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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

Reference number
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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).

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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.

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[7].

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

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[7].

INTERNATIONAL STANDARD **ISO 22854:2021(E)**

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 0,61 % (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 TAEE 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 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
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 ($C_{12}H_{26}$) or tridecane ($C_{13}H_{28}$) 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.

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.

8.6 Preparation of the test sample

Prepare the test sample as specified in 8.2.

8.7 Preparation of the apparatus and test conditions

Set up the apparatus in accordance with 8.1 and check it in accordance with 8.4.

9 Calculation

9.1 General

For Procedure A, this clause shall be followed in full.

For Procedure B, in the final calculations the peak area of the diluting solvent (5.4) shall not be integrated 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 % (m/m)

The integrated peak areas are employed for the calculations. The peaks are arranged according to their presence in the groups described in Clause 3. Tables 1 and 2 give the relative response factors of hydrocarbon groups and for oxygenated compounds.

After correcting with the response factors, the mass contributions for all hydrocarbon groups are calculated and normalized to 100 % (m/m). The hydrocarbon groups are then classified according to the hydrocarbon type and carbon number.

Table 1 — FID relative response factors of hydrocarbon groups

Carbon number	**Relative response factor** $F_{\text{RR,HG}}$				
	Paraffins, *n*- **plus** *iso*-	**Naphthenes**	**Olefins,** *n*- **plus** *iso*-	**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 2 — FID relative response factors for oxygenated compounds

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

[a] The relative response factors for the oxygenate compounds have been determined experimentally.

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):

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

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;

0,748 7 is the correction factor to set the response of methane to unity.

For each hydrocarbon group (HG) the % (*m*/*m*), 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 % (*V*/*V*)

The conversion from % (*m*/*m*) to % (*V*/*V*) 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 3 and of oxygenate compounds at 15 °C in Table 4.

Table 3 — Density at 15 °C of hydrocarbon groups

Carbon number	Density ρ_{HG} kg/m^3				
	Paraffins, ***n*- plus *iso*-**	**Naphthenes**	**Olefins,** ***n*- plus *iso*-**	**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

Table 4 — Density at 15 °C of oxygenate compounds

Oxygenate 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
n-propanol	813,3
iso-propanol	789,5
n-butanol	813,3
iso-butanol	805,8
sec-butanol	810,6
tert-butanol	791,0
2-methyl-2-butanol	813,5

The % (V/V), φ_{HG}, of the hydrocarbon group (HG) is obtained from the % (m/m), w_{HG}, as given in Formula (3):

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

where

ρ_{HG} is the density of the hydrocarbon group (HG) in kg/m^3;

w_{HG} is the % (m/m) of the hydrocarbon group (HG).

9.4 Calculation of total oxygen content in % (*m*/*m*)

Calculate the oxygen content, w_O, from all identified oxygenate compounds, *i*, according to Formula (4):

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

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 molecular mass of the oxygenated compound, in g/mol;

w_i is the % (*m*/*m*) 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: 1,000

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

9.5 Data report according to automotive motor gasoline specification

For reporting of conformity to current automotive motor gasoline specifications, 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, naphthenes and high-boiling poly-naphthenes.
- The total olefin content is determined by summation of the (volume fraction) of the olefins and the cyclic olefins.
- The total aromatic content is reported unchanged.
- The benzene content is reported in % (*V*/*V*).
- The oxygenated compound contents are reported in % (*V*/*V*).
- The total oxygen content is calculated according to 9.4. It is reported in % (*m*/*m*).

10 Expression of results

10.1 Procedure A

The results are reported as a volume fraction expressed in % or a mass fraction expressed in % (see 9.5) according to the following requirements:

- saturates content, aromatics content and olefins content to the nearest 0,1 %;
- benzene content, oxygenate content and total oxygen content to the nearest 0,01 %.

10.2 Procedure B

The results for ethanol, ethers and higher alcohols are reported to the nearest 0,1 % (*V*/*V*).

11 Precision

11.1 General

The precision is given as determined by statistical examination of inter-laboratory test results in accordance with ISO 4259[1]. Precision values calculated from the formulae given in Table 5 or Table 6 shall be rounded to the appropriate number of decimal places as specified in Clause 10.

The values in Table 6 (Procedure B) are applicable for samples that have a content of ethers up to 11,0 % (*V*/*V*) and C3 – C5 alcohols up to 6,0 % (*V*/*V*).

Supporting data are documented in CEN/TR 15745[6] (calculations according to ISO 4259:2006[1]) and Reference [10] (calculations according to ISO 4259-1:2017[2]).

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 5 for Procedure A and Table 6 for Procedure B.

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 5 for Procedure A and Table 6 for Procedure B.

NOTE The reproducibility of *iso*-propanol can be higher than for the other components, particularly when it appears as a double peak; it is then necessary to identity both peaks properly (see warning notice in 4.3). The repeatability indicates that a better precision can be obtained when comparing the ratio of the reproducibility to the repeatability, *R*/*r*, with the ratio for *iso*-butanol. Reference can also be made to CEN/TR 15745,[6] which cites the research report on work done by CEN.

12 Test report

The test report shall contain at least the following information:

a) a reference to this document, i.e. ISO 22854:2021;

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) date of the test.

Table 5 — Repeatability and reproducibility for Procedure A

Component or group	Repeatability [a] r	Reproducibility [a] R	Covered range
Saturates %(*V*/*V*)	0,5	1,6	26,85 – 79,31
Aromatics %(*V*/*V*)	$(0{,}009\,5\,X + 0{,}195\,2)$	$(0{,}045\,0\,X + 0{,}138\,4)$	19,32 – 46,29
Olefins %(*V*/*V*)	$(0{,}018\,5\,X + 0{,}141\,5)$	$(0{,}117\,6\,X + 0{,}511\,8)$	0,40 – 26,85
Benzene %(*V*/*V*)	$6{,}740 \cdot 10^{-3} \cdot (X+1)$	$1{,}912 \cdot 10^{-2} \cdot (X+1)$	0,38 – 1,98
Toluene %(*V*/*V*)	$5{,}261 \cdot 10^{-3} \cdot (X+4)$	$1{,}893 \cdot 10^{-2} \cdot (X+4)$	5,85 – 31,65
Oxygenated compounds (as individual component or group) %(*V*/*V*)	$(0{,}019\,3\,X + 0{,}002\,4)$	$(0{,}025\,1\,X + 0{,}351\,5)$	0,61 – 9,85
Total oxygen content %(*m*/*m*)	$9{,}028 \cdot 10^{-3}\ (X+7{,}5)$	$1{,}851 \cdot 10^{-2} \cdot (X+7{,}5)$	2,01 – 12,32
Methanol %(*V*/*V*)	$3{,}019 \cdot 10^{-2} \cdot X$	$8{,}863 \cdot 10^{-2} \cdot X$	1,05 – 16,96
Ethanol %(*V*/*V*)	0,06 $8{,}275 \cdot 10^{-3} \cdot (X+11)$	0,37 $2{,}175 \cdot 10^{-2} \cdot (X+11)$	1,5 – 4,0 4,01 – 17,86
MTBE %(*V*/*V*)	$1{,}735 \cdot 10^{-2} \cdot X^{0.8}$	$6{,}203 \cdot 10^{-2} \cdot X^{0.8}$	0,99 – 15,70
ETBE %(*V*/*V*)	$3{,}138 \cdot 10^{-3} \cdot (X+6)$	$1{,}293 \cdot 10^{-2} \cdot (X+6)$	0,99 – 15,49
TAME %(*V*/*V*)	$6{,}063 \cdot 10^{-3} \cdot (X+0{,}8)$	$2{,}659 \cdot 10^{-2} \cdot (X+0{,}8)$	0,99 – 5,92
TAEE %(*V*/*V*)	$6{,}401 \cdot 10^{-3} \cdot (X+0{,}8)$	$5{,}438 \cdot 10^{-2} \cdot (X+0{,}8)$	0,98 – 15,59

[a] *X* is the mean of the two results being compared unless otherwise stated.

Table 6 — Repeatability and reproducibility for Procedure B (high ethanol gasolines)

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

[a] *X* is the mean of the two results being compared in % (*V*/*V*) 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.

Annex A
(informative)

Instrument specifications

A.1 General

A specific column specification is given in Table A.1. Not all columns may be required, the actual columns used may 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 — Suggested column specification

Name	Length cm	I.D. mm	Phase	Description
Sulfate column I	30	2	50 % sulfate on Chromosorb 750[a], (80 to 100) mesh	Absorption of alcohols and higher-boiling aromatics
Polar column (4)	270	2	30 % OV 275 on Chromosorb[a] PAW, (60 to 80) mesh	Separation of aliphatic and aromatic compounds
Non-polar column (12)	1 500	0,53	5 µm methyl silicone	Elution of aromatics
Molecular sieve 13X (13)	170	1,7	3 % molecular sieve 13X on Chromosorb 750[a], (80 to 100) mesh	Separation of paraffins and naphthenes
Sulfate column II (6)	30	3	50 % sulfate on Chromosorb 750[a], (80 to 100) mesh	Adsorption of ethers
Olefine trap (7)	30	3	8 % silver salt on silica gel, (80 to 120) mesh	Adsorption of olefins
Porapak[b] column	90	2	Porapak P[b], (80 to 100) mesh	Elution of aromatics, alcohols and ethers
Hydrogenation catalyst (9)	5,5	1,7	2 % Pt on alumina	Hydrogenation of unsaturated compounds

[a] Chromosorb is the trade name of a product distributed 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 distributed 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.

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 of the 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 requires reproducible temperature programming. The indicated temperatures are typical. Temperature control can be by any means that will meet the requirements listed in Table A.2

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 – 2 80	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.

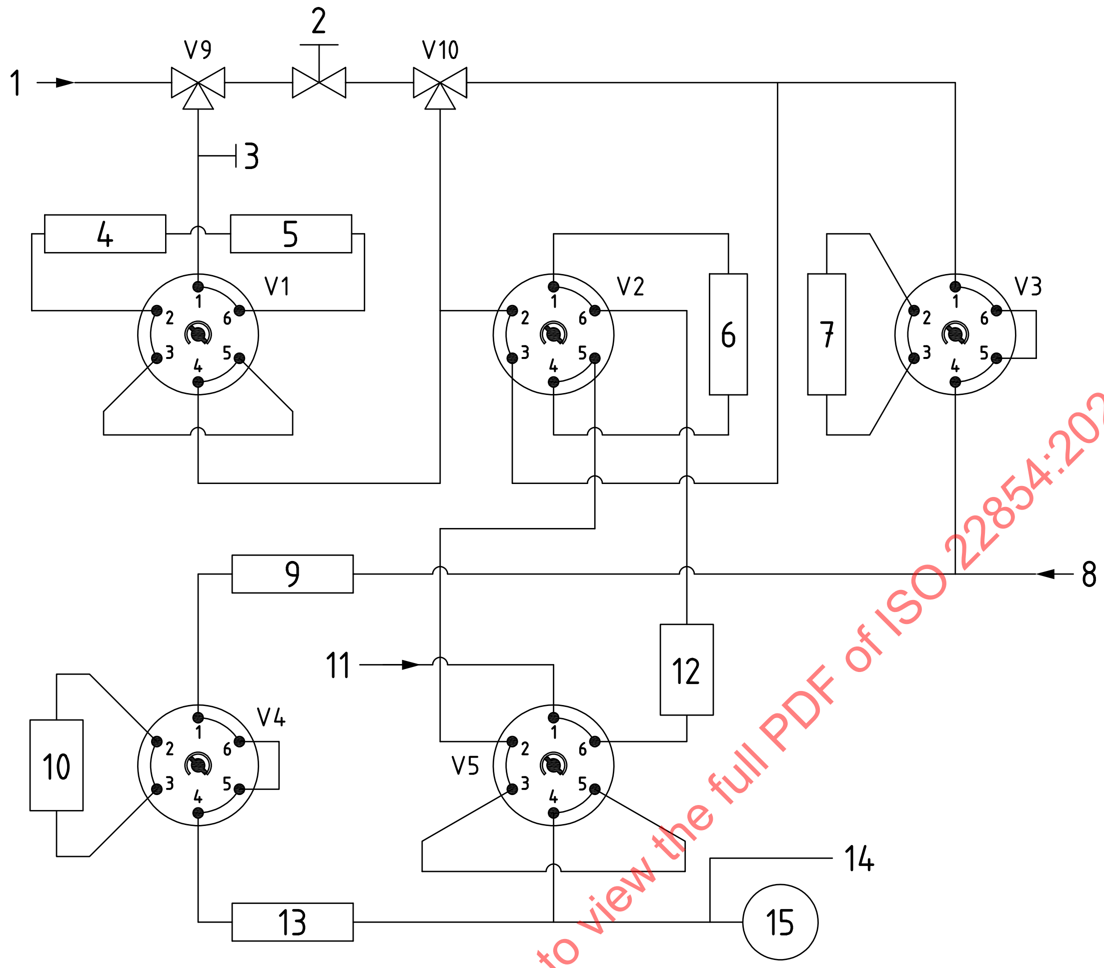
The carrier gas (Flows A and B, see 5.1.2) may be either helium or nitrogen. Table A.3 contains the typical flow rates for both options.

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
H2 (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	V9, V10	3-way valve
1	front inlet (Flow A)	9	platinum (Pt) column
2	needle valve	10	molecular sieve 5A
3	injection port	11	back inlet (Flow B)
4	polar column	12	non-polar column
5	pre-column	13	molecular sieve 13X
6	alcohol/ether trap	14	back end split
7	olefin trap	15	flame ionization detector
8	platinum column hydrogen flow		

Figure A.1 — Typical instrument configuration

Annex B
(informative)

Examples of typical chromatograms

B.1 General

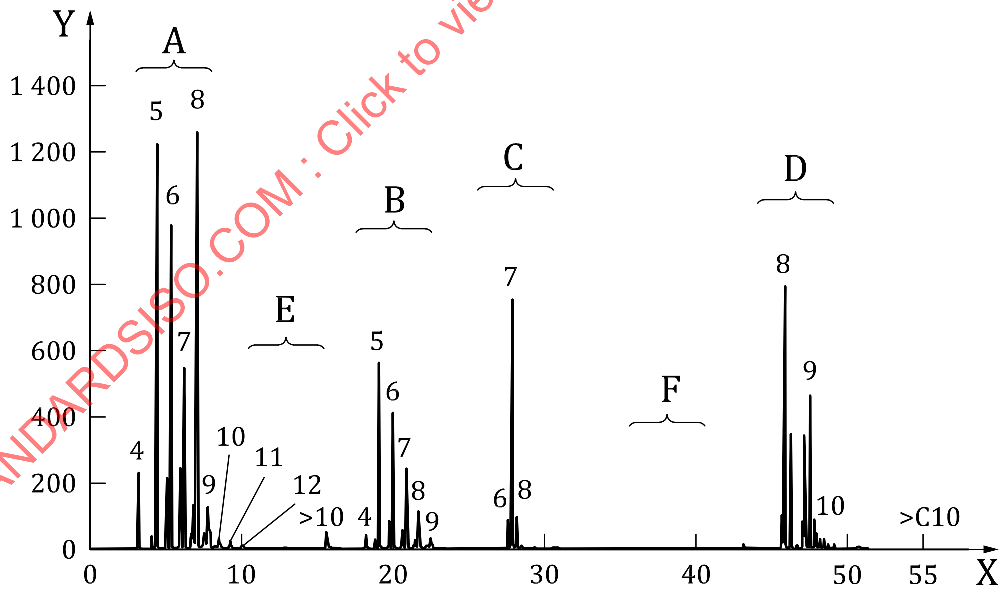
This annex contains example chromatograms with a typical elution order of the hydrocarbon and oxygenates fractions as mentioned in 6.3. This is intended to be used as a guideline for the identification of unknown peaks. The retention times in these example chromatograms depend on the analysis mode and 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 guidelines are given with information on what to expect of the specific type of gasoline and on 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 BOB is the most straight forward analysis. This type of samples is good for verifying the performance of the instrument (Figure B.1)



Key

X time, in minutes

A saturates carbon number C4 - C11

B olefins carbon number C4 - C10

C aromatics carbon number C6 - C8

Y instrument response, in picoamperes (pA)

D aromatics carbon number C7 - C10

E oxygenates (ethers), if the gasolines contain ethers, they will elute here

F oxygenates (alcohols and ethers), peaks are seen because gasoline contains oxygenates

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

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

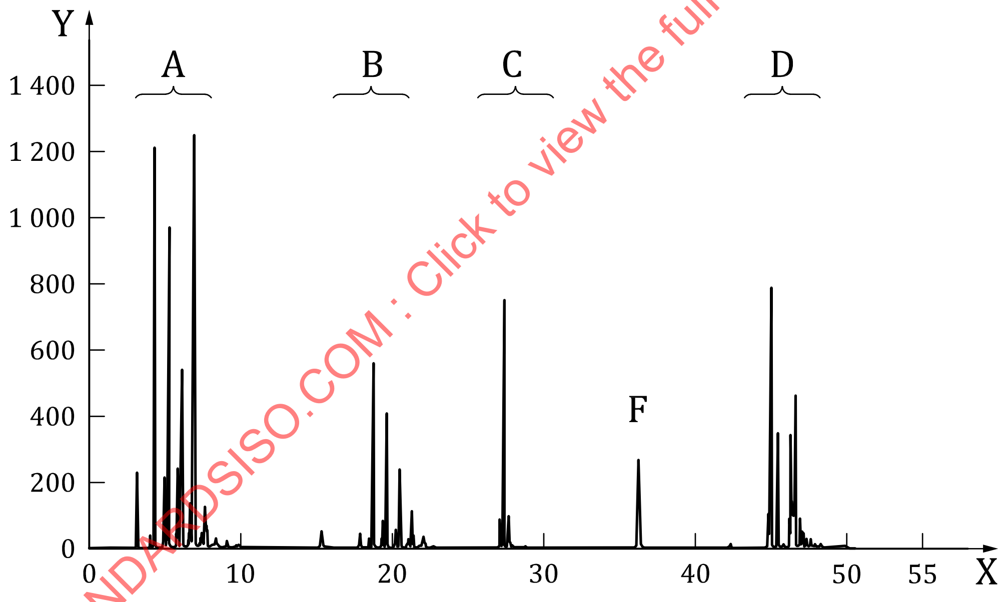
B.2.2.1 Benzene: benzene elutes as the first aromatic component at about 28 min. When the instrument valve switch time is not adjusted well, it can appear in the saturates fraction (between 6,5 min and 9 min). Correct the valve switch time such that all benzene elutes.

B.2.2.2 The profile of saturates and olefins: check and compare the profile of the saturates and olefins. Be alerted when e.g. there is no olefins C4 and C5, although there is saturated C4 and C5. Also, be alerted when there is e.g. C5 and C7, but no C6. In these cases, check the identification, and the column temperature settings.

B.2.2.3 Oxygenates: although no oxygenates are expected in BOB, check the region 12 min - 17 min and 31 min - 35 min for traces of ethers and alcohols, the BOB might be polluted with low level oxygenates.

B.3 A gasoline with one or two known oxygenates

B.3.1 Before running the gasolines with known oxygenates, run a standard 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 - 17 min) or in the alcohol fraction (between 31 min - 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

B olefins carbon number C4 - C10

C aromatics carbon number C6 - C8

D aromatics carbon number C7 - C10 plus hydrocarbons with a boiling point > 185 °C

F oxygenates (alcohols and ethers), if the gasolines contain ethers and alcohols, they will elute here

Figure B.2 — Chromatogram of a gasoline with 5 % (*V*/*V*) ethanol