



**International
Standard**

ISO 22854

**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*

**Fifth edition
2025-01**

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Published in Switzerland

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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 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 optimization 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.

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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, 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
$F_{\text{RR,HG}}$	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
TAEF	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		
<i>n</i> -Hexane, % (volume fraction)			0,1 – 2,1
Total naphthenes (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		
TAEF, % (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.

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 as follows:

- 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 (e.g. 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 (e.g. silver salt) in two steps. This is important 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 cyclo alkanes (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 the 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 (e.g. OV 101 methyl silicone) and detected according to the 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](#). For Procedure C, exemplary chromatograms of the tuning are shown in [Figure B.6](#).

WARNING — 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 when handling automotive motor gasoline samples with high levels of sulfur.

7 Sampling

Samples shall be taken in accordance with ISO 3170 for manual sampling or in accordance with ISO 3171 for automatic pipeline sampling.

NOTE National fuel specification standards or legal requirements for the sampling of automotive motor gasoline can apply.

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 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 a volume fraction of 50 % and a volume fraction of 85 %.

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 (see [5.6](#)) 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 a volume fraction of 20 %. If the ethanol content is unknown, it is recommended to use a dilution ratio of 4:1 when analysing the sample.

8.2.2 All procedures — Sample cooling

Cool the test sample to prevent loss by evaporation. Transfer a sufficient portion of the test sample to a vial (5.4) and immediately tightly close and seal it using the self-sealing PTFE cap (see 5.4). It is recommended 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 the linearity of the detector is valid.

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

8.4 Tuning of the apparatus (Procedure C)

This tuning step is required for type of products using small engine petrol fuel which are low in olefin content and are substantially free of aromatic compounds, especially benzene. This step requires optimizing the pre-column temperatures and valve settings.

Run the tuning solution (5.7) and check for correct instrument parameters, cutting times and grouping times. Verify whether all individual components have been identified correctly, like the examples in Figure B.6.

Some deviation from the target values is allowed but special attention should be paid to the MTBE and ETBE values in conjunction with the benzene value. MTBE and ETBE tend to coelute with benzene when the precolumn temperature is too high. Lower the precolumn temperature by steps of 10 °C and rerun the tuning solution until each component can be correctly identified.

8.5 Verification of the apparatus and test conditions

Run the reference solution (see 5.5) 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.

WARNING — 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.

NOTE The recent study, see CEN/TR 15745,^[6] has shown that *iso*-propanol often eludes in two peaks. Notwithstanding the notice of importance in 4.3, this elution can happen. In this case, it is important to identify both peaks properly. When the peaks are correctly identified, the reproducibility in 11.3 applies.

8.6 Validation

Reprocess the validation reference solution (see 5.5) 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 given in Clause 11.

It is strongly recommended to run the validation reference solution weekly to check the proper functioning of the equipment.

The validation reference solution(s) should contain the components in amounts similar to those found in the test samples. Validation of the apparatus should be performed prior to the analysis of any new oxygenates.

8.7 Preparation of the test sample

Prepare the test sample as specified in 8.2.

8.8 Preparation of the apparatus and test conditions

Set up the apparatus in accordance with 8.1 and check it in accordance with 8.5.

For Procedure C, check the areas in between the fractions on “unexpected peaks”. These can be components eluting in the wrong fraction and adjustment of the temperature(s) can be required. Also check peak shapes, such as double peaks or skewed peaks, which can indicate an incorrect elution order. Adjust the valve times using the tuning and reference solutions.

9 Calculation

9.1 General

For Procedure A and C, 9.2 to 9.5 shall be followed.

For Procedure B, in the final calculations, the peak area of the diluting solvent (see 5.6) shall not be integrated. This is so that the final report, after normalization to 100 %, gives the results for all groups and components for the undiluted sample.

NOTE Analysing high-ethanol samples using this application can require specific analysis and reporting procedures and competences (see manufacturer’s instructions).

9.2 Calculation as a mass fraction in per cent

The integrated peak areas are employed for the calculations. The peaks are arranged according to their presence in the hydrocarbon group. Tables 3 and 4 give the relative response factors of hydrocarbon groups and for oxygenated compounds.

NOTE The response factors are normalized to methane and those for the oxygenated compounds have been determined experimentally.

After correcting with the relative response factors, the mass contributions for all hydrocarbon groups are calculated and normalized to a mass fraction of 100 %. The hydrocarbon groups are then classified according to the hydrocarbon type and carbon number.

Table 3 — FID relative response factors of hydrocarbon groups

Carbon number	Relative response factor				
	Paraffins, <i>n-</i> plus <i>iso-</i>	Cyclo-alkanes (naphthenes)	Olefins, <i>n-</i> plus <i>iso-</i>	Olefins, cyclics	Aromatics
3	0,916	—	0,916	—	—
4	0,906	—	0,906	—	—
5	0,899	0,874	0,899	0,874	—
6	0,895	0,874	0,895	0,874	0,811
7	0,892	0,874	0,892	0,874	0,820
8	0,890	0,874	0,890	0,874	0,827
9	0,888	0,874	0,888	0,874	0,832
10	0,887	0,874	0,887	0,874	0,837
11+	0,887	—	—	—	0,840

Table 4 — FID relative response factors for oxygenated compounds

Oxygenated compound	Relative response factor $F_{RR,HG}$
MTBE	1,334
DIPE	1,317
ETBE	1,242
TAME	1,242
Methanol	3,000
Ethanol	1,870
<i>n</i> -propanol	1,867
<i>iso</i> -propanol	1,742
<i>n</i> -butanol	1,546
<i>iso</i> -butanol	1,390
<i>sec</i> -butanol	1,390
<i>tert</i> -butanol	1,230
2-methyl-2-butanol	1,400

If single compounds, e.g. oxygenate compounds, are determined by a different but accepted method, e.g. EN 1601,^[4] ASTM D4815,^[8] EN 13132,^[5] or ASTM D5599,^[9] they shall be excluded from integration. The total area is then not normalized to 100 %, but to 100 % minus the excluded quantified component. The external quantification shall be noted in the report.

Calculate the theoretical relative response factors, $F_{RR,HG}$, of a particular carbon number for a hydrocarbon type group (response of methane set to unity) as given in [Formula \(1\)](#); (see [Tables 1](#) and [2](#)):

$$F_{RR,HG} = \frac{[(M_C \cdot n_C) + (M_H \cdot n_H)] \cdot 0,7487}{M_C \cdot n_C} \quad (1)$$

where

M_C is the molar mass of carbon, equal to 12,011, in g/mol;

n_C is the number of carbon atoms in the group;

M_H is the molar mass of hydrogen, equal to 1,008, in g/mol;

n_H is the number of hydrogen atoms in the group;

0,7487 is the correction factor to set the response of methane to unity.

For each hydrocarbon group (HG) the mass fraction in per cent, w_{HG} , is calculated as given in [Formula \(2\)](#):

$$w_{HG} = \frac{100 \cdot A_{HG} \cdot F_{RR,HG}}{\sum_i (A_{HG,i} \cdot F_{RR,HG,i})} \quad (2)$$

where A_{HG} is the total, corrected signal area for the hydrocarbon group (HG).

9.3 Calculation as a volume fraction in per cent

The conversion from mass fraction to volume fraction is done using the density of the hydrocarbon groups. The density values at 15 °C of hydrocarbon groups, expressed in kilograms per cubic metre, are shown in [Table 5](#). The density values of oxygenate compounds at 15 °C are shown in [Table 6](#) (derived from Reference [\[10\]](#)).

Table 5 — Density at 15 °C of hydrocarbon groups

Carbon number	Density ρ_{HG} kg/m ³				
	Paraffins, <i>n-</i> plus <i>iso-</i>	Cyclo-alkanes (naphthenes)	Olefins, <i>n-</i> plus <i>iso-</i>	Olefins, cyclics	Aromatics
3	506,5	—	520,4	—	—
4	577,9	—	613,7	—	—
5	626,9	750,3	656,5	773,3	—
6	662,2	760,6	685,9	785,3	884,3
7	688,8	762,1	704,0	790,5	871,6
8	708,4	780,5	719,3	805,2	871,9
9	728,1	792,5	738,2	812,5	878,0
10	734,0	812,8	748,6	817,6	892,8
11+	759,0	—	—	—	894,4

SOURCE: Reference [10], reproduced with the permission of the authors.

Table 6 — Density at 15 °C of oxygenated compounds

Oxygenated compound	Density ρ_{HG} kg/m ³
MTBE	745,3
DIPE	729,2
ETBE	745,6
TAME	775,2
Methanol	795,8
Ethanol	794,8
<i>n</i> -propanol	813,3
<i>iso</i> -propanol	789,5
<i>n</i> -butanol	813,3
<i>iso</i> -butanol	805,8
<i>sec</i> -butanol	810,6
<i>tert</i> -butanol	791,0
2-methyl-2-butanol	813,5

SOURCE: Reference [10], reproduced with the permission of the authors.

The volume fraction in per cent, ϕ_{HG} , of the hydrocarbon group (HG) is obtained from the mass fraction, w_{HG} , as given in Formula (3).

$$\phi_{\text{HG}} = \frac{100 \cdot \frac{w_{\text{HG}}}{\rho_{\text{HG}}}}{\sum_i \left(\frac{w_{\text{HG},i}}{\rho_{\text{HG},i}} \right)} \quad (3)$$

where

ρ_{HG} is the density of the hydrocarbon group (HG) in kg/m³;

w_{HG} is the mass percentage of the hydrocarbon group (HG).

9.4 Calculation of total oxygen content in mass fraction in per cent

Calculate the oxygen content, w_O , from all identified oxygenate compounds, i , according to [Formula \(4\)](#):

$$w_O = \sum_i \left(\frac{n_O \cdot M_O}{M_i} \cdot w_i \right) \quad (4)$$

where

n_O is the number of oxygen atoms in the molecule, generally 1;

M_O is the molar mass of oxygen, in g/mol;

M_i is the molar mass of the oxygenated compound, in g/mol;

w_i is the mass percentage of the compound in the mixture.

EXAMPLE This example calculation uses MTBE ($C_5H_{12}O$) as the only oxygenate compound and the following molar masses:

- C: 12,011
- H: 1,008
- O: 16,000

$$w_O = \sum_i \left(\frac{n_O \cdot M_O}{M_i} \cdot w_i \right) = \frac{1 \cdot 16,000}{5 \cdot 12,011 + 12 \cdot 1,008 + 1 \cdot 16,000} \cdot w_i = 0,1815 \cdot w_i$$

9.5 Data report according to automotive motor gasoline specifications

For the reporting of conformity to automotive motor gasoline specifications, such as EN 228,^[3] specific rounding or summation of results can be necessary. The following results are reported.

- The total content of saturates is determined by summation of (volume fraction) of the paraffins, cycloalkanes (naphthenes) and high-boiling poly-cyclic alkanes. The content of separate saturates (such as *n*-hexane) are reported in volume fraction percentage).
- The total olefin content is determined by summation of the (volume fraction) of the olefins and the cyclic olefins and is reported in volume fraction percentage.
- The total aromatic content is reported unchanged in volume fraction percentage.
- The benzene content is reported in volume fraction percentage.
- The oxygenated compound contents are reported in volume fraction percentage.
- The total oxygen content is calculated according to [9.4](#). It is reported in mass fraction percentage.

10 Expression of results

10.1 Procedure A and C

The results are reported as a volume fraction percentage or a mass fraction percentage (see [9.5](#)) according to the following requirements:

- saturates content, aromatics content and olefins content to the nearest 0,1 %;
- benzene content, oxygenates content and total oxygen content to the nearest 0,01 %;
- *n*-hexane and total C6- to C8-naphthenes to the nearest 0,1 %.

10.2 Procedure B

The results for ethanol, ethers and higher alcohols are reported to the nearest 0,1 %.

11 Precision

11.1 General

The precision is given as determined by statistical examination of inter-laboratory test results in accordance with ISO 4259:2006¹⁾.^[1] Precision values calculated from the formulae given in [Table 7](#), [Table 8](#) or [Table 9](#) shall be rounded to the appropriate number of decimal places as specified in [Clause 10](#).

Supporting data for Procedures A and B are documented in CEN/TR 15745,^[6] which consists of calculations according to ISO 4259:2006^[1] and Reference [\[11\]](#), which consists of calculations according to ISO 4259-1:2017.^[2]

The precision values calculated from [Table 8](#) (Procedure B) are applicable for the ranges given in that table.

NOTE 1 For the higher alcohol fraction, too few data were obtained to derive a full precision statement. The data presented in [Table 8](#) are therefore only indicative.

Supporting data for Procedure C are documented in Reference [\[12\]](#). The calculations were performed according to ISO 4259-1:2017, but the effective resulting precision statements retained insufficient degrees of freedom as required by that standard. The precision as in [Table 9](#) is deemed to be intermediate until more data can be gathered from the field.

NOTE 2 For total oxygen content no precision statement could be determined.

11.2 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 intervals of time, in the normal and correct operation of the method that is expected to be exceeded with a probability of 5 % due to random variation, conforms to the value given in [Table 7](#) for Procedure A, [Table 8](#) for Procedure B and [Table 9](#) for Procedure C.

11.3 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 exceeded with a probability of 5 % due to random variation, conforms to the value given in [Table 7](#) for Procedure A, [Table 8](#) for Procedure B and [Table 9](#) for Procedure C.

Table 7 — Repeatability and reproducibility for Procedure A

Component or group content	Repeatability ^a <i>r</i>	Reproducibility ^a <i>R</i>	Covered range
Saturates, % (volume fraction)	0,5	1,6	26,85 – 79,31
Aromatics, % (volume fraction)	$(0,009\ 5\ X + 0,195\ 2)$	$(0,045\ 0\ X + 0,138\ 4)$	19,32 – 46,29
Olefins, % (volume fraction)	$(0,018\ 5\ X + 0,141\ 5)$	$(0,117\ 6\ X + 0,511\ 8)$	0,40 – 26,85
Benzene, % (volume fraction)	$6,740 \cdot 10^{-3} \cdot (X+1)$	$1,912 \cdot 10^{-2} \cdot (X+1)$	0,38 – 1,98
Toluene, % (volume fraction)	$5,261 \cdot 10^{-3} \cdot (X+4)$	$1,893 \cdot 10^{-2} \cdot (X+4)$	5,85 – 31,65
Methanol, % (volume fraction)	$3,019 \cdot 10^{-2} \cdot X$	$8,863 \cdot 10^{-2} \cdot X$	1,05 – 16,96
^a <i>X</i> is the mean of the two results being compared, unless otherwise stated.			

1) Withdrawn.

Table 7 (continued)

Component or group content	Repeatability ^a <i>r</i>	Reproducibility ^a <i>R</i>	Covered range
Ethanol, % (volume fraction)	0,06 $8,275 \cdot 10^{-3} \cdot (X+11)$	0,37 $2,175 \cdot 10^{-2} \cdot (X+11)$	0,50 – 4,00 4,01 – 17,86
MTBE, % (volume fraction)	$1,735 \cdot 10^{-2} \cdot X^{0,8}$	$6,203 \cdot 10^{-2} \cdot X^{0,8}$	0,99 – 15,70
ETBE, % (volume fraction)	$3,138 \cdot 10^{-3} \cdot (X+6)$	$1,293 \cdot 10^{-2} \cdot (X+6)$	0,99 – 15,49
TAME, % (volume fraction)	$6,063 \cdot 10^{-3} \cdot (X+0,8)$	$2,659 \cdot 10^{-2} \cdot (X+0,8)$	0,99 – 5,92
TAAE, % (volume fraction)	$6,401 \cdot 10^{-3} \cdot (X+0,8)$	$5,438 \cdot 10^{-2} \cdot (X+0,8)$	0,98 – 15,59
Individual other oxygenated compounds, % (volume fraction)	(0,019 3 <i>X</i> + 0,002 4)	(0,025 1 <i>X</i> + 0,351 5)	0,61 – 9,85
Total oxygenates, % (volume fraction)	(0,019 3 <i>X</i> + 0,002 4) 0,010 7 (<i>X</i> + 10,727 7)	(0,025 1 <i>X</i> + 0,351 5) 0,019 1 (<i>X</i> + 10,727 7)	0,61 – 9,03 9,03 – 27,42
Total oxygen content, % (mass fraction)	$9,028 \cdot 10^{-3} (X+7,5)$	$1,851 \cdot 10^{-2} \cdot (X+7,5)$	0,50 – 12,32

^a *X* is the mean of the two results being compared, unless otherwise stated.

Table 8 — Repeatability and reproducibility for Procedure B (high ethanol gasolines)

Component or group content	Repeatability ^a <i>r</i> % volume fraction	Reproducibility ^a <i>R</i> % volume fraction
Ethanol [>50 % (volume fraction) and < 85 % (volume fraction)]	1,24	4,85
Ethers [>0,5 % (volume fraction) and < 1,6 % (volume fraction)]	0,03	0,33
C3 – C5 alcohols [>1,4 % (volume fraction) and < 2,5 % (volume fraction)]	$0,103\ 2\ X + 0,001\ 1\ ^b$	$0,696\ 3\ X + 0,073\ 1\ ^b$

^a *X* is the mean of the two results being compared, unless otherwise stated.

^b Limited data was obtained for the calculation of these precision data. The values should therefore be considered as an indication only.

Table 9 — Repeatability and reproducibility (interim) for Procedure C

Content of component or group	Repeatability ^a <i>r</i>	Reproducibility ^a <i>R</i>	Covered range
Total aromatics % (volume fraction)	$0,037(X+1)$	$0,12(X+1)$	0,38 - 2,69
Total olefins % (volume fraction)	$0,004(X+2)$	$0,022(X+2)$	0,08 - 2,37
Benzene, % (volume fraction)	$0,006(X+0,35)$	$0,042(X+0,35)$	0,04 - 0,11
n-hexane, % (volume fraction)	$0,004 \cdot X^{0,5}$	$0,036 \cdot X^{0,25}$	0,10 - 2,05
Total naphtenes (C6-C8), % (volume fraction)	$0,002\ 7(X+4)$	$0,007\ 6(X+4)$	0,18 – 3,83
Total oxygenates, % (volume fraction)	0,012	0,041	0,08 - 0,86
Methanol, % (volume fraction)	$0,022(X+1,71)$	$0,082(X+1,71)$	0,07 - 0,39
Ethanol, % (volume fraction)	$0,020\ X^{0,4}$	$0,061 \cdot X^{0,4}$	0,07 - 0,39
MTBE, % (volume fraction)	$0,006(X+0,1)$	$0,041(X+0,1)$	0,13 - 0,70
ETBE, % (volume fraction)	$0,003(X+0,3)$	$0,024(X+0,3)$	0,09 - 0,73

^a *X* is the mean of the two results being compared, unless otherwise stated.

12 Test report

The test report shall contain at least the following information:

- a) a reference to this document, i.e. ISO 22854:2025;
- b) type and complete identification of the product tested;
- c) sampling method used (see [Clause 7](#));
- d) result of the test (see [Clause 10](#));
- e) if applicable, the external quantification (see [9.2](#));
- f) any deviation, by agreement or otherwise, from the procedure specified;
- g) any unusual features observed;
- h) date of the test.

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Annex A (informative)

Instrument specifications

A.1 General

A specific column specification is given in [Table A.1](#) indicating length, internal diameter (ID), phase and further description. It is possible that not all columns are required and the actual columns used can vary depending on the instrument configuration. The test equipment should be set up to work according to the information in this annex and should have all the necessary items installed according to the requirements of the supplier's specifications.

Table A.1 — Example of column specification

Name	Length cm	ID mm	Phase	Description
Sulfate column I	30	2	50 % sulfate on Chromosorb 750 ^a , mesh size 150 µm to 180 µm (no. 80 to no. 100) ^c	Absorption of alcohols and higher-boiling aromatics
Polar column (key reference 4 in Figure A.1)	270	2	30 % OV 275 on Chromosorb ^a PAW, mesh size 180 µm to 250 µm (no. 80 to no. 100) ^c	Separation of aliphatic and aromatic compounds
Non-polar column (key reference 12 in Figure A.1)	1 500	0,53	5 µm methyl silicone	Elution of aromatics
Molecular sieve 13X (key reference 11 in Figure A.1)	170	1,7	3 % molecular sieve 13X on Chromosorb 750 ^a , mesh size 150 µm to 180 µm (no. 80 to no. 100) ^c	Separation of paraffins and cyclo-alkanes (naphthenes)
Sulfate column II (key reference 6 in Figure A.1)	30	3	50 % sulfate on Chromosorb 750 ^a , mesh size 160 µm to 180 µm (no. 80 to no. 100) ^c	Adsorption of ethers
Olefin trap (key reference 7 in Figure A.1)	30	3	8 % silver salt on silica gel, mesh size 125 µm to 180 µm (no. 80 to no. 100) ^c	Adsorption of olefins
Porapak ^b column	90	2	Porapak Pb, mesh size 150 µm to 180 µm (no. 80 to no. 100) ^c	Elution of aromatics, alcohols and ethers
Hydrogenation catalyst (key reference 9 in Figure A.1)	5,5	1,7	2 % Pt on alumina	Hydrogenation of unsaturated compounds

^a Chromosorb is the trade name of a product supplied by Johns-Manville Corp. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products can be used if they can be shown to lead to the same results.

^b Porapak is the trade name of a product supplied by Waters Associates, Inc. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products can be used if they can be shown to lead to the same results.

^c These numbers provide another way to describe the mesh size, derived from ASTM E11-24, Table 1.

A typical instrument configuration is shown in [Figure A.1](#).

A.2 Temperature control ranges of system components

The independent temperature control of numerous columns and traps, the hydrogenation catalyst, column switching valves, and sample lines is required. All system components that contact the sample shall be heated to a temperature that will prevent condensation of any sample component. [Table A.2](#) lists the system components and operating temperatures. Some of the components require isothermal operation, some require rapid heating and cooling, while one component requires reproducible temperature programming. The indicated temperatures are typical. Temperature control may be performed by any means, granted the requirements listed in [Table A.2](#) are met.

Table A.2 — Temperature control ranges of system components

Component	Typical operating temperature range °C	Maximum heating time min	Maximum cooling time min
Sulfate column I (Alcohol trap)	60 – 280	2	5
Polar column	130	Isothermal	
Non-polar column	130	Isothermal	
Olefin trap	120 – 280	1	5
Molsieve 13X	90 – 430	Temperature programmed	
Sulfate column II (Ether-alcohol trap)	70 – 280	1	5
Hydrogenation catalyst	180	Isothermal	
Column switching valves	130	Isothermal	
Sample lines	130	Isothermal	

A.3 Gas flow rates

The gas flow rates on commercial instruments are normally set prior to shipment and normally require little adjustment. Optimize flow rates on other systems to achieve the required separations. Typical flow rates for the commercial instrument used in the precision study are given in [Table A.3](#); however, the flows can differ somewhat from system to system.

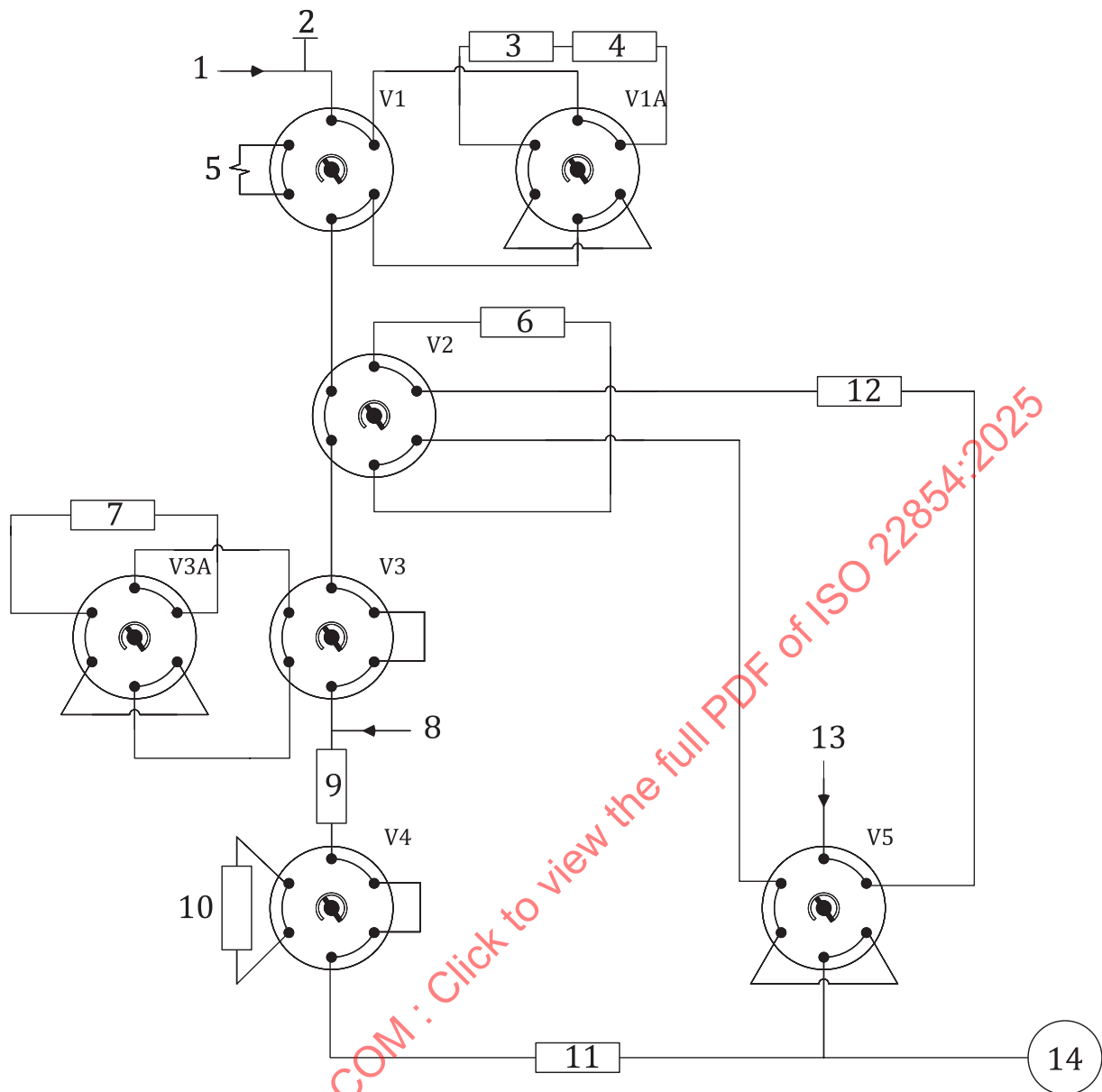
The carrier gas (Flows A and B, see [5.2](#)) may be either helium or nitrogen. [Table A.3](#) contains the typical flow rates for both options.

Table A.3 — Typical gas flow rates

Gas	Flow rate ml/min
Flow A (Helium)	22 ± 1
Flow B (Helium)	12 ± 1
Flow A (Nitrogen)	6
Flow B (Nitrogen)	8
H ₂ (hydrogenator)	14 ± 2
Hydrogen (FID)	30 – 35
Air (FID)	400 – 450

A.4 Typical instrument configuration

See [Figure A.1](#).



Key

V1 to V5 column switching/bypass valves

1 front inlet (Flow A)

2 injection port

3 fixed restriction

4 polar column

5 pre-column

6 alcohol/ether trap

7 olefin trap

8 platinum column hydrogen flow

9 platinum (Pt) column

10 molecular sieve 5A

11 molecular sieve 13X

12 non-polar column

13 back inlet (Flow B)

14 flame ionization detector

Figure A.1 — Typical instrument configuration

Annex B (informative)

Examples of typical chromatograms

B.1 General

This annex contains examples of chromatograms with a typical elution order of the hydrocarbon and oxygenates fractions as mentioned in [6.3](#). This annex is intended to be used as guidelines for identifying unknown peaks. The retention times in these example chromatograms depend on the analysis mode and can differ from other modes or instrument versions. This annex is not intended to replace the manufacturer's manual or instruction.

For each type of gasoline, information is given on what to expect from the specific type of gasoline and what to check for when evaluating the results.

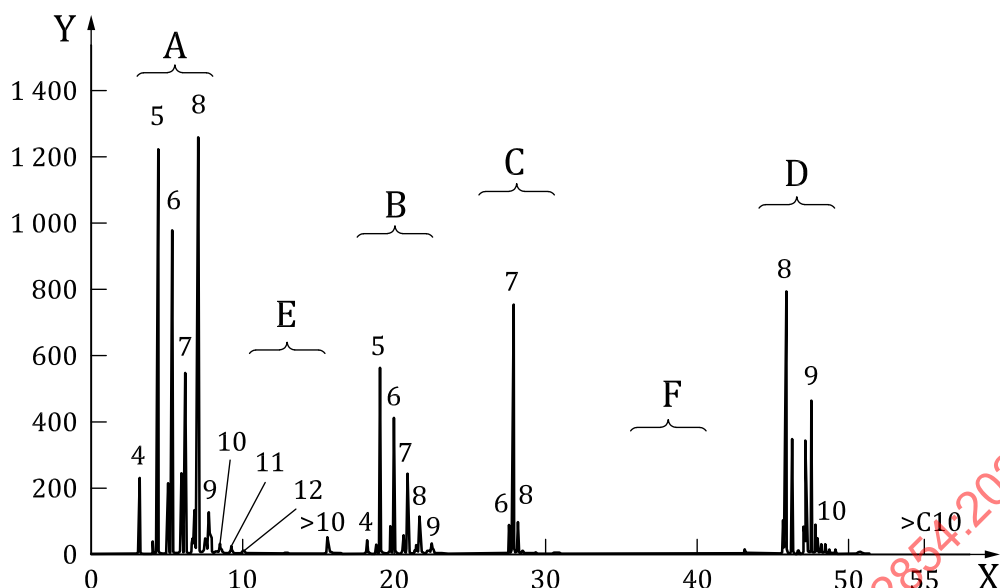
Finally, this annex contains information on general good laboratory practices.

B.2 Conventional gasoline or BOB

B.2.1 Conventional gasoline or before oxygenate blending (BOB) is the most straight forward analysis. This type of samples is useful for verifying the performance of the instrument (see [Figure B.1](#)).

B.2.2 Evaluation of the results includes verifying the peaks of some key components, including:

- a) Benzene: benzene elutes as the first aromatic component at about 28 min. When the instrument valve switch time is not adjusted well, it can appear in the saturates fraction (between 6,5 min and 9 min). Correct the valve switch time so that all benzene elutes.
- b) The profile of saturates and olefins: check and compare the profile of the saturates and olefins. Be aware of when, for example, there is no olefins C4 and C5, although there is saturated C4 and C5. Also, be aware of when there is for example, C5 and C7, but no C6. In these cases, check the identification, and the column temperature settings.
- c) Oxygenates: although no oxygenates are expected in BOB, check the time regions in the chromatogram from 12 min to 17 min and from 31 min to 35 min for traces of ethers and alcohols. The BOB can be polluted with low level oxygenates.



Key

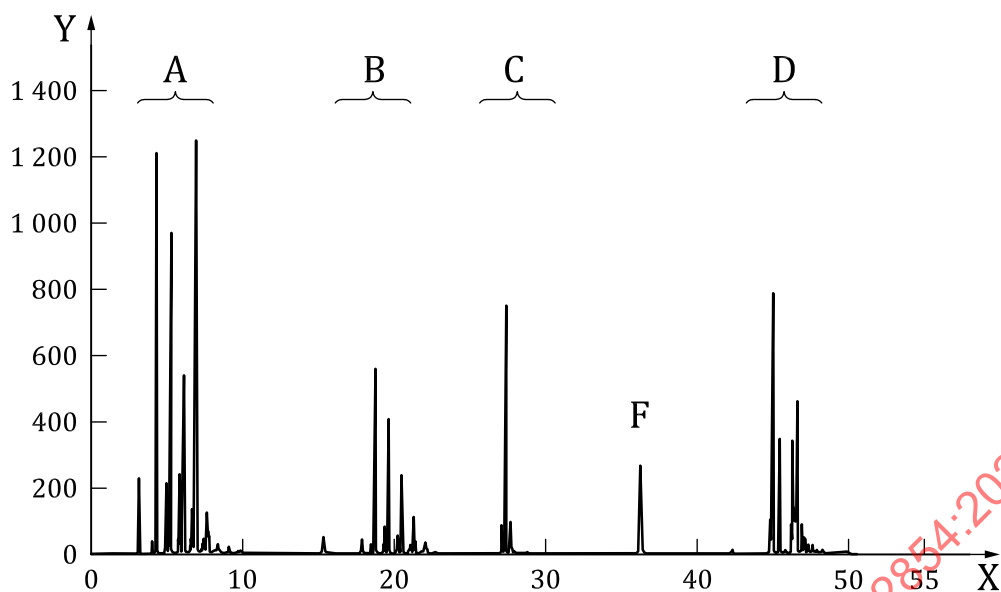
X	time, in minutes	Y	instrument response, in picoamperes (pA)
A	saturates carbon number C4 - C11	D	aromatics carbon number C7 - C10
B	olefins carbon number C4 - C10	E	oxygenates (ethers), if the gasolines contain ethers, they will elute here
C	aromatics carbon number C6 - C8	F	oxygenates (alcohols and ethers), peaks are seen because gasoline contains oxygenates

NOTE The numbers in the figure correspond to the carbon number lengths listed under A, B, C and D, e.g. 4 = C4 (carbon length of 4 Cs).

Figure B.1 — Chromatogram of a conventional gasoline or blend stock for oxygenate blending (BOB)

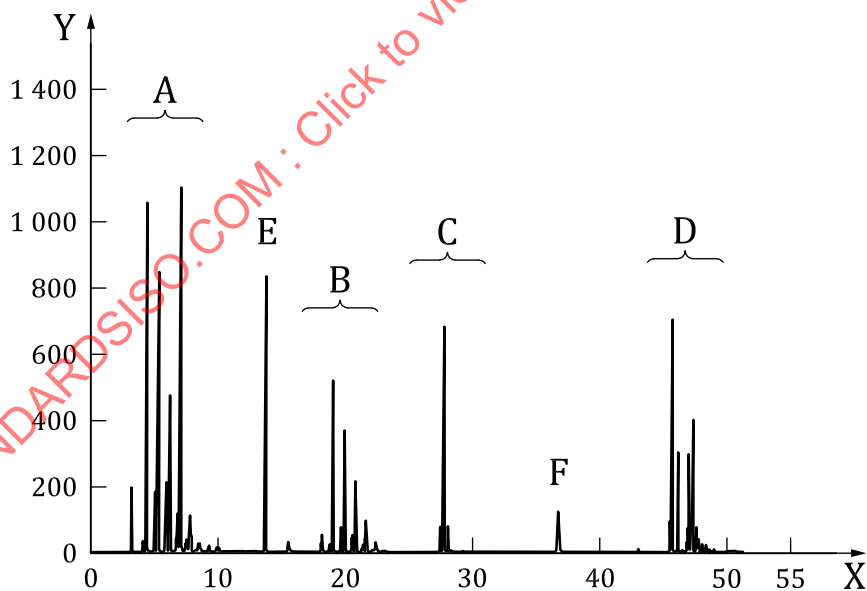
B.3 Gasoline with one or two known oxygenates

B.3.1 Before running the gasolines with known oxygenates, run a reference standard (a gasoline with known composition and concentration) containing the expected oxygenate concentrations to confirm the good performance of the instrument and the software setup (see [Figures B.2](#) and [B.3](#)). The ethers can elute either between the saturates and olefins (between 12 min to 17 min) or in the alcohol fraction (between 31 min to 35 min). At both locations they can be identified and quantified.

**Key**

X	time, in minutes	Y	instrument response, in picoamperes (pA)
A	saturates carbon number C4 - C11	D	aromatics carbon number C7 - C10 plus hydrocarbons with a boiling point > 185 °C
B	olefins carbon number C4 - C10	F	oxygenates (alcohols and ethers), if the gasolines contain ethers and alcohols, they will elute here
C	aromatics carbon number C6 - C8		

Figure B.2 — Chromatogram of a gasoline with a volume fraction of 5 % ethanol

**Key**

X	time, in minutes	Y	instrument response, in picoamperes (pA)
A	saturates carbon number C4 - C11	D	aromatics carbon number C7 - C10
B	olefins carbon number C4 - C10	E	ETBE
C	aromatics carbon number C6 - C8	F	ethanol

Figure B.3 — Chromatogram of a gasoline with a volume fraction of 10 % ETBE and 1 % ethanol

B.3.2 Evaluation of the results includes verifying the peaks of some key components.

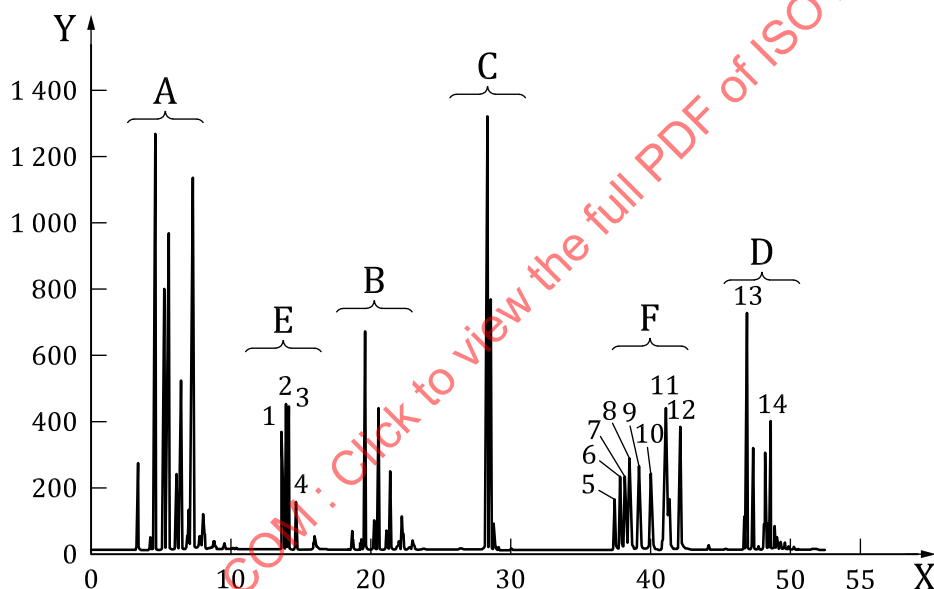
B.3.3 Additional peaks before benzene (<28 min) require attention. When it is expected to be an ether (because the sample contains a high percentage of ethers), it shall be identified in the software as an ether. When this additional peak is expected to be ethanol, the pre-column temperature shall be increased, causing ethanol to move to its proper location.

B.3.4 Once this pre-column temperature is set with a validation sample, it is correct for the unknown samples.

B.4 Gasoline with a mix of (unknown) oxygenates

When no information is known about the sample, use the chromatogram in [Figure B.4](#) as a reference. It shows the elution order and time of 4 ethers and 7 alcohols.

Compare each section of the sample chromatogram with the corresponding section of the example chromatogram in [Figure B.4](#). If additional peaks are found in sections where no peak is expected, analyse known samples or consult the manufacturer for identifying the unknowns.



Key

X	time, in minutes	Y	instrument response, in picoamperes (pA)
A	saturates carbon number C4 - C11	D	aromatics carbon number C7 - C10
B	olefins carbon number C4 - C10	E	ethers
C	aromatics carbon number C6 - C8	F	alcohols and ethers
1	MTBE	8	<i>tert</i> -butanol
2	DIPE	9	<i>n</i> -propanol
3	ETBE	10	ETBE
4	TAME	11	2-butanol
5	methanol	12	<i>tert</i> -amylalcohol
6	ethanol	13	toluene
7	<i>iso</i> -propanol	14	C8-aromatics

Figure B.4 — Gasoline with a mix of (unknown) oxygenates

Additional confirmation of the correct elution of oxygenates can be obtained by running a mix of pure oxygenates which are commercially available.