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Incorporating corrigendum October 2014

BSI Standards Publication

Liquid petroleum products — Unleaded petrol — Determination of organic oxygenate compounds and total organically bound oxygen content by gas chromatography (O-FID)

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National foreword

This British Standard is the UK implementation of EN 1601:2014, incorporating corrigendum October 2014. It supersedes BS EN 1601:1997 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee PTI/15, Natural Gas and Gas Analysis.

A list of organizations represented on this committee can be obtained on request to its secretary.

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This British Standard was published under the authority of the Standards Policy and Strategy Committee on 30 September 2013.

BS 2000 Series

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Amendments/corrigenda issued since publication

Date	Text affected
31 December 2014	Implementation of CEN corrigendum October 2014: Table 1 replaced

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NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 1601

April 2014

ICS 75.160.20

Incorporating corrigendum October 2014
Supersedes EN 1601:1997

English Version

Liquid petroleum products - Unleaded petrol - Determination of organic oxygenate compounds and total organically bound oxygen content by gas chromatography (O-FID)

Produit pétroliers liquides - Essence sans plomb - Détermination des composés oxygénés organiques et de la teneur totale en oxygène organiquement lié par chromatographie en phase gazeuse (O-FID)

Flüssige Mineralölerzeugnisse - Unverbleite Ottokraftstoffe - Bestimmung sauerstoffhaltiger organischer Verbindungen und des Gesamtgehalts an organisch gebundenem Sauerstoff mittels Gaschromatographie (O-FID)

This European Standard was approved by CEN on 18 January 2014.

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COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Contents

Foreword

This document (EN 1601:2014) has been prepared by Technical Committee CEN/TC 19 “Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin”, the secretariat of which is held by NEN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by October 2014, and conflicting national standards shall be withdrawn at the latest by October 2014.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document supersedes EN 1601:1997.

The major updates towards the former version are:

— Inclusion of a dilution procedure to measure an oxygenate compound content higher than 15 % (*m/m*). In this procedure detailed in Clause 9, the sample is diluted (1:1 or 1:2 mass/mass) with an oxygenate free petrol, before the addition of the internal standard and the analysis. Precision data have not been evaluated for this procedure;

— The previous precision data for oxygen content covered the range 1,5 % (*m/m*) to 3,0 % (*m/m*). The data precision for oxygen content has been updated for the range 2,1 % (*m/m*) to 3,9 % (*m/m*), based on Round Robins data from 2005 to 2011 available from DIN-FAM, Germany;

— The scope of the test method has been updated to include petrol with higher total oxygen content and with higher oxygenate contents than mentioned in the former edition; the test method is now applicable for petrol (automotive motor gasoline) with a total oxygen content up to 3,9 % (*m/m*), and/or with an individual oxygenate compound content higher than 15 % (*m/m*). Such petrol is specified in EN 228 [1]. Precision data have not been evaluated for this procedure and consequently the previous precision data for a individual oxygenate compound content in the range of 0,17 % (*m/m*) higher thanto 15 % (*m/m*) have not been updated or extended above 15 % (*m/m*), in order to introduce for instance automotive ethanol (E85) fuel in the scope.

— Deletion of the original Annex A on densities of oxygenate compounds and inclusion of some of them in Table 1;

— Updated chromatograms and improved description of the gas chromatographic equipment with inclusion of a schematic instrument O-FID instrument configuration in the new Annex A.

According to the CEN-CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

1 Scope

This European Standard specifies a gas chromatographic method for the quantitative determination, in unleaded petrol having a final boiling point not greater than 220 °C, of individual organic oxygenate compounds in the range 0,17 % (*m/m*) to 15 % (*m/m*) in a direct analysis (without dilution), and total organically bound oxygen up to 3,9 % (*m/m*).

For samples for which one of the oxygenate compounds content is higher than 15 % (*m/m*), a procedure with a dilution of the sample before the analysis is given.

NOTE 1 Precision data are not available for an oxygenate compound content higher than 15 % (*m/m*); see Foreword.

NOTE 2 For the purposes of this European Standard, the terms "% (*m/m*)" and "% (*V/V*)" are used to represent respectively the mass fraction, μ, and the volume fraction, φ.

WARNING — The use of this European Standard may involve hazardous materials, operations and equipment. This European Standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this European Standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

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.

EN ISO 3170, *Petroleum liquids - Manual sampling (ISO 3170)*

EN ISO 3171, *Petroleum liquids - Automatic pipeline sampling (ISO 3171)*

EN ISO 3675, *Crude petroleum and liquid petroleum products - Laboratory determination of density - Hydrometer method (ISO 3675)*

EN ISO 3838, *Crude petroleum and liquid or solid petroleum products - Determination of density or relative density - Capillary-stoppered pyknometer and graduated bicapillary pyknometer methods (ISO 3838)*

EN ISO 12185, *Crude petroleum and petroleum products - Determination of density - Oscillating U-tube method (ISO 12185)*

3 Principle

After separation using a capillary column, the organic oxygenate compounds are selectively converted to carbon monoxide, hydrogen and carbon in a pyrolytic cracking reactor.

In a hydrogenation reactor, carbon monoxide is then converted to methane and subsequently detected using a flame ionization detector (FID).

NOTE Guidance on the oxygen selective detection (O-FID) technique is given in Annex A.

4 Reagents and materials

4.1 Gases

4.1.1 Carrier gas, helium, or nitrogen, free of hydrocarbons and oxygen and water.

Few percentages of hydrogen (used as auxiliary gas) shall be mixed to the carrier gas (see Figure A.1). Hydrogen shall not be used as a carrier gas because it will interfere with the cracking reaction.

IMPORTANT — It is important to minimize oxygen in the carrier gas. To reduce the background signal, it is essential to use oxygen and moisture filters.

4.1.2 Detector gases, hydrogen and air suitable for flame ionization detector.

WARNING — Hydrogen is explosive when mixed with air at concentrations ranging approximately from 4 % (*V/V*) to 75 % (*V/V*). All joints and lines carrying hydrogen shall be made gas tight to prevent leakage of hydrogen into a confined space.

4.1.3 Cracking reactor gas, helium or nitrogen, used as purge gas to protect the platinum/rhodium element (see Figure A.1).

4.2 Reagents for the preparation of calibration samples

Use only reagents of recognized analytical grade. Reagents shall be not less than 99,0 % (*m/m*) pure.

Calibration samples should be combinations of the following reagents:

4.2.1 methanol (MeOH);

4.2.2 ethanol (EtOH);

4.2.3 propan-1-ol (NPA);

4.2.4 propan-2-ol (IPA);

4.2.5 butan-1-ol (NBA);

4.2.6 butan-2-ol (SBA);

4.2.7 2-methylpropan-2-ol (TBA);

4.2.8 2-methylpropan-1-ol (IBA);

4.2.9 pentan-2-ol (SAA);

4.2.10 *tert*-butyl methyl ether (MTBE);

4.2.11 methyl *tert*-pentyl ether (TAME);

4.2.12 Diisopropyl ether (DIPE);

4.2.13 *tert*-butyl ethyl ether (ETBE);

4.2.14 butan-2-one (MEK);

4.2.15 acetone.

4.3 Internal standards

Use one of the reagents listed in 4.2. If all of these reagents are likely to be present in the sample under test, use a different organic oxygenate compound of the same purity. The internal standard of choice shall elute at a different retention time as components present in the test sample.

4.4 Oxygenate free petrol

Petrol examined to ensure that it contains no organic oxygenate compounds detectable by this test method.

Cool the oxygenate free petrol to between 5 °C and 10 °C before the preparation of the calibration samples and test samples.

5 Apparatus

5.1 Gas chromatographic assembly

5.1.1 Gas chromatograph, equipped with a variable split flow injector, an oxygen selective detection system (O-FID), and computer-controlled or other system permitting the recording of chromatograms and execution of quantitative calculations. A typical O-FID instrument configuration is given in Annex A.

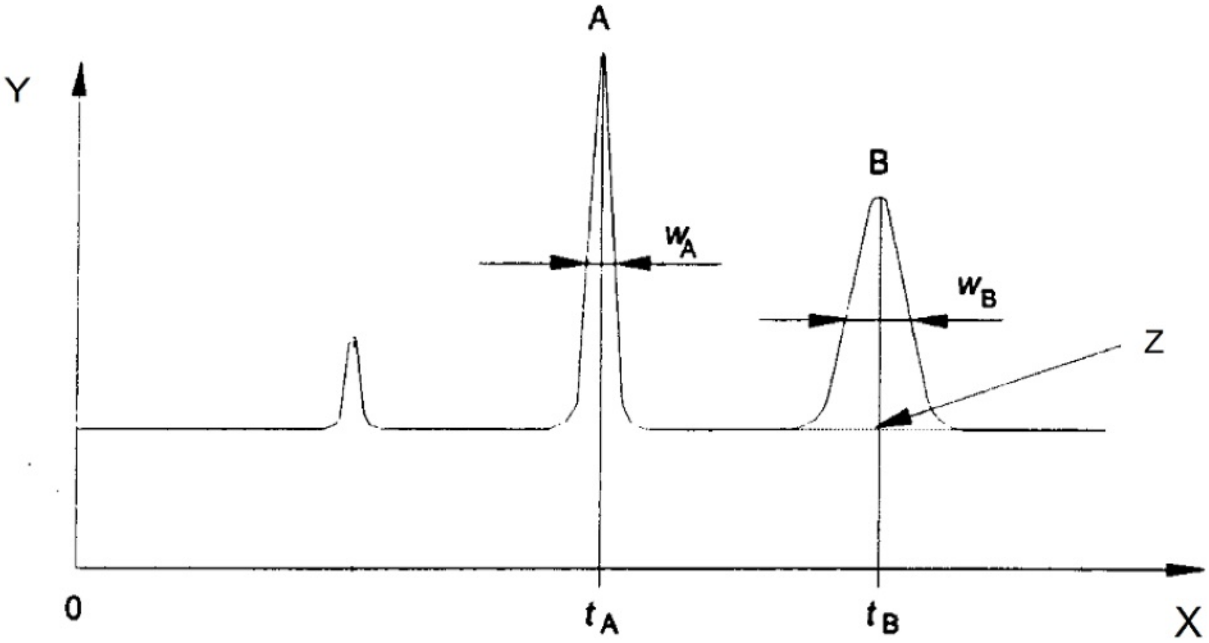
5.1.2 Columns, the separation column shall consist of a capillary column, coated with a suitable phase for achieving the required resolution.

NOTE By way of indication, an example of elution order of some oxygenate compounds is shown in Figure A.3.

The resolution between the compounds to be determined, and between water and oxygen, shall be at least 1.

The resolution, *R*, between peaks A and B (see Figure 1) shall be calculated using Formula (1):

$$R = 1{,}18 \frac{t_B - t_A}{w_A + w_B} \tag{1}$$



Key

X	retention time
Y	instrument response
Z	baseline
t_A	is the retention time of component A, in seconds;
t_B	is the retention time of component B, in seconds;
w_A	is the peak width at half-height of component A, in seconds;
w_B	is the peak width at half-height of component B, in seconds.

Figure 1 — Calculation of the resolution between peaks A and B

5.2 Other equipment

5.2.1 Balance for weighting, maximum mass depending of the sample container, with an accuracy of 1 mg or better.

5.2.2 Glassware, usual laboratory glassware, that shall be cleaned carefully before use.

5.2.3 Test sample container, normally with a capacity of between 10 ml and 100 ml, fitted with rubber membrane cap covered with self-sealing polytetrafluoroethylene (PTFE).

6 Sampling

Unless otherwise specified in the commodity specification, samples shall be taken as described in EN ISO 3170 or EN ISO 3171 and/or in accordance with the requirements of national standards or regulations for the sampling of petrol.

The samples shall be filled into clean containers.

7 Procedure

7.1 Setting up the apparatus

Prepare the equipment and set the test conditions in accordance with the manufacturer's instructions (cracking reactor temperature, hydrogenation reactor temperature, addition of hydrogen in the carrier gas).

The chromatographic analysis conditions shall be chosen taking into account the characteristics of the column being used and the type of carrier gas. Any satisfactory method that produces a column meeting the requirements of 5.1.2 may be used. The injection parameters (volume, split flow rate) for the test sample and the calibration sample will be chosen in such a way that the capacity of the column and other components of the gas chromatograph are not exceeded and that the linearity of the detector is valid.

NOTE By way of indication, an example of analysis conditions is described in A.2.

7.2 Calibration

Prepare the calibration sample by combining known masses of organic oxygenate compounds (4.2) with the internal standard (4.3) and diluting them to a known mass with the oxygenate free petrol (4.4). The calibration sample should contain the same oxygenates in similar proportions as present in the sample under test. These proportions may be determined by a first qualitative analysis.

Cool the oxygenate free petrol (4.4) to between 5 °C and 10 °C.

Weigh, to the nearest 1 mg, the test sample container (5.2.3) and its cap without sealing it.

Transfer a quantity of the internal standard (4.3) to the test sample container and weigh, to the nearest mg, the test sample container with contents and cap, without sealing the sample container.

The mass, m_{Cst}, in grams, of the internal standard shall amount to between 2 % (*m/m*) and 5 % (*m/m*) of the oxygenate free petrol, but shall not be less than 0,050 g.

Record the mass, m_{Cst}, of the internal standard added.

Transfer a quantity of each oxygenate compound of interest to the test sample container and weigh, to the nearest 1 mg, the test sample container with contents and cap, without sealing the sample container.

Record the mass m_{Ci} of each oxygenate compound added.

Transfer a quantity, normally between 5 ml and 100 ml, of the cooled oxygenate free petrol to the test sample container and seal immediately with the cap. Weigh, to the nearest 1 mg, the test sample container and contents. Record the mass of the oxygenate free petrol added, to the nearest 1 mg.

Mix the contents of the test sample container by shaking until homogeneous.

Inject the prepared calibration sample into the gas chromatograph using the injection volume and recommended operation parameters (see 7.1).

Determine and record the retention time, t_{i}, for all the components i to be evaluated. Calculate the calibration factor, f_{i}, for all the components i to be evaluated, using Formula (2).

$$f_i = \frac{m_{\mathrm{C}i} \times A_{\mathrm{st}}}{A_i \times m_{\mathrm{Cst}}} \qquad (2)$$

where

m_{Ci} is the mass, in grams, of component *i* in the calibration sample;

A_{st} is the peak area of the internal standard;

A_i is the peak area of component *i*;

m_{Cst} is the mass, in grams, of the internal standard in the calibration sample.

Record the calibration factor for each component.

7.3 Determination of density of the sample

Determine the density at 15 °C, ρ_{s}, of the sample in accordance with EN ISO 3675, EN ISO 3838 or EN ISO 12185 and record the result to the nearest 0,1 kg/m^3.

7.4 Preparation of test sample

If the content of one of the oxygenate compounds is or is expected higher than 15 % (*m/m*), refer to the procedure in Clause 9 for the determination of the content of this component. Otherwise, apply the procedure below.

Weigh, to the nearest 1 mg, the test sample container (5.2.3) and its cap without sealing it.

Transfer a quantity of the internal standard (4.3) to the test sample container and weigh, to the nearest 1 mg, the test sample container with contents and cap, without sealing the test sample container. The mass, m_{st}, in grams, of the internal standard shall amount to between 2 % (*m/m*) and 5 % (*m/m*) of the test sample, m_{s}, but shall not be less than 0,050 g. Record the mass, m_{st}, of the internal standard added.

Transfer a quantity, normally between 5 ml and 100 ml, of the cooled sample to the test sample container and seal immediately with the cap. Weigh, to the nearest 1 mg, the test sample container and contents. Record the mass, m_{s}, in grams, of the portion of test sample added, to the nearest 1 mg.

Mix the contents of the test sample container by shaking until homogeneous.

7.5 Introduction of test portion

Inject the prepared test sample (7.4) into the gas chromatograph using the injection volume and recommended operation parameters (see 7.1).

7.6 Examination of chromatogram

Examine the chromatogram and identify the components of the test sample by means of their retention times (see 7.2). Ensure proper integration of the peaks of interest.

8 Calculation

8.1 Calculation of mass of each component in the test sample

Calculate the mass, m_i, in grams, of each component *i* of the test sample using Formula (3).

$$m_i = \frac{A_i \times f_i \times m_{st}}{A_{\mathrm{st}}} \qquad (3)$$

where

A_i is the peak area of component *i*;

f_i is the calibration factor for component *i* (see 7.2);

m_{st} is the mass, in grams, of the internal standard included in the test sample (7.4);

A_{st} is the peak area of the internal standard.

8.2 Calculation of each component in the sample as a percentage by mass

Calculate as a percentage by mass, μ_i, each component i in the sample using Formula (4).

$$\mu_i = \frac{m_i}{m_s} x\,100 \quad (4)$$

where

m_i is the mass, in grams, of each component *i* of the test sample (see 8.1);

m_s is the mass, in grams, of the test sample (see 7.4).

8.3 Calculation of each component in the sample as a percentage by volume

Calculate as a percentage by volume, φ_i, of each component *i* in the sample using Formula (5).

$$\varphi_i = \frac{V_i}{V_s} x\,100 \quad (5)$$

where

V_i is the volume, in millilitres, of component *i*;

V_s is the volume, in millilitres, of the sample taken (7.4).

The volume, V_i, of component *i* is calculated from the mass of each component, the densities given in Table 1 and the density of the sample (7.3), using the general formula (see Formulae (6) and (7)):

$$volume = \frac{mass}{density} \quad (6)$$

For component, *i*, this becomes:

$$V_i = \frac{m_i\ x\,1000}{\rho_i} \quad (7)$$

where

ρ_i is the density at 15 °C in kg/m^3 of component *i* (see Table 1);

m_i is the mass, in grams, of each component *i* of the test sample (see 8.1).

The density values of oxygenate compounds are shown in Table 1.

The volume, V_s, of the sample taken is calculated using Formula (8).

$$V_s = \frac{m_s\, x\,1000}{\rho_s} \quad (8)$$

where

m_s is the mass, in grams, of the test sample (see 7.4);

ρ_s is the density at 15 °C in kg/m^3 of the test sample (see 7.3).

Table 1 — Densities of oxygenate compounds

Oxygenate compound	**Density at 15 °C** kg/m^3
methanol	795,8
ethanol	794,8
propan-1-ol	813,3
propan-2-ol	789,5
butan-1-ol	813,3
butan-2-ol	810,6
2-methylpropan-2-ol	791,0
2-methylpropan-1-ol	805,8
pentan-2-ol	813,5
tert-butyl methyl ether	745,3
methyl *tert*-pentyl ether	775,2
tert-butyl ethyl ether	745,6
diisopropyl ether	729,2
acetone	795,8
butan-2-one	810,0

9 Procedure for the determination of a higher oxygenate compound content

9.1 General

The procedure as described in Clause 9 should be used to analyse petrol samples for which one of the oxygenate compounds content is higher than 15 % (*m/m*). This procedure applies to samples for which the content of this oxygenate compound is known before the analysis, or for which the oxygenate compound content has been evaluated in a previous qualitative analysis, or for which the oxygenate content has been measured in a first quantitative analysis.

9.2 Dilution of the sample

The sample is diluted (1:1 to 1:2 mass/mass) with an oxygenate free petrol (4.4), dependent on the samples (see 9.1).

Weigh, to the nearest 1 mg, the test sample container (5.2.3) and its cap without sealing it.

By way of indication, an example of preparation is described hereafter.

Prepare 20 ml by filling a test sample container with around 10 ml of sample and weigh with a precision of 1 mg, the mass (m_s) of the sample.

Complete with around 10 ml of an oxygenate free petrol (4.4). Weigh with a precision of 1 mg, the mass (m_{OF}) of the oxygenate free petrol, and seal the test container immediately with the cap. This new sample is called hereafter sample D.

Shake the sample D to homogenize it. This test sample D is stored between 0 °C and 10 °C, if the step described in 9.3 is not performed immediately.

9.3 Preparation of the sample D for analysis

Transfer a quantity of the internal standard to the sample D. The mass of the internal standard shall amount to between 2 % (*m/m*) and 5 % (*m/m*) of sample D. Refer to 7.4 for analytical advices for the preparation of this test sample D.

9.4 Analysis of the test sample D

Inject the prepared test sample (9.3) into the gas chromatograph using the operation parameters (see 7.1).

Examine the chromatogram, identify the component of interest and the internal standard by means of their retention times. Ensure proper integration of the peaks.

9.5 Calculation and expression of results

9.5.1 Calculation of the component of interest in the sample D as a percentage by mass

The content (x_{Di}) of the component *i* of interest in the sample D is calculated according to 8.1 and 8.2.

9.5.2 Calculation of the component of interest in the test sample as a percentage by mass

Calculate in % *(m/m)* the content (C_{im}) of the component i of interest in the sample using Formula (9).

$$c_{\mathrm{im}} = x_{\mathrm{D}i} \frac{m_{\mathrm{s}} + m_{\mathrm{OF}}}{m_{\mathrm{s}}} \qquad (9)$$

where

$x_{\mathrm{D}i}$ is the content of the component i in the sample D, expressed in % (*m/m*) (see 9.5.1);

m_{s} is the mass of the test sample , expressed in grams (see 9.2);

m_{OF} is the mass of the oxygenate free petrol, expressed in grams (see 9.2).

9.5.3 Calculation of the component of interest in the test sample as a percentage by volume

Calculate in % (*V/V*) the content (C_{iv}) of the component *i* of interest in the sample using Formula (10).

$$C_{\mathrm{iv}} = C_{\mathrm{im}} \frac{\rho_{\mathrm{s}}}{\rho_{\mathrm{i}}} \qquad (10)$$

where

C_{im} is the content of the component i, in % (*m/m*) (see 9.5.2);

ρ_{s} is the density at 15 °C of the test sample, in kg/m^3 (see 7.3);

ρ_{i} is the density at 15 °C of the component *i*, in kg/m^3 (see Table 1).

10 Total organically bound oxygen content

Calculate the total content of organically bound oxygen, μ_{ox}, as a percentage by mass, from the percentages by mass of the individual components, after identification, using Formula (11) and the atomic mass of oxygen.

$$\mu_{\mathrm{ox}} = \sum \frac{\mu_i \times 16{,}00}{M_i} \tag{11}$$

where

M_i is the molar mass of component i.

μ_i is the percentage by mass of component i (see 8.2 and/or 9.5.2)"

EXAMPLE If the sample has been determined to contain 2 % (*m/m*) methanol and 4 % (*m/m*) ethanol. Then μ_i for methanol is 2 % (*m/m*), M_i is 32,04 and μ_i for ethanol is 4 % (*m/m*), M_i is 46,07.

$$\mu_{\mathrm{ox}} = \frac{2 \text{ x } 16{,}00}{32{,}04} + \frac{4 \text{ x } 16{,}00}{46{,}07} = 1{,}00 + 1{,}39 = 2{,}39\,\%\,(m/m)$$

11 Expression of results

Report the contents of each component to the nearest 0,1 % (*m/m*) or 0,1 % (*V/V*).

Report the total content of organically bound oxygen to the nearest 0,01 % (*m/m*).

12 Precision

12.1 General

The precision given in 12.2 and 12.3 was determined by statistical examination of interlaboratory test results in accordance with EN ISO 4259 [2]. For more details on precision data, see the Foreword.

12.2 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, would in the long run, in the normal and correct operation of the test method, exceed the values given in Table 2 and Table 3 only in one case in twenty.

12.3 Reproducibility, *R*

The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values given in Table 2 and Table 3 only in one case in twenty.

Table 2 — Precision for organic oxygenate compound content

Organic oxygenates content % (*m/m*) or % (*V/V*)	**Repeatability (*r*)** % (*m/m*) or % (*V/V*)	**Reproducibility (*R*)** % (*m/m*) or % (*V/V*)
0,1 to 1,0	0,05	0,1
> 1,0 to 3,0	0,1	0,3
> 3,0 to 5,0	0,1	0,4
> 5,0 to 7,0	0,2	0,5
> 7,0 to 9,0	0,2	0,6
> 9,0 to 11,0	0,2	0,8
> 11,0 to 13,0	0,3	0,9
> 13,0 to 15,0	0,3	1,0

Table 3 — Precision for total organically bound oxygen content

Total organically bound oxygen content μ_{ox} % (*m/m*)	**Repeatability (*r*)** % (*m/m*)	**Reproducibility (*R*)** % (*m/m*)
1,50 to 2,10	0,08	0,30
2,11 to 3,90	0,05	0,41

13 Test report

The test report shall specify:

a) the type and identification of the product under test;

b) the reference to this European Standard, i.e. EN 1601;

c) the sampling procedure used (see Clause 6);

d) the density of the sample (see 7.3);

e) the result of the test (see Clause 11);

f) all operating details not specified in this European Standard, or regarded as optional, together with details of any incidents which may have influenced the test result(s);

g) the date of test.

Annex A
(informative)

Guidance on the oxygen selective detection (O-FID) technique

A.1 Description

In this technique, a gas chromatograph is equipped with a cracking reactor, a hydrogenation reactor and a flame ionization detector. The technique permits the determination of organic oxygenate compounds and the total oxygen content in petrol. An example of test equipment is shown in Figure A.1.

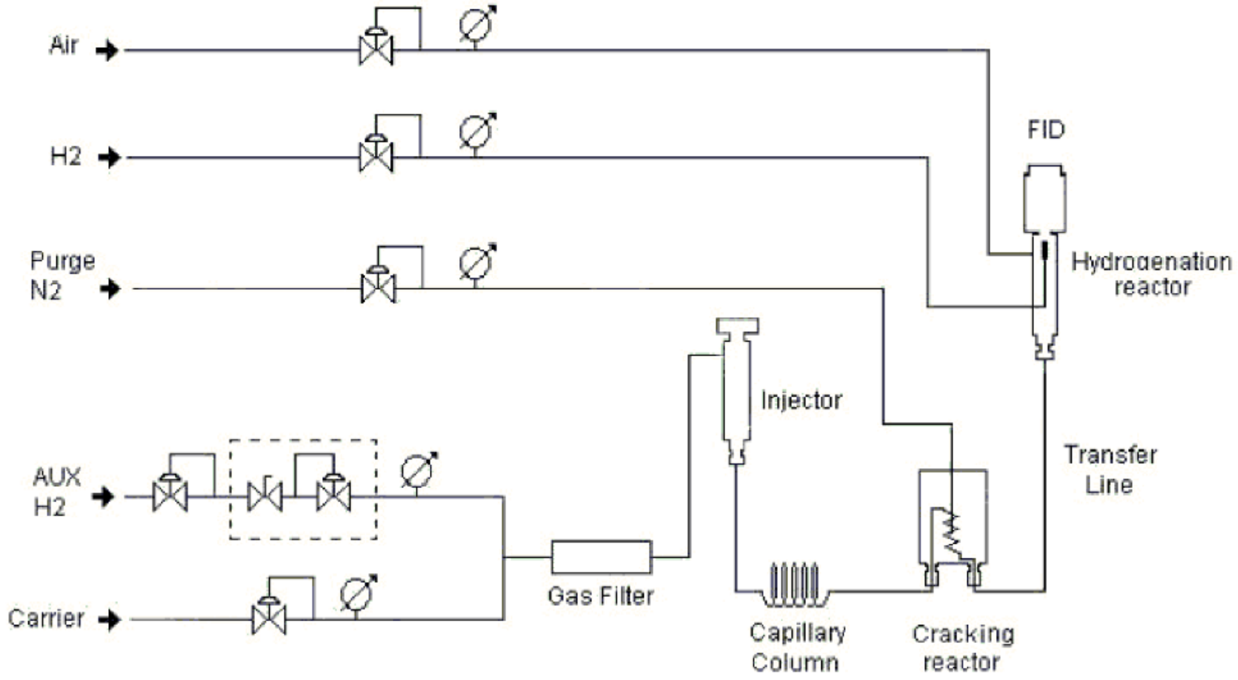


Figure A.1 — Typical O-FID instrument configuration

The cracking reactor, connected immediately after the separation capillary column consists of a platinum/rhodium capillary tube heated and temperature controlled, as recommended by the manufacturer's instructions. Under these conditions when an organic oxygenate compound, eluted by the capillary column, enters the reactor any atom of oxygen will produce a molecule of CO according to the reaction:

$$\mathrm{C}_n\mathrm{H}_m\mathrm{O}_x \xrightarrow{\mathrm{T1(°C)}} x\mathrm{CO} + \frac{\mathrm{m}}{2}\ \mathrm{H}_2 + (n-x)\mathrm{C}$$

T1 depends on the manufacturer (850 °C to 1 200 °C).

The catalytic hydrogenation reactor converts the carbon monoxide produced by the cracking reactor into methane according to the reaction:

$$\mathrm{CO} + 3\mathrm{H}_2 \xrightarrow{\mathrm{T2(°C)}} \mathrm{CH}_4 + \mathrm{H}_2\mathrm{O}$$

T2 depends on the manufacturer (300 °C to 350 °C).

The methane (CH_4) produced in the hydrogenation reactor is quantitatively measured by means of a flame ionization detector (FID).

A.2 Summary of the analysis conditions

By way of indication, an example of analysis conditions is described:

Capillary column, coated with polydimethylsiloxane

- length: 30 m
- internal diameter: 0,32 mm
- film thickness: 1 µm

Variable flow split injector:

- split flow rate: 200 ml/min
- temperature: 250 °C

Injected volume: 0,5 µl

Carrier gas:

- helium + 4 % H_2
- pressure: 50 kPa
- flow rate: 1,5 ml/min

Hydrogenation reactor:

- temperature: 300 °C

Cracking reactor:

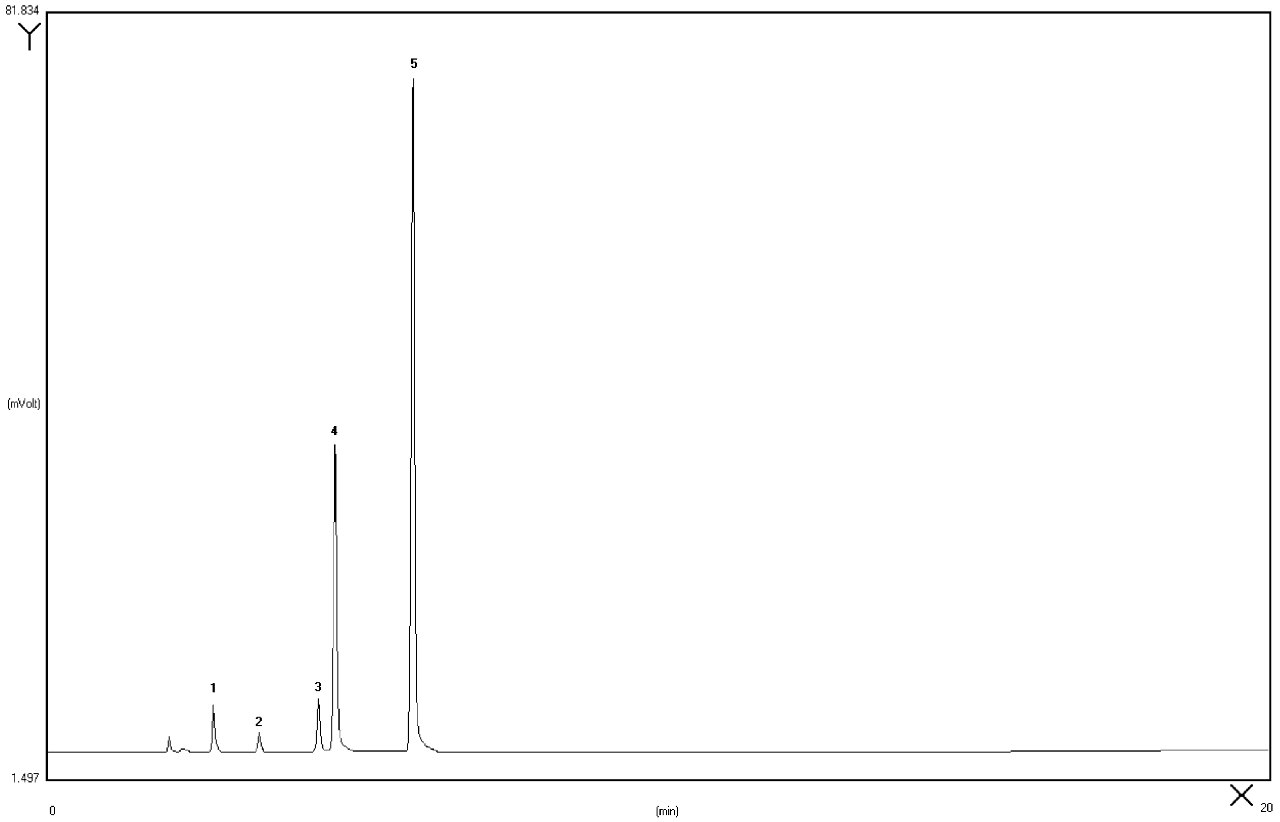
- temperature: 850 °C

Oven:

- temperature: 40 °C hold for 5 min, programmed at 5 °C min^{-1} up to 100 °C and hold 3 min.

These conditions apply to the chromatograms given as examples in Annex A.

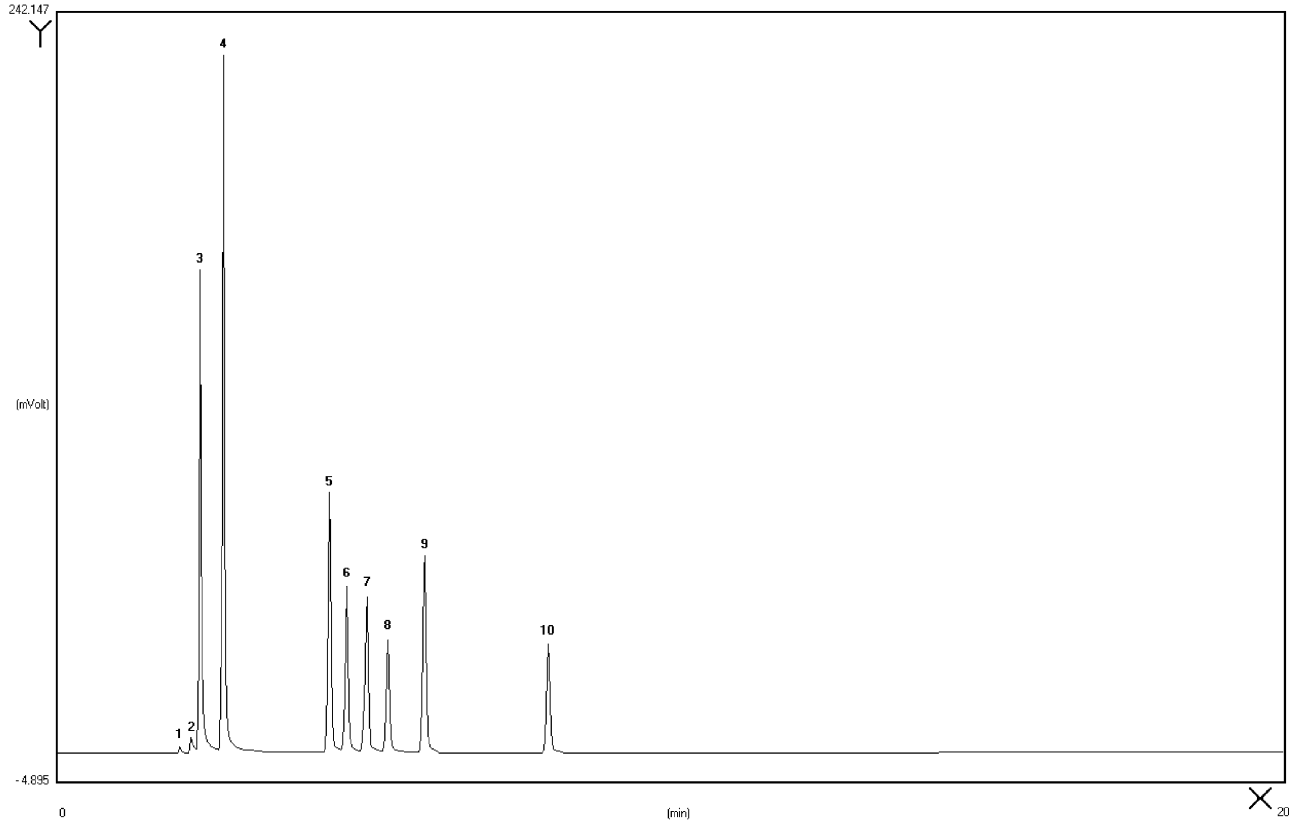
Figure A.2 shows a chromatogram of a European commercial petrol RON 98 using the oxygen selective detector. Figure A.3 shows a chromatogram of a reference sample (oxygenate compounds in petrol) with an elution order of some oxygenate compounds.



Key

X	time, expressed in minutes
Y	instrument response, expressed in millivolts
1	ethanol
2	TBA
3	MTBE
4	internal standard
5	ETBE

Figure A.2 — Chromatogram of an automotive unleaded petrol RON 98



Key

X	time, expressed in minutes
Y	instrument response, expressed in millivolts
1	air
2	water
3	methanol
4	ethanol
5	MTBE
6	internal standard
7	butan-2-ol
8	DIPE
9	ETBE
10	TAME

Figure A.3 — Chromatogram of a reference sample

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[1] EN 228, *Automotive fuels - Unleaded petrol - Requirements and test methods*

[2] EN ISO 4259:2006, *Petroleum products - Determination and application of precision data in relation to methods of test (ISO 4259:2006)*

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