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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

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

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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 document 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*, 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 fifth edition cancels and replaces the fourth edition (ISO 22854:2021), which has been technically revised.

The main changes are as follows:

— the Scope (Clause 1) and precision (Clause 11) have been clarified in terms of total oxygenates and corrected for previous mistakes in oxygen and ethanol contents, as well as corrected for rounding as required by the reporting requirements;

— a new procedure C has been implemented (and precision thereof determined by an interlaboratory study) to allow determination of very low aromaticity, benzene, toluene and hexane contents required for small engine petrol fuel for which CEN/TC 19 has developed a specification;

— the text has been further harmonized with ASTM D6839.

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.

Introduction

Originally, this document was used for the determination of saturated, olefinic, aromatic and oxygenated hydrocarbons in automotive motor gasoline according to European fuel specifications, such as EN 228.[3]

An interlaboratory study has shown that the method described in this document 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. A further study focused on higher ether contents. Annex B includes example chromatograms of gasolines with a variety of oxygenates, which can be used to correctly identify these oxygenates.

Another interlaboratory study has shown that the method is applicable for gasolines with a very low content of aromatic compounds, such as those described in EN 17867.[13] The study delivered optimalization of a validation step (Procedure C).

This document lays down three procedures: A, B and C. The application ranges of each are given in Table 1. Procedure A is the normal procedure for motor gasoline, whereas Procedure B describes the procedure for the analysis of oxygenated groups (ethanol, methanol, ethers, C3 – C5 alcohols) in ethanol (E85) automotive fuel. Procedure C describes the analysis of small engine petrol fuel containing low contents of aromatics and olefins.

The test method described in this document is harmonized with ASTM D6839,[7] except for Procedure C which focuses on European products only.

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, small engine petrol and ethanol (E85) automotive fuel. Additionally, the benzene and toluene content, oxygenated compounds and the total oxygen content can be determined.

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.

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, definitions, symbols and abbreviated terms

3.1 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/

3.1.1
hydrocarbon group
HG
family of hydrocarbons

EXAMPLE *Saturated hydrocarbons* (3.1.2) or *olefinic hydrocarbons* (3.1.3).

3.1.2
saturate
saturated hydrocarbon
type of hydrocarbon that contains no double bonds with a carbon number of 3 to 12

EXAMPLE *n*-paraffins, *iso*-paraffins, cyclo-alkanes and poly-cyclic alkanes.

3.1.3
olefin
olefinic hydrocarbon
type of hydrocarbon that contains double or triple bonds with a carbon number of 3 to 10

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

3.1.4
aromatic
aromatic hydrocarbon
type of cyclic hydrocarbon 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 polycyclic aromatic hydrocarbons, with a carbon number of up to 12.

3.1.5
oxygenate
oxygenated compound
type of hydrocarbon that contains one or more oxygen atoms, the addition of which is allowed according to fuel specifications

EXAMPLE Alcohols and ethers.

3.2 Symbols and abbreviated terms

For the purposes of this document, the following symbols and abbreviations apply.

A_{HG}	total, corrected signal area for the hydrocarbon group
BOB	before oxygenate blending
DIPE	di-isopropyl ether
E85	ethanol automotive fuel
ETBE	ethyl-tert-butyl ether
FID	flame ionization detector
$F_{RR,HG}$	theoretical relative response factor of a particular carbon number for a hydrocarbon type group
φ_{HG}	volume fraction in per cent for a hydrocarbon group
GC	gas chromatography
H_2	helium
HG	hydrocarbon group
ID	Internal diameter
M_C	molar mass of carbon
M_H	molar mass of hydrogen
M_i	molar mass of the oxygenated compound
M_O	molar mass of oxygen
MTBE	methyl-tert-butyl ether

n_C number of carbon atoms in the group

n_H number of hydrogen atoms in the group

n_O number of oxygen atoms in the molecule

PTFE polytetrafluoroethylene

QC quality control

ρ_{HG} density of the hydrocarbon group

r repeatability

R reproducibility

TAEE tertiary amyl-ethyl ether

TAME tertiary amyl-methyl ether

w_{HG} mass fraction in per cent for a hydrocarbon group

w_i mass percentage of the compound in the mixture

X the mean of the two results being compared

4 Principle

4.1 The application ranges for each procedure are given in Table 1. All procedures specified use the same separation technique and analysis procedure.

Table 1 — Application ranges for each procedure[a]

Component or group	Procedure A	Procedure B	Procedure C
Saturates, % (volume fraction)	26,9 – 79,3		
Total aromatics, % (volume fraction)	19,3 – 46,3		0,4 – 2,7
Total olefins, % (volume fraction)	0,4 – 26,9		0,1 – 2,4
Benzene, % (volume fraction)	0,38 – 1,98	0,1 – 0,5	0,04 – 0,11
Toluene, % (volume fraction)	5,85 – 31,65		
n-Hexane, % (volume fraction)			0,1 - 2,1
Total napthenes (C6-C8), % (volume fraction)			0,2 - 3,8
Oxygenates[b], % (volume fraction)	0,61 – 27,42		0,08 – 0,86
Total oxygen content, % (mass fraction)	0,50 – 12,32		0,02 – 0,16
Methanol, % (volume fraction)	1,05 – 16,96		
Ethanol, % (volume fraction)	0,50 – 17,86	> 50,0 and < 85,0	0,06 - 0,39
C3 – C5 alcohols, % (volume fraction)		> 1,4 and < 6,0	
Ethers, % (volume fraction)		> 0,5 and < 11,0	
MTBE, % (volume fraction)	1,0 – 15,7		0,01 – 0,70
ETBE, % (volume fraction)	1,0 – 15,5		0,09 – 0,73
TAME, % (volume fraction)	1,0 – 5,9		
TAEE, % (volume fraction)	1,0 – 15,6		

[a] Empty cells indicate that the application range has not been determined.

[b] Oxygenated compounds (as individual component or as total oxygenates).

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

The 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 %.

WARNING — To ensure the method is executed correctly, it is essential to carefully verify that all compounds are correctly identified. This is especially true for the identification of oxygenated compounds because of their wide range of response factors. To ensure correct identification, it is therefore highly recommended 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.

4.5 Procedure A assesses the total oxygenates content and individual oxygenates. The ranges given are considered to apply to individual oxygenated compounds or the total group of (unidentified, not further precised) oxygenates. For Procedure A, applicability of this document has been verified for the determination of *n*-propanol, acetone, and di-isopropyl ether (DIPE). However, no precision data have been determined for these compounds.

4.6 Procedure B involves the analysis of oxygenated groups (ethanol, methanol, ethers, C3 – C5 alcohols) in ethanol (E85) automotive fuel containing ethanol with a mass fraction of between 50 % and 85 %. Procedure B differs from Procedure A, in that the sample is diluted with an oxygenate-free component to lower the ethanol content to a value below 20 % before the analysis by GC. 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 %.

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

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.

4.7 Procedure C is applicable to the analysis of small engine petrol fuel containing low contents of aromatics and olefins. Procedure C differs from Procedure A, in that it requires an additional tuning step to ensure that the individual oxygenates, aromatics and olefins are correctly identified by optimizing the pre-column temperatures and valve settings.

5 Reagents and materials

5.1 Hydrogen, 99,995 % pure.

WARNING — Hydrogen is explosive when mixed with air at a concentration between 4 % and 75 % volume fraction. Refer to the equipment manufacturers' manuals concerning leaks in the system.

Installation of suitable moisture filters is recommended for hydrogen lines.

5.2 Helium or **nitrogen,** 99,995 % pure.

The system's operating parameters such as column and trap temperatures, carrier gas flows and valve switching times depend 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.

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

5.3 Compressed air.

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

5.5 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 an interlaboratory or proficiency test, or by other methods.

For Procedure C, make sure that the contents of aromatics, benzene and olefins in the solution are sufficiently low and comparable to those of the test sample.

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

5.6 Diluting solvent, used in Procedure B, shall not interfere with any other component in gasoline being analysed. Dodecane ($C_{12}H_{26}$) or tridecane ($C_{13}H_{28}$) are recommended solvents.

5.7 Tuning solution, used in Procedure C, containing a mixture of oxygenates (ethanol, MTBE and ETBE) and benzene, at levels at the end or just above those of this methods range (see Table 1) and complemented with a base solution containing various aromatics and olefins.

As a base solution, a regular oxygen-free (BOB) refinery stream is recommended. An example of a tuning solution is given in Table 2.

Table 2 — Example of a tuning solution composition

Component or group	Content volume fraction %
Ethanol	0,87
MTBE	0,87
ETBE	0,87
Benzene	1,00

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.