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Petroleum products and other liquids — Standard test method for ethanol determination in gasoline blends by gas chromatography

Produits pétroliers et autres liquides - Éthanol — Détermination de l'éthanol dans les mélanges d'essence par chromatographie en phase gazeuse

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 28, *Petroleum and related products, fuels and lubricants from natural or synthetic sources*, Subcommittee SC 7, *Liquid Biofuels*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Petroleum products and other liquids — Standard test method for ethanol determination in gasoline blends by gas chromatography

1 Scope

This document establishes a method for determining the ethanol content in gasoline blends by gas chromatography (GC). This method is applicable to gasoline samples with ethanol contents ranging from 1,02 % to 52,3 %, in volume fraction.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

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

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
gasoline
hydrocarbon fuel or blends thereof, which is liquid at atmospheric pressure and is used in spark ignition engines

4 Principle

A sample is analysed by gas chromatography, using a flame ionization detector, split/splitless injector, nonpolar column, and external standardization technique for quantifying the ethanol content in gasoline blends.

5 Apparatus

5.1 Gas chromatograph equipped with a flame ionization detector, split/splitless inlet, automatic sampler, and oven with programmable temperature.

5.2 Electronic instrument for data acquisition, integrated with software for data processing.

5.3 Fused-silica capillary column with nonpolar stationary phase, 100 % dimethylpolysiloxane, and dimensions of 50 m x 0,20 mm x 0,50 µm.

5.4 Analytical balance, with minimum resolution of 0,1 mg.

5.5 GC autosampler vials (e.g 2 ml of volume capacity) with cap and septa [e.g septa of rubber-membrane/self-sealing polytetrafluoroethylene (PTFE)].

5.6 Micro syringe, with a volume of 5 µl or 10 µl, for automatic GC sampler.

5.7 Calibrated volumetric flasks.

5.8 Calibrated pipettes.

6 Reagents

6.1 Ethanol, 99,8 % minimum purity.

In cases of doubt about the ethanol's purity, it is recommended that the water content be verified by coulometric Karl Fischer method, and the result considered in 7.2.7.

6.2 *n*-Heptane or isooctane, 99,5 % minimum purity.

6.3 Carrier gas, hydrogen or helium, 99,995 % minimum purity, gas chromatography quality, dried, and free from organic impurities.

6.4 Auxiliary gases, hydrogen, nitrogen and air, 99,995 % minimum purity, gas chromatography quality, free from organic impurities.

7 Procedure

7.1 Preparation of the apparatus

7.1.1 Install column ends in the chromatograph's injector and detector in accordance with the procedures described in the equipment manufacturer's manual.

7.1.2 Establish a constant pressure at the column inlet, of about 88,25 kPa if using hydrogen as carrier gas, or 171,6 kPa if using helium.

7.1.3 Adjust the following operating conditions on the chromatograph:

a) oven temperature programming, in accordance with Table 1;

Table 1 — Oven temperature programming

Heating rate (°C min^{-1})	Temperature (°C)	Time (min)
_ _	35	6
20	250	10

b) detector temperature: 300 °C;

c) auxiliary nitrogen (make-up gas), hydrogen and synthetic air flows;

It is recommended to use the flow values provided by the manufacturer. The recommended values are nitrogen 35 ml min^{-1}, hydrogen 30 ml min^{-1} and synthetic air 350 ml min^{-1}.

d) injector temperature: 250 °C;

e) injector split ratio: 300:1;

f) injection volume: 1,0 µl;

g) analysis time: 26,75 minutes.

7.2 Preparation of the analytical curve

7.2.1 Analyse the *n*-heptane (or isooctane) (6.2), using the chromatographic conditions described in 7.1.3 to ensure that there are no impurities that can coelute with ethanol. The total impurities of *n*-heptane (or isooctane) shall not be greater than 0,5 %.

7.2.2 Prepare, using the apparatus listed in 5.7 and 5.8, five standard solutions of ethanol in *n*-heptane or isooctane in the following volume fractions: 15 %, 25 %, 30 %, 40 % and 55 %. For samples with ethanol content ranging from 1,02 % to 15 %, in volume fraction, prepare other five standard solutions that include the expected target content in samples.

NOTE Alternatively, the standard solutions can be gravimetrically prepared using an analytical balance with 0,1 mg minimum resolution, which are then converted into volumes from the ethanol and *n*-heptane (or isooctane) densities for the calculation of final concentrations by volume fraction (see Annex A).

7.2.3 Homogenize the standard solutions and transfer aliquots of each one to vials.

7.2.4 Place the vials in the GC automatic sampler and program the analysis sequence.

7.2.5 Analyse the standard solutions, in triplicate, in separate vials, using conditions from 7.1.3.

7.2.6 Identify and integrate the ethanol peak area in each standard solution chromatogram. Calculate the average value of the areas in the triplicates of each standard solution.

7.2.7 Draw a calibration curve by plotting the average ethanol peak areas (Y-axis) versus the average ethanol concentration (X-axis). The purity of ethanol (6.1) as well as calibration corrections of volumetric flasks (5.7) and pipettes (5.8) shall be considered to calculate the concentrations of the standard solutions.

7.2.8 Use linear regression to determine the best formula. The coefficient of determination, R^2, obtained for the curve shall be at least 0,995.

7.3 Sample analysis

7.3.1 Homogenize the sample and transfer an aliquot to a vial.

7.3.2 Place the vial in the GC automatic sampler and program the analysis sequence.

7.3.3 Analyse the sample using conditions from 7.1.3.

7.3.4 Identify the ethanol peak in the chromatogram, from the comparison with the retention time obtained for the standards, under the same operating conditions. Figures B.1 to B.3 show the separation expected for the ethanol peak in relation to the other components of gasoline.

7.3.5 Integrate the ethanol peak area identified in 7.3.4 and determine the ethanol content in the sample by interpolation on the analytical curve.

8 Expression of results

Express the ethanol content in the sample with two decimal places for results less than a volume fraction of 10 % and with one decimal place for results greater than or equal to a volume fraction of 10 %.

9 Precision

9.1 General

The precision, as determined by statistical examination according to ISO 4259-1:2017, of interlaboratory test results on gasoline samples containing ethanol, is given in 9.2 and 9.3.

The interlaboratory study was carried out in 2019, with the participation of 11 laboratories. Ten samples, each with a distinct gasoline matrix, comprising domestic and imported ones, were distributed to each laboratory. The lowest and highest non-rejected results were respectively 0,91 % and 54,3 % of ethanol content, in volume fraction. The degrees of freedom for repeatability and reproducibility were 97 and 39, respectively.

9.2 Repeatability (r)

The difference between two independent results obtained using this method for test material considered to be the same in the same laboratory, by the same operator using the same equipment within short interval of time, in the normal and correct operation of the method that is expected to be exceeded with an approximate probability of 5 % due to random variation, can be calculated using Formula (1):

$$r = 0{,}101\,4\,x^{0{,}7} \tag{1}$$

where x is the average of the two test results being compared.

9.3 Reproducibility (R)

The difference between two independent results obtained using this method for test material considered to be the same in different laboratories, where different laboratory means a different operator, different equipment, different geographic location, and under different supervisory control, in the normal and correct operation of the method that is expected to be exceed with an approximate probability of 5 % due to random variation, can be calculated using Formula (2):

$$R = 0{,}406\,5\,x^{0{,}7} \tag{2}$$

where x is the average of the two test results being compared.

9.4 Reporting limits

Due to testing variation, the lowest and highest acceptable single results that are deemed as valid results of the test method are respectively 0,53 % and 60,0 %, in volume fraction.

Annex A
(informative)

Example of preparation

A.1 Example of preparation of a standard solution 40 % ethanol in *n*-heptane, in volume fraction

Transfer, with a calibrated pipette, a volume of 40 ml of ethanol to a calibrated 100 ml volumetric flask and complete the volume with *n*-heptane, until the printed mark of the volumetric flask.

A.2 Example of preparation of a standard solution 40 % ethanol in *n*-heptane, in mass fraction

Weigh initially approximately 3,00 g of *n*-heptane (w_s). Then, weigh approximately 2,00 g of ethanol (w_e), totalling approximately 5,00 g of solution. Record the exact values of the weighed masses of ethanol and *n*-heptane.

A.3 Conversion of standard solutions: from mass fraction to volume fraction

Using the densities of *n*-heptane (or isooctane) (D_s) and ethanol (D_e), calculate the volume equivalent to the measured mass of ethanol (V_e) and *n*-heptane (V_s) and, subsequently, the volume concentration ($C_{v/v}$), using Formulae (A.1) to (A.3):

$$V_e = \frac{w_e}{D_e} \tag{A.1}$$

$$V_s = \frac{w_s}{D_s} \tag{A.2}$$

$$C_{v/v} = \frac{V_e}{V_e + V_s} \tag{A.3}$$

where

w_x is the weight of a compound "*x*";

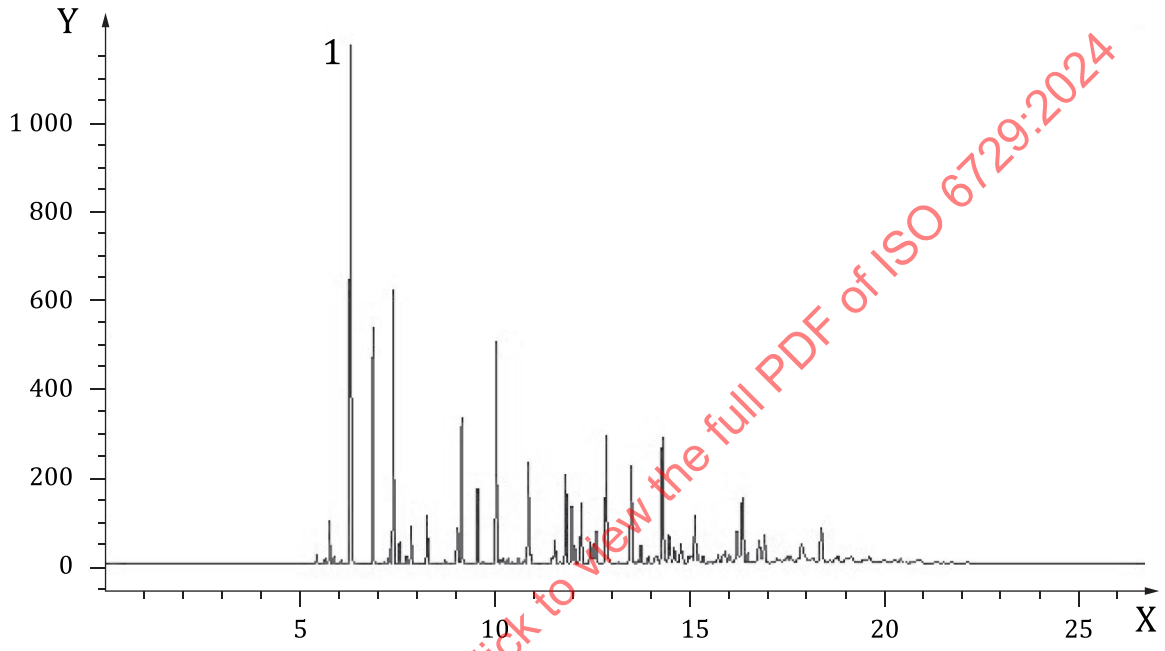
D_x is the density of a compound "*x*";

V_x is the volume equivalent to the measured mass of a compound "*x*".

Annex B
(informative)

Reference chromatograms

Figures B.1 to B.3 show the selectivity in the separation of the ethanol peak in relation to the gasoline matrix, using the column indicated in this document. Example chromatograms of samples containing ethanol in a volume fraction of 27 % and 2 % are shown.



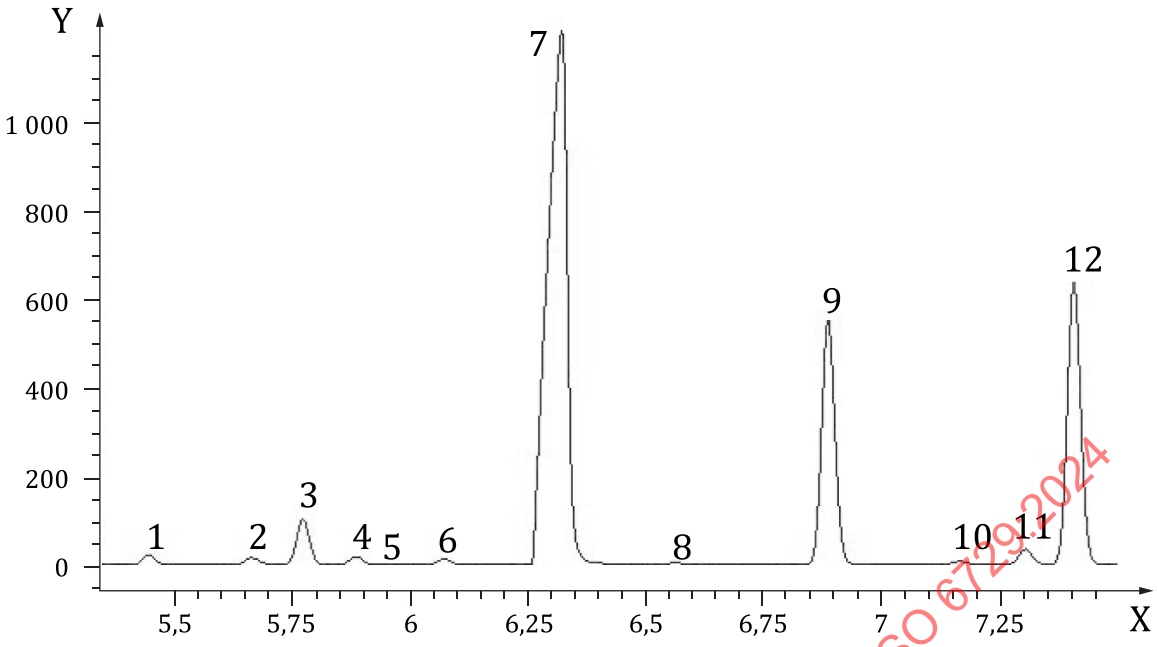
Key

Y detector response, expressed in picoamperes (pA)

X time, expressed in minutes (min)

1 ethanol

Figure B.1 — Overall chromatogram profile of an ethanol-gasoline blend in a 50 m column, where the ethanol volume fraction = 27%



Key

Y detector response, expressed in picoamperes (pA)
X time, expressed in minutes (min)
1 iso-butane
2 1-butene
3 *n*-butane
4 trans-2-butene
5 neo-pentane
6 cis-2-butene
7 ethanol
8 3-methyl-1-butene
9 iso-pentane
10 1-pentene
11 2-methyl-1-butene
12 *n*-pentane

Figure B.2 — Chromatogram of Figure B.1 enlarged in the ethanol elution region (6,321 minutes)