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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 automobile pour moteurs et du carburant à l'éthanol (E85) — Méthode par chromatographie multidimensionnelle en phase gazeuse

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Foreword

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ISO 22854 was prepared by the European Committee for Standardisation (CEN) Technical Committee CEN/TC 19, *Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin*, in collaboration with Technical Committee ISO/TC 28, *Petroleum and petroleum products*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 22854:2008), which has been technically revised.

Introduction

This International Standard is an update of the first edition (ISO 22854:2008). Originally ISO 22854:2008 was used for determination of saturated, olefinic, aromatic and oxygenated hydrocarbons in automotive motor gasoline according to European fuel specifications. Recent round-robin work has shown that the scope of the method can be updated without alteration to include petrol with higher oxygen percentages than mentioned in the first edition and will now be applicable for automotive motor gasoline up to and including E10.

An interlaboratory study organized by CEN has shown that the method can also be used for high-ethanol gasoline [also called ethanol (E85) automotive fuel], provided that the sample is diluted with a component that will not interfere with any of the components or group of components that need to be analysed. Details of how to perform such analysis are given in 8.2.

The derived precision data for methanol do not comply with the precision calculation as presented in this International Standard. No precision calculation for methanol has been established as the need for such data has not been expressed. If methanol is present in the automotive motor gasoline sample, it is recommended that its contents is verified by the use of an appropriate test method, for instance as given in EN 228.[1]

The test method described in this International Standard is harmonized with ASTM D6839.[2]

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 International Standard 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 content, oxygenate 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, μ, and the volume fraction, φ.

This International Standard defines two procedures, A and B.

Procedure A is applicable to automotive motor gasoline with total aromatics of up to 50 % (*V*/*V*); total olefins from about 1,5 % (*V*/*V*) up to 30 % (*V*/*V*); oxygenates from 0,8 % (*V*/*V*) up to 15 % (*V*/*V*); total oxygen from about 1,5 % (*V*/*V*) to about 3,7 % (*V*/*V*); and benzene of up to 2 % (*V*/*V*). The system may be used for ethers with 5 or more C atoms up to 22 % (*V*/*V*) but the precision has not been established up to this level.

Although this test method may be used to determine higher-olefin contents of up to 50 % (*V*/*V*), the precision for olefins was tested only in the range from about 1,5 % (*V*/*V*) to about 30 % (*V*/*V*).

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

NOTE 2 For Procedure A, precision data have been established for the oxygenate compounds in automotive motor gasoline samples containing ethyl-tert-butyl ether (ETBE), methyl-tert-butyl ether (MTBE), tert-amyl-methyl ether (TAME), iso-propanol, iso-butanol, tert-butanol, methanol and ethanol. The derived precision data for methanol do not comply with the precision calculation as presented in this International Standard. Applicability of this International Standard 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 procedure for 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. If the ethanol content is unknown, it is advised to use a dilution of 4:1 when analysing the sample.

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

NOTE 3 For Procedure B, the precision may be used for an ethanol fraction from about 50 % (*V*/*V*) up to 85 % (*V*/*V*). For the ether fraction, the precision as specified in Table 6 may 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 While developing this test method, the final boiling point was limited to 215 °C.

NOTE 5 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, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3170:2004, *Petroleum liquids — Manual sampling*

ISO 3171:1998, *Petroleum liquids — Automatic pipeline sampling*

3 Terms and definitions

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

3.1
hydrocarbon group
family of hydrocarbons such as saturated hydrocarbons, olefinic hydrocarbons, etc

3.1.1
saturated hydrocarbon
saturate
type of hydrocarbon 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
olefinic hydrocarbon
olefin
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.

3.1.3
aromatic hydrocarbon
aromatic
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 naphthalenes, with a carbon number of up to 12.

3.2
oxygenate
oxygenated compound
type of hydrocarbon 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 Clause 1, Note 2.

3.3
partial group
PG
one carbon number in an individual group, being either a single compound like toluene or an isomeric mixture

EXAMPLE *n*-Butane and *iso*-butane.

4 Principle

4.1 Procedure A and Procedure B use the same separation technique and analysis procedure, the difference between the parts 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 gas chromatographic analysis using special column-coupling and column-switching procedures.

The automotive motor gasoline sample is injected into the gas chromatographic 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 oxygen - containing 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. By the use of 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

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

5.1.1 Hydrogen, 99,995 % pure.

DANGER — Hydrogen is explosive when mixed with air at concentration between 4 % (*V*/*V*) and 75 % (*V*/*V*). See 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.

DANGER — Flammable. 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:

- First, 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 may be performed in one step.
- Next, 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 and B.2. Specifically for Procedure B, a typical chromatogram is shown in Figure B.6.

IMPORTANT — Sulfur-containing compounds are irreversibly adsorbed in the olefins trap and can reduce its capacity to retain olefins. Sulfur can also be adsorbed 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 required by national fuel specification standards or by the 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 section 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 dilutant (5.4) shall not interfere with the analysis. The level of dilution should be chosen in such 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 oxygen-containing 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 function 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 out in accordance with 8.4.

9 Calculation

9.1 General

For Procedure A, this Clause shall be followed in total.

For Procedure B, in the final calculations the peak area of the dilutant (5.4) shall not be integrated so that the final report, after normalization to 100 %, will give the results for all groups and components for the undiluted sample.

NOTE Analysing high-ethanol samples using this application may require specific analysis and reporting procedure and competences. Follow the specific manufacturer's instructions for details on this.

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

If single compounds, e.g. oxygenate compounds, are determined by a different but accepted method, e.g. EN 1601,[3] ASTM D4815,[4] EN 13132,[5] or ASTM D5599,[6] 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.

Table 1 — FID relative response factors of partial groups

Carbon number	**Relative response factor** $F_{RR,PG}$				
	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

Calculate the theoretical relative response factors, $F_{RR,PG}$, 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):

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

where

M_C is the atomic 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 atomic 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 partial group, PG, the % (*m*/*m*), w_{PG}, is calculated as given in Formula (2):

$$w_{PG} = \frac{100 \cdot A_{PG} \cdot F_{RR,PG}}{\sum_i \left(A_{PG,i} \cdot F_{RR,PG,i}\right)} \tag{2}$$

where A_{PG} is the total, corrected signal area for the partial group, PG.

Table 2 — FID relative response factors for oxygenated compounds

Oxygenate compound	**Relative response factor** $F_{\mathrm{RR,PG}}$[a]
MTBE	1,33
DIPE	1,32
ETBE	1,24
TAME	1,24
Methanol	3,80
Ethanol	1,87
n-propanol	1,87
iso-propanol	1,74
n-butanol	1,55
iso-butanol	1,39
sec-butanol	1,39
tert-butanol	1,23
2-methyl-2-butanol	1,40

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

9.3 Calculation as % (*V*/*V*)

The conversion from % (*m*/*m*) to % (*V*/*V*) is done using the density of the partial groups. The density values at 15 °C of partial groups, expressed in kilograms per cubic metre, is shown in Table 3 and of oxygenate compounds at 15 °C in Table 4.

Table 3 — Density of partial groups at 15 °C

Carbon number	**Density** ρ_{PG} 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 of oxygenate compounds at 15 °C

Oxygenate compound	**Density** ρPG 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_{PG}, of the partial group PG is obtained from the % (m/m), w_{PG}, as given in Formula (3):

$$\phi_{\text{PG}} = \frac{100 \cdot \dfrac{w_{\text{PG}}}{\rho_{\text{PG}}}}{\sum\limits_{i} \left(\dfrac{w_{\text{PG},i}}{\rho_{\text{PG},i}} \right)} \tag{3}$$

where

ρ_{PG} is the density of the partial group, PG, in kg/m^3;

wPG is the % (m/m) of the partial group, PG.

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):

$$w_{\text{O}} = \sum_{i} \left(\frac{n_{\text{O}} \cdot M_{\text{O}}}{M_i} \cdot w_i \right) \tag{4}$$

where

n_{O} is the number of oxygen atoms in the molecule, generally 1;

M_{O} is the atomic 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 atomic 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 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 (*V*/*V*) of the paraffins, naphthenes and high-boiling poly-naphthenes.
- The total olefin content is determined by summation of the (*V*/*V*) 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 in % (*V*/*V*) or % (*m*/*m*) (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.[8] Precision values calculated from the equations 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 which have a content of ethers up to 11,0 % (*V*/*V*) and C3 – C5 alcohols up to 6,0 % (*V*/*V*).

11.2 Repeatability, *r*

The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, in the long run for the normal and correct operation of the test method, is expected to exceed the values given in Table 5 for Procedure A and Table 6 for Procedure B in only one case in twenty.

11.3 Reproducibility, *R*

The difference between two single and independent test results, obtained by different operators working in different laboratories on identical test material, in the long run for the normal and correct operation of the test method, is expected to exceed the values given in Table 5 for Procedure A and Table 6 for Procedure B in only one case in twenty.

NOTE 1 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,[9] which cites the research report on work done by CEN.

NOTE 2 The derived reproducibility data for methanol is much higher than can be expected from the repeatability. Due to the fact that methanol is an active component, it is necessary to take care during sampling and to ensure the proper operation of the pre-column. Reference can also be made to CEN/TR 15745,[9] which cites the research report on work done by CEN.

Table 5 — Repeatability and reproducibility for Procedure A

Component or group		Repeatability [a] r % (V/V)	Reproducibility [a] R % (V/V)
Saturates		0,5	1,6
Aromatics		$0{,}009\,5\,X + 0{,}195\,2$	$0{,}045\,0\,X + 0{,}138\,4$
Olefins		$0{,}018\,5\,X + 0{,}141\,5$	$0{,}117\,6\,X + 0{,}511\,8$
Benzene	for $w_{\text{benzene}} \geq 0{,}8$	$0{,}014\,7\,X + 0{,}003\,1$	$0{,}077\,7\,X - 0{,}025\,0$
	for $w_{\text{benzene}} < 0{,}8$	0,02	0,04
Oxygenated compounds (as individual component or group)		$0{,}019\,3\,X + 0{,}002\,4$	$0{,}025\,1\,X + 0{,}351\,5$
Total oxygen content		0,04 % (m/m)	0,31 % (m/m)

[a] X is the mean of the two results being compared in % (V/V) 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]	$0{,}696\,3\,X + 0{,}073\,1$

[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.

12 Test report

The test report shall contain at least the following information:

a) a reference to this International Standard, i.e. ISO 22854;

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.

Annex A
(informative)

Instrument specifications

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.

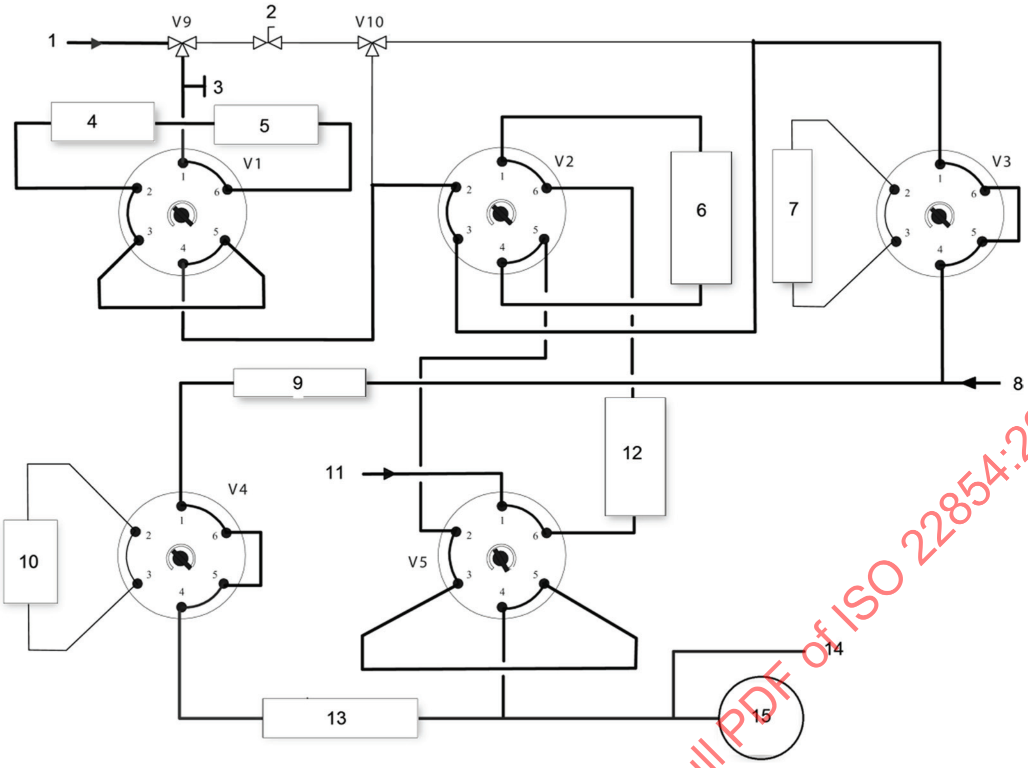
Table A.1 — Suggested column specification

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 may 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 may be used if they can be shown to lead to the same results.

A typical instrument configuration is shown in Figure A.1.



Key

V1 to V5	column switching/bypass valves
1	front inlet
2	needle valve
3	injection port
4	polar column
5	pre-column
6	alc/ether trap
7	olefine trap
8	Pt hydrogen
V9, V10	3-way valve
9	Pt column
10	molecular sieve 5A
11	back inlet
12	non-polar column
13	molecular sieve 13X
14	back end split
15	flame ionization detector

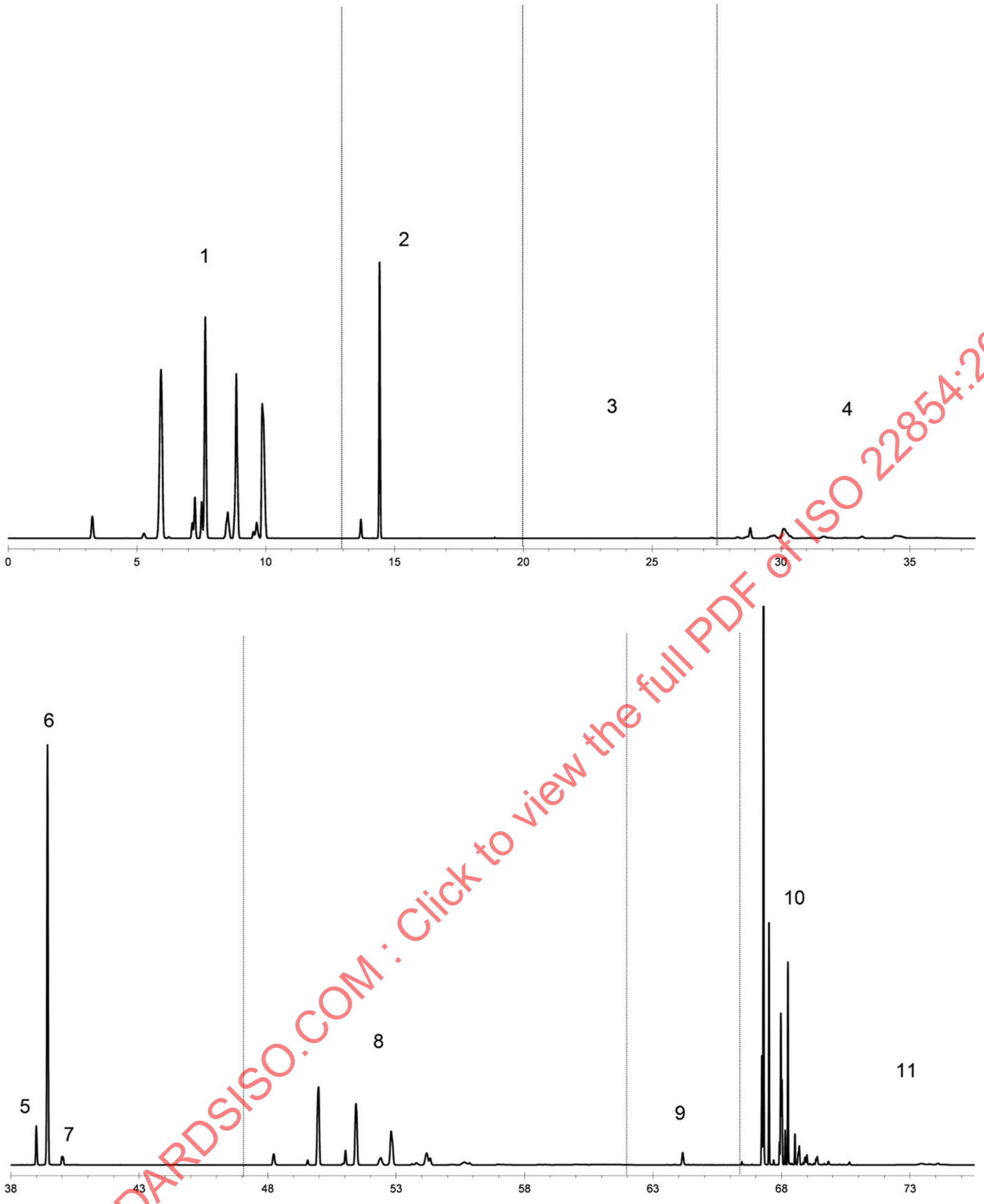
Figure A.1 — Typical instrument configuration

Annex B
(informative)

Examples of typical chromatograms

Figures B.1 and B.2 show example chromatograms with a typical elution order of the hydrocarbon fractions as mentioned in 6.3. Figure B.3 is a more detailed presentation of the elution of ethanol, showing that ethanol elutes just before the C9 aromatics (indicated as 2 in the chromatograms).

Reference is made to CEN/TR 15745,[9] which cites the research report on work done by CEN or the manufacturer's manual for additional detailed chromatograms.



Key

x-axis	time, in minutes (min)
y-axis	instrument response, in picoamperes (pA)
1	light saturates: C3 to C8
2	ETBE
3	C4 to C6 olefins
4	heavy saturates: C7 to C10
5	benzene
6	toluene
7	C8 aromatics
8	olefins
9	ethanol
10	C8 to C10 aromatics
11	high-boiling aromatics

Figure B.1 — Typical chromatogram of an automotive motor gasoline containing ETBE