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**Liquid petroleum products —  
Determination of hydrocarbon  
types and oxygenates in automotive-  
motor gasoline and in ethanol (E85)  
automotive fuel — Multidimensional  
gas chromatography method**

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*Produits pétroliers liquides — Détermination des groupes  
d'hydrocarbures et de la teneur en composés oxygénés de l'essence  
pour moteurs automobiles et du carburant éthanol pour automobiles  
E85 — Méthode par chromatographie multidimensionnelle en phase  
gazeuse*

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## Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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](http://www.iso.org/directives)).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see [www.iso.org/patents](http://www.iso.org/patents)).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see [www.iso.org/iso/foreword.html](http://www.iso.org/iso/foreword.html).

This document was prepared by Technical Committee ISO/TC 28, *Petroleum and related products, fuels and lubricants from natural or synthetic sources*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 19, *Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This fourth edition cancels and replaces the third edition (ISO 22854:2016), which has been technically revised.

The main changes compared to the previous edition are as follows:

- the Scope and precision have been extended in concentration range;
- the precision statement has been updated;
- new examples of typical chromatograms have been added to [Annex B](#);
- the text has been further harmonized with ASTM D6839<sup>[Z]</sup>.

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](http://www.iso.org/members.html).

## Introduction

Previous editions of this document were used for determination of saturated, olefinic, aromatic and oxygenated hydrocarbons in automotive motor gasoline according to European fuel specifications.

An interlaboratory study has shown that the method can be used for gasolines with a higher concentration of oxygenated compounds, including methanol. The interlaboratory study also provided data to calculate precision for toluene in gasoline.

[Annex B](#) now includes example chromatograms of gasolines with a variety of oxygenates which can be used for the correct identification of these oxygenates.

The test method described in this document is harmonized with ASTM D6839<sup>[Z]</sup>.

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# Liquid petroleum products — Determination of hydrocarbon types and oxygenates in automotive-motor gasoline and in ethanol (E85) automotive fuel — Multidimensional gas chromatography method

## 1 Scope

This document specifies the gas chromatographic (GC) method for the determination of saturated, olefinic and aromatic hydrocarbons in automotive motor gasoline and ethanol (E85) automotive fuel. Additionally, the benzene and toluene content, oxygenated compounds and the total oxygen content can be determined.

NOTE 1 For the purposes of this document, the terms % (*m/m*) and % (*V/V*) are used to represent respectively the mass fraction, *w*, and the volume fraction, *φ*.

This document defines two procedures, A and B.

Procedure A is applicable to automotive motor gasoline with total aromatics of 19,32 % (*V/V*) up to 46,29 % (*V/V*); total olefins from 0,40 % (*V/V*) up to 26,85 % (*V/V*); oxygenates from 0,62 % (*V/V*) up to 9,85 % (*V/V*); oxygen content from 1,50 % (*m/m*) to 12,32 % (*m/m*); benzene content from 0,38 % (*V/V*) up to 1,98 % (*V/V*) and toluene content from 5,85 % (*V/V*) up to 31,65 % (*V/V*).

The method has also been tested for individual oxygenates. A precision has been determined for a total volume of methanol from 1,05 % (*V/V*) up to 16,96 % (*V/V*); a total volume of ethanol from 0,50 % (*V/V*) up to 17,86 % (*V/V*); a total volume of MTBE from 0,99 % (*V/V*) up to 15,70 % (*V/V*), a total volume of ETBE from 0,99 % (*V/V*) up to 15,49 % (*V/V*), a total volume of TAME from 0,99 % (*V/V*) up to 5,92 % (*V/V*), and a total volume of TAAE from 0,98 % (*V/V*) up to 15,59 % (*V/V*).

Although this test method can be used to determine higher-olefin contents of up to 50 % (*V/V*), the precision for olefins was tested only in the range from 0,40 % (*V/V*) to 26,85 % (*V/V*).

Although specifically developed for the analysis of automotive motor gasoline that contains oxygenates, this test method can also be applied to other hydrocarbon streams having similar boiling ranges, such as naphthas and reformates.

NOTE 2 For Procedure A, applicability of this document has also been verified for the determination of *n*-propanol, acetone, and di-isopropyl ether (DIPE). However, no precision data have been determined for these compounds.

Procedure B describes the analysis of oxygenated groups (ethanol, methanol, ethers, C3 – C5 alcohols) in ethanol (E85) automotive fuel containing ethanol between 50 % (*V/V*) and 85 % (*V/V*). The gasoline is diluted with an oxygenate-free component to lower the ethanol content to a value below 20 % (*V/V*) before the analysis by GC.

The sample can be fully analysed including hydrocarbons. Precision data for the diluted sample are only available for the oxygenated groups.

NOTE 3 For Procedure B, the precision can be used for an ethanol fraction from about 50 % up to 85 % (*V/V*). For the ether fraction, the precision as specified in [Table 6](#) can be used for samples containing at least 11 % (*V/V*) of ethers. For the higher alcohol fraction, too few data were obtained to derive a full precision statement and the data presented in [Table 6](#) are therefore only indicative.

NOTE 4 An overlap between C9 and C10 aromatics can occur. However, the total is accurate. Isopropyl benzene is resolved from the C8 aromatics and is included with the other C9 aromatics.

## 2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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.

ISO 3170, *Petroleum liquids — Manual sampling*

ISO 3171, *Petroleum liquids — Automatic pipeline sampling*

## 3 Terms and definitions

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

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

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <http://www.electropedia.org/>

### 3.1

#### hydrocarbon

#### hydrocarbon group

#### HG

family of hydrocarbons such as saturated hydrocarbons, olefinic hydrocarbons

#### 3.1.1

##### saturate

##### saturated hydrocarbon

type of *hydrocarbon* (3.1) that contains no double bonds with a carbon number of 3 to 12

EXAMPLE *n*-Paraffins, *iso*-paraffins, naphthenes and poly-naphthenes.

#### 3.1.2

##### olefin

##### olefinic hydrocarbon

type of *hydrocarbon* (3.1) that contains double or triple bonds with a carbon number of 3 to 10

EXAMPLE *n*-Olefins, *iso*-olefins and cyclic olefins.

#### 3.1.3

##### aromatic

##### aromatic hydrocarbon

type of cyclic *hydrocarbon* (3.1) with alternating double and single bonds between carbon atoms forming the rings

EXAMPLE Benzene, toluene and higher homologous series with a carbon number of 6 to 10 and naphthalenes, with a carbon number of up to 12.

### 3.2

#### oxygenate

#### oxygenated compound

type of *hydrocarbon* (3.1) that contains an oxygen group, the addition of which is allowed according to current petrol specifications

EXAMPLE Alcohols and ethers.

Note 1 to entry: See Note 2 to [Clause 1](#).



## 4 Principle

**4.1** Procedure A and Procedure B use the same separation technique and analysis procedure. The difference between the two procedures is that for Procedure B the sample is diluted. The diluting solvent is not considered in the integration. This makes it possible to report the results of the undiluted sample after normalization to 100 %.

**4.2** The automotive motor gasoline sample being analysed is separated into hydrocarbon groups by means of GC analysis using special column-coupling and column-switching procedures.

The automotive motor gasoline sample is injected into the GC system and, after vaporization, is separated into the different groups. Detection is always done by a flame ionization detector (FID).

**4.3** The mass concentration of each detected compound or hydrocarbon group is determined by the application of relative response factors (see 9.2) to the area of the detected peaks, followed by normalization to 100 %. For automotive motor gasoline samples containing oxygenates that cannot be determined by this test method, the hydrocarbon results are normalized to 100 % minus the value of oxygenates as determined by another method. The liquid volume concentration of each detected compound or hydrocarbon group is determined by the application of density values (see 9.3) to the calculated mass concentration of the detected peaks followed by normalization to 100 %.

**IMPORTANT — It is essential to the correct execution of the method that great care be taken to ensure that all compounds are correctly identified. This is especially true for the identification of oxygenated compounds because of their wide range of response factors. It is, therefore, highly recommended for correct identification to verify possibly unknown oxygenates using a reference mixture that contains these pure compounds.**

**4.4** After this analysis, the automotive motor gasoline is separated into hydrocarbon groups and then by carbon number. Using the corresponding relative response factors, the mass distributions of the groups in the automotive motor gasoline sample can be calculated.

## 5 Reagents and materials

### 5.1 Gases

Installation of suitable moisture filters is recommended for hydrogen, helium and nitrogen lines.

#### 5.1.1 Hydrogen, 99,995 % pure.

**WARNING — Hydrogen is explosive when mixed with air at concentration between 4 % (V/V) and 75 % (V/V). Refer to the equipment manufacturers' manuals concerning leaks in the system.**

#### 5.1.2 Helium or nitrogen, 99,995 % pure.

The system's operating parameters such as column and trap temperatures, carrier gas flows and valve switching times are depending on the type of carrier gas used. The use of nitrogen as carrier gas is not possible on all configurations. Contact the equipment manufacturer for specific information or instructions on the use of nitrogen.

#### 5.1.3 Compressed air.

**5.2 Vials**, airtight and inert, e.g. with rubber-membrane caps covered with self-sealing polytetrafluoroethylene (PTFE).

**5.3 Reference solutions**, finished automotive motor gasoline(s) used as reference and which contain components and concentration levels comparable to those of the test sample.

The composition of the reference solution should have been determined in a round robin or by other methods.

**WARNING — The reference solutions are flammable and harmful if inhaled.**

**5.4 Diluting solvent**, used in Procedure B, shall not interfere with any other component in gasoline being analysed. Dodecane (C<sub>12</sub>H<sub>26</sub>) or tridecane (C<sub>13</sub>H<sub>28</sub>) are recommended solvents.

## 6 Apparatus

**6.1 Gas chromatograph**, computer-controlled, multidimensional GC equipment, injector, FID, suitable columns, traps and hydrogenation catalysts, of which an example is given in [Annex A](#).

**6.2 Switching valves**, suitable switching valves that are used for the transfer of compounds from one column to the other in the gas chromatograph.

They shall have a chemically inactive surface and a small dead volume.

**6.3 Traps**, suitable short columns (see [Annex A](#) for an example) used for retaining certain selected chemical groups of the automotive motor gasoline using temperature control.

The absorption of the trapped compounds shall be reversible.

**EXAMPLE** A typical sequence is the following:

- The alcohols and higher-boiling aromatics are absorbed in a trap (sulfate column I). The remaining aromatics are separated from the other components by means of a polar column (for example, OV 275).
- The ethers are separated from the remaining fraction by means of another trap (sulfate column II).
- The olefins are separated from the saturates by the olefin trap (for example, silver salt) in two steps. This is necessary due to the limited capacity of such traps to retain high amounts of butene or total olefins. If the trap capacity is sufficient for the olefin concentration, the separation can be performed in one step.
- The remaining saturated hydrocarbons are separated into paraffins and naphthenes according to their carbon number using a 13X molecular sieve column.
- The ethers are then eluted from the trap (sulfate column II) and separated and detected according to boiling point.
- The olefins are desorbed from the olefin trap and hydrogenated in the Pt-column. They are separated and detected as the corresponding saturated compounds using a 13X molecular sieve.
- The alcohols and higher-boiling aromatics are eluted from the polar column and the trap (sulfate column I), separated using a non-polar column (for example, OV 101 methyl silicone) and detected according to boiling point.

Examples of typical chromatograms with this order of elution of the hydrocarbon fractions are shown in [Figures B.1](#) to [B.4](#). Specifically, for Procedure B, a typical chromatogram is shown in [Figure B.5](#).

**IMPORTANT — Sulfur-containing compounds are irreversibly adsorbed in the olefins trap and can reduce its capacity to retain olefins. Sulfur can also adsorb in the alcohol and ether-alcohol-aromatic traps. Although the effect of low amounts of sulfur components on the various traps or columns is very small, it is important to exercise care with automotive motor gasoline samples with high levels of sulfur.**

## 7 Sampling

Unless otherwise specified, e.g. in national fuel specification standards or regulations for the sampling of automotive motor gasoline, samples shall be taken in accordance with ISO 3170 for manual sampling or in accordance with ISO 3171 for automatic pipeline sampling.

## 8 Procedure

### 8.1 Conditioning

Condition the apparatus according to the manufacturer's instructions after shutdowns.

### 8.2 Sample preparation

#### 8.2.1 Procedure B only — Sample dilution

The procedure as described in this subclause is used to analyse gasoline samples containing higher amounts of ethanol such as ethanol (E85) automotive fuel with ethanol content between 50 % (V/V) and 85 % (V/V).

As the sulfate column I trap (see [Table A.1](#)) cannot trap high amounts of ethanol, the sample shall be diluted. The selected diluting solvent ([5.4](#)) shall not interfere with the analysis. The level of dilution should be chosen in such a way that the final amount of ethanol does not exceed 20 % (V/V). If the ethanol content is unknown, it is advised to use a dilution ratio of 4:1 when analysing the sample.

#### 8.2.2 Procedure A and B — Sample cooling

Cool the test sample to prevent loss by evaporation. Transfer a sufficient portion of the test sample to a vial ([5.2](#)) and immediately tightly close and seal it using the self-sealing PTFE cap (see [5.2](#)). It is advised to cool the test sample to a temperature between 0 °C and 5 °C.

### 8.3 Test sample injection volume

Size the injection volume of the test sample in such a way that the capacity of the columns is not exceeded and that the linearity of the detector is valid.

NOTE An injection volume of 0,1 µl has proven to be satisfactory.

### 8.4 Verification of the apparatus and test conditions

Run the reference solution ([5.3](#)) and check for correct instrument parameters, cutting times and grouping times. If they are not correct, adjust the apparatus to the manufacturer's recommendations and rerun the reference solution.

Attention should be paid to components, such as benzene, olefins and oxygenates, that are near the boundaries of separation on the group-selective columns. Care should be taken to accurately identify the oxygenated compounds. It is recommended to verify the identity of possible oxygenates using a reference material that contains the pure component of interest. [Annex B](#) shows several chromatograms specifically for oxygenate compounds, providing evidence of their elution times and possible interferences.

### 8.5 Validation

Reprocess the validation reference solution and compare the obtained results with the consensus values. The absolute deviation from the consensus values shall not be greater than the reproducibility for the parameters as given in [Clause 11](#).