram. Therefore, if "alcohol content" is called up in a specification, water needs to be considered separately in the calculations.

NOTE 2 For the purposes of this European Standard, the term “% (*m/m*)” is used to represent the mass fraction (*ω*).

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

EN ISO 3696, *Water for analytical laboratory use — Specification and test methods (ISO 3696)*

3 Principle

The compounds specified in the scope are determined by direct injection of a test portion into a gas chromatograph (GC) system. An internal standard is added to the sample prior to the injection. The compounds are separated with suitable GC equipment using temperature programming with the option to also use flow programming on a suitable column. They are detected using a flame ionisation detector (FID). The concentration of each compound is determined from response factors with respect to the internal standard.

The response factors are obtained during calibration using the same chromatographic conditions as those for the analysis of the ethanol samples.

Two procedures ("Procedure A" and "Procedure B") are specified which differ mainly in the optional use of a water dilution step prior to the analysis. Both variants have been validated to produce identical results and precision in extensive RR tests.

4 Reagents and materials

All reagents shall be of recognised analytical grade (minimum 99 %) or of higher purity, if commercially available. They shall be stored in closed dark glass bottles and can be used for some long time. Other internal standards may also be used when there is sufficient proof that their GC signal does not interfere with the other signals in the chromatogram.

4.1 **Water** which, for analytical laboratory use, shall conform to grade 2 of EN ISO 3696.

4.2 Compounds

The compounds used for calibration and peak identification are listed in Table 1.

Table 1 — Compounds for calibration, used as solvents and other related information

Compound	Attributed to group
Calibration compounds	
Methanol	Methanol
Propan-1-ol	Higher Alcohols
Butan-1-ol	Higher Alcohols
Butan-2-ol	Higher Alcohols
2-Methylpropan-1-ol	Higher Alcohols
2-Methylbutan-1-ol	Higher Alcohols
3-Methylbutan-1-ol	Higher Alcohols
Internal standards	
Pentan-3-ol	Internal standard for Procedure A
4-Methylpentan-2-ol	Internal standard for Procedure B
Solvent	
Ethanol [a]	Solvent
[a] Ethanol is needed in Procedure "A" and "B" as a solvent for the calibration solutions. The purity of the ethanol should be taken into account when preparing the mixtures. It should not contain any impurities that may interfere with the analysis and the results shall be corrected for the purity of the ethanol	

5 Apparatus

5.1 Gas chromatograph, equipped with a Flame Ionisation Detector (FID), a split injector and connected to a PC or other system permitting the recording of chromatograms and execution of quantitative calculations.

5.2 Gas chromatographic column

5.2.1 General

Bonded capillary column with a suited phase, permitting the complete separation of all requested compounds for the analysis, except for 2-methylbutan-1-ol and 3-methylbutan-1-ol, for which a minimum peak resolution of 1,0 (see 5.2.2) is required. The internal standard shall be perfectly separated from all other compounds. Additional detail, including sample chromatograms, is given in Annex A.

5.2.2 Chromatographic resolution

The column resolution (as measured for 2-methylbutan-1-ol and 3-methylbutan-1-ol) shall be at least 1,0. Determine the column resolution, *CR*, with the calibration solutions (7.3) or (7.4) for the 2-methylbutan-1-ol and 3-methylbutan-1-ol peaks using the following Formula (1):

$$CR = \frac{2(t_2 - t_1)}{1{,}699(W_1 + W_2)} \quad (1)$$

where

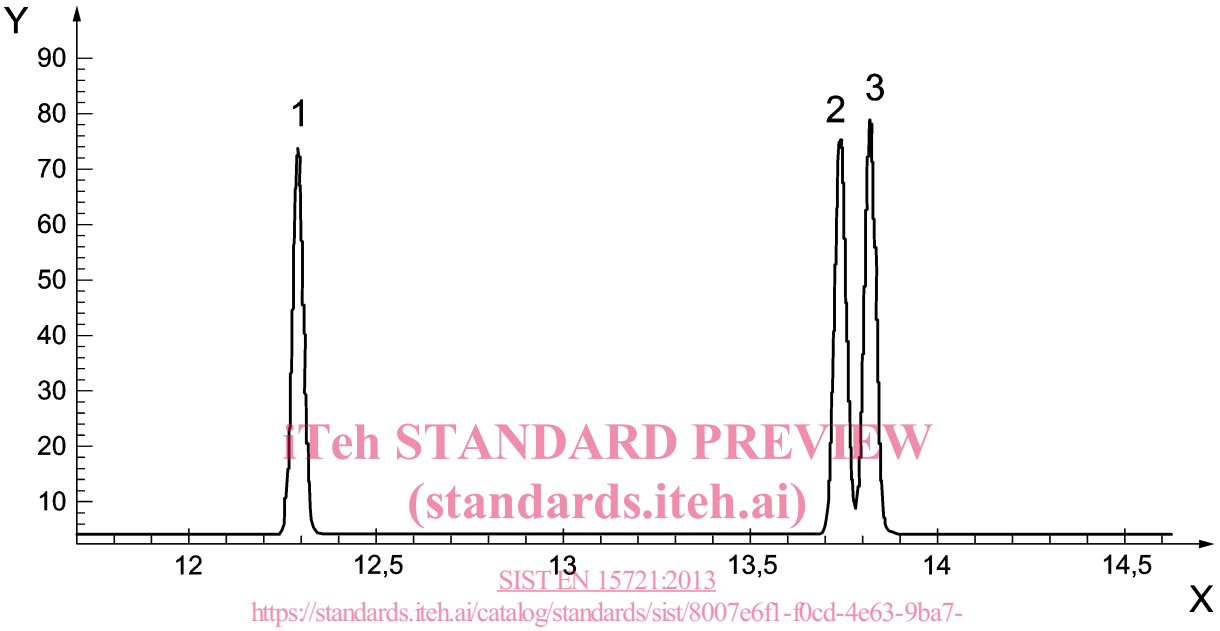
t_1 is the retention time, in seconds, for the 2-methylbutan-1-ol peak;

t_2 is the retention time, in seconds, for the 3-methylbutan-1-ol peak;

W_1 is the width, in seconds, at half-height of 2-methylbutan-1-ol peak;

W_2 is the width, in seconds, at half-height of 3-methylbutan-1-ol peak.

Figure 1 presents further clarification on the calculation of column resolution, *CR*, of 2-methylbutan-1-ol and 3-methylbutan-1-ol according to procedure “B” (example: *CR* = 1,30).



Key

1	Pentan-3-ol	(retention time 12,292 min)	X	retention time (min)
2	2-methylbutan-1-ol	(retention time 13,741 min)	Y	FID signal
3	3-methylbutan-1-ol	(retention time 13,820 min)		

Figure 1 — Typical chromatogram for calculation of column resolution

5.3 Analytical balance, capable of weighing to the nearest 0,1 mg.

5.4 Vials, having seals and used for test portions and calibration solutions.

6 Sampling

Unless otherwise specified, laboratory samples shall be obtained by the procedures specified in EN ISO 3170.

Glass bottles shall be used for taking samples. The glass bottles shall be meticulously cleaned and rinsed at least twice with the product to be sampled. Special care shall be taken during all further manipulations with the samples to avoid any risk of further contamination, e.g. with water.

7 Procedure

7.1 General

Two method variants are defined in this document:

a) "Procedure A", using direct injection of a test portion;

b) "Procedure B", using injection after one additional preparation step, i.e. dilution of the sample with water.

Which of the two method variants is used is subject to decision in the laboratory. It may also depend on a particular request for solution to a specific problem. See the examples of chromatograms in Annex A for additional detail.

7.2 General considerations for preparation and handling of solutions

Several precautions shall be observed in the preparation and handling of stock solutions and calibration solutions to avoid loss of material due to the high volatility of all used compounds. Therefore, preparations should always be done starting with the least volatile compound.

All solutions are prepared gravimetrically.

Septum caps shall only be removed immediately before adding the next component and replaced immediately after.

It is strongly recommended to replace a used cap by a new one. This change should be done after cooling the sample to about 4 °C.

The glass vials containing the prepared calibration solutions shall be stored at 4 °C and may be used for six months at maximum.

7.3 Preparation of solutions for Procedure A

7.3.1 Calibration stock solution (E) for Procedure A

Put a 100 ml septum vial (5.4) on the analytical balance (5.3), close the vial with a cap, and record the mass.

Open the vial and fill 80 ml of ethanol solvent (see 4.2) in, put the cap on the vial and record the mass of the ethanol added.

Successively add 1 ml of each of the following compounds through the septum and record the individual added mass to the nearest 0,1 mg:

a) 3-methylbutan-1-ol,

b) 2-methylbutan-1-ol,

c) butan-1-ol,

d) 2-methylpropan-1-ol (iso-butanol),

e) propan-1-ol,

f) butan-2-ol,

g) methanol.

CAUTION — Care shall be taken to avoid loss of volatile components during preparation of the standard.

7.3.2 Internal standard stock solution (ES) for Procedure A

In a 10 ml vial add about 8 ml of ethanol solvent and weigh to the nearest 0,1 mg.

Add 80 µl of the internal standard pentan-3-ol (4.2) and record the mass to the nearest 0,1 mg.

7.3.3 Calibration solution (FS1) for Procedure A

In a 2 ml vial add about 1 ml of ethanol solvent and weigh to the nearest 0,1 mg.

Add 100 µl of calibration stock solution (E, 7.3.1) and weigh to the nearest 0,1 mg.

Add 80 µl of the internal standard solution (ES, 7.3.2) and weigh to the nearest 0,1 mg.

7.3.4 Preparation of sample (S) for Procedure A

In a 2 ml vial add about 1 ml of sample and weigh to the nearest 0,1 mg.

Add 80 µl of the internal standard stock solution (ES, 7.3.2) and weigh to the nearest 0,1 mg.

7.4 Preparation of solutions for Procedure B

7.4.1 Calibration stock solution (E) for Procedure B

Put a 100 ml septum vial on the analytical balance, close the vial with a cap, and record the mass to the nearest 0,1 mg.

Open the vial and fill 50 ml of ethanol solvent (see 4.2) in, put the cap on the vial and record to the nearest 0,1 mg the mass of the ethanol added.

Successively add the indicated quantity in µl of each of the following compounds through the septum and record the individual added mass to the nearest 0,1 mg:

a)	3-methylbutan-1-ol	500 µl
b)	2-methylbutan-1-ol	200 µl
c)	butan-1-ol	100 µl
d)	2-methylpropan-1-ol	400 µl
e)	propan-1-ol	250 µl
f)	butan-2-ol	100 µl
g)	methanol	500 µl

Fill up to 100 ml with pure water (4.1) and shake vigorously.

CAUTION — Care shall be taken to avoid loss of volatile components during preparation of the standard.