

SLOVENSKI STANDARD

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Liquid petroleum products - Determination of hydrocarbon types and oxygenates in petrol
- Multidimensional gas chromatography method

Flüssige Mineralölerzeugnisse - Bestimmung der Kohlenwasserstoffgruppen und
sauerstoffhaltigen Verbindungen in Ottokraftstoffen - Multidimensionales
gaschromatographisches Verfahren

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Produits pétroliers liquides - Détermination des familles d'hydrocarbures et de la teneur
en composés oxygénés de l'essence automobile - Méthode par chromatographie
multidimensionnelle en phase gazeuse

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EUROPEAN STANDARD
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English version

**Liquid petroleum products - Determination of hydrocarbon types
and oxygenates in petrol - Multidimensional gas chromatography
method**

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d'hydrocarbures et de la teneur en composés oxygénés de
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multidimensionnelle en phase gazeuse

Flüssige Mineralölerzeugnisse - Bestimmung der
Kohlenwasserstoffgruppen und sauerstoffhaltigen
Verbindungen in Ottokraftstoffen - Multidimensionales
gaschromatographisches Verfahren

This European Standard was approved by CEN on 21 June 2004.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

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Foreword

This document (EN 14517:2004) has been prepared by Technical Committee CEN/TC 19 “Petroleum products, lubricants and related products”, 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of an identical text or by endorsement, at the latest by March 2005, and conflicting national standards shall be withdrawn at the latest by March 2005.

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

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EN 14517:2004 (E)

1 Scope

This document specifies the gas chromatographic determination of saturated, olefinic and aromatic hydrocarbons in finished petrol according to EN 228. Additionally, the benzene content, oxygenate compounds and the total oxygenate content can be determined.

The method is applicable for finished petrol with total aromatic content up to 50 % (V/V), total olefin content from about 1,5 % (V/V) up to 30 % (V/V), oxygenate compounds up to 15 % (V/V), total oxygen content from about 1,5 % (m/m) to about 3 % (m/m) and benzene content less than 2 % (V/V).

NOTE 1 For the purposes of this European Standard, the terms “% (m/m)” and “% (V/V)” are used to represent respectively the mass fraction and the volume fraction.

NOTE 2 While developing this method the final boiling point was limited to 215 °C.

NOTE 3 For oxygenate compounds, precision data has only been established on samples containing ethyl-*tert*-butyl ether (ETBE), methyl-*tert*-butyl ether (MTBE), *tert*-amyl-methyl ether (TAME) and ethanol. Applicability of this test method has also been verified for the determination of methanol, n-propanol, i-propanol, i-butanol, *tert*-butanol, acetone, and *di*-isopropyl ether (DIPE). However, no precision data have been determined for these compounds. If any of these oxygenate compounds are present in the sample, their contents should be determined by use of the appropriate test methods given in EN 228.

NOTE 4 Although this test method may be used to determine higher olefin contents up to 50 % (V/V), the precision for olefins was only tested in the range from about 1,5 % (V/V) to about 30 % (V/V).

NOTE 5 Although specifically developed for the analysis of finished petrol that contains oxygenates, this test method may also be applied to other hydrocarbon streams having similar boiling ranges such as naphthas and reformates.

2 Normative references

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The following referenced documents are indispensable for the application 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.

EN 228, *Automotive fuels – Unleaded petrol – Requirements and test methods*.

EN 1601, *Liquid petroleum products – Unleaded petrol – Determination of organic oxygenate compounds and total organically bound oxygen content by gas chromatography (O-FID)*.

EN 13132, *Liquid petroleum products – Unleaded petrol – Determination of organic oxygenate compounds and total organically bound oxygen content by gas chromatography using column switching*.

EN ISO 3170, *Petroleum liquids – Manual sampling (ISO 3170:2004)*.

EN ISO 3171, *Petroleum liquids – Automatic pipeline sampling (ISO 3171:1988)*.

3 Terms and definitions

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

3.1

hydrocarbon group (singular)

family of hydrocarbons such as saturated hydrocarbons, olefinic hydrocarbons, etc.

3.1.1

saturated hydrocarbon

hydrocarbon type such as the n-paraffins, iso-paraffins, naphthenes and poly-naphthenes with 3 to 12 carbon number

3.1.2

olefinic hydrocarbon

hydrocarbon type such as the n-olefins, i-olefins and cyclic olefins with 3 to 10 carbon number

3.1.3

aromatic hydrocarbon

hydrocarbon type benzene, toluene and higher homologous series with 6 to 10 carbon number and naphthalenes up to 12 carbon number

3.1.4

oxygenated hydrocarbon

hydrocarbon type alcohols and ethers, which addition is allowed according to EN 228 (see NOTE 3 in Clause 1).

3.2

partial group

one carbon number in an individual group, being either a single compound like toluene or an isomeric mixture like n-butane and i-butane

4 Principle

4.1 The sample to be analyzed is separated into hydrocarbon groups by means of gas chromatographic analysis using special column-coupling and column-switching procedures.

The sample is injected in the gas chromatographic system and after vaporization separated into the different groups. Detection is always done by a flame ionization detector (FID).

4.2 The mass concentration of each detected compound or hydrocarbon group is determined by the application of relative response factors (see 10.1) to the area of the detected peaks, followed by normalization to 100 %. For 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 such as EN 1601 or EN 13132. The liquid volume concentration of each detected compound or hydrocarbon group is determined by application of density values (see 10.2) to the calculated mass concentration of the detected peaks followed by normalization to 100 %.

4.3 After this analysis the petrol is separated into hydrocarbon groups and carbon numbers. By the use of the corresponding relative response factors (see Table 1 and Table 2) the mass distributions of the groups can be calculated.

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5 Reagents and Materials

5.1 Gases

5.1.1 Hydrogen, 99,999 % pure

5.1.2 Helium, 99,999 % pure

5.1.3 Compressed air

NOTE Installation of suitable moisture filters is recommended for Helium and Hydrogen lines.

5.2 Vials

Use airtight and inert vials, e.g. with rubber-membrane caps covered with self-sealing *poly-tetra-fluorethylene* (PTFE).

5.3 Test mixtures

Finished petrol(s) as reference containing components and concentration levels as in practice.

6 Apparatus

6.1 Gas chromatograph

Computer controlled multidimensional GC equipment, injector, FID, suitable columns, traps and hydrogenation catalysts as described in annex A. The test equipment shall be set up to work according to the above mentioned method and have all the necessary items installed according to the requirements of the supplier's specifications.

6.2 Switching valves

Suitable switching valves which are used for the transfer of compounds in the gas chromatograph from one column to the other. They shall have a chemically inactive surface and a small dead volume.

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6.3 Traps

Suitable short columns (see annex A) used for retaining certain selected chemical groups of the petrol using temperature control. The absorption of the trapped compounds shall be reversible.

EXAMPLE A typical sequence is for example:

- 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 for high amounts of butene or high total olefin contents. Permitting trap capacity and 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 atom number using a molecular sieve 13X 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 molecular sieve 13X.
- The alcohols and higher-boiling aromatics are eluted from the polar column and the trap (Sulfate I column), separated using a non-polar column (for example OV 101 Methyl Silicone), and detected according to boiling point.

Figures B.1 and B.2 show a sample chromatogram with a typical elution order of the hydrocarbon fractions mentioned above.

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7 Sampling

Unless otherwise specified, 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.

8 Procedure

8.1 Preparing the apparatus

Condition the instrument according to the manufacturer's instructions after shutdowns.

8.2 Preparation of a sample for analysis

Cool the sample to prevent loss by evaporation. Transfer the test portion to a vial (5.2) and immediately tightly close and seal using the self sealing PTFE cap (5.2).

8.3 Injection volume

The injection volume shall be sized 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 been proven satisfactory.

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8.4 Verification of proper function**8.4.1** Take a test mixture (5.3) of known composition.

NOTE The composition of the test mixture should have been determined in a round robin or by other methods. The known composition should show the same properties as are to be determined.

8.4.2 Run the test mixture and check for correct instrument parameters, cutting times and grouping times. If they are not correct adjust your instrument to the manufacturer's recommendations and rerun the sample.

NOTE Attention should be paid to components that are on the boundary of separation on the group selective columns. Examples are benzene, olefins and oxygenates. Annex B shows several chromatograms specifically for oxygenate compounds, enclosing evidence of their elution times and possible interferences.

8.5 Validation

Reprocess the validation test mixture and compare the obtained contents with the consensus values. The absolute difference to the consensus values shall not be greater than the reproducibility for the parameters in Table 5.

It is strongly recommended to run the validation test mixture weekly to check the proper function of the equipment.

NOTE The validation test mixture or test mixtures should contain components and amounts as found in the samples to be analyzed. Validation of the instrument should be performed prior any new oxygenates are analyzed.

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9 Preparation**9.1 Preparation of the analysis sample** [SIST EN 14517:2004](https://standards.iteh.ai/catalog/standards/sist/dce20358-0672-47ba-8602-367ced9e3c1d/en-14517-2004)

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Submit the laboratory sample to the preparation procedure specified in 8.2 and 8.3.

9.2 Preparation of the instrument and test conditions

The instrument shall be checked according to 8.4 and has to be set up according to 8.1.

10 Calculation**10.1 Calculation as % (m/m)**

By means of integration the areas under the peaks are determined. The peaks are arranged according to their presence in the groups described in Clause 4. 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 now classified according to the hydrocarbon type and carbon number.

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

Table 1 — FID Relative Response Factors of partial groups

Carbon number	RRF_{PG}				
	Paraffins n + iso	Naphthenes	Olefins n + iso	Olefins cycl.	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	0,812
7	0,892	0,874	0,892	0,874	0,821
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+	0,840				0,880

Calculation of theoretical relative response factors (response of methane set to unity).

$$RRF_{PG} = \frac{((C_{aw} \times C_n) + (H_{aw} \times H_n)) \times 0,7487}{C_{aw} \times C_n} \quad (1)$$

where

RRF_{PG} = relative response factor for a hydrocarbon type group of a particular carbon number (see Tables 1 and 2);

C_{aw} = atomic mass of carbon, 12,011;

C_n = number of carbon atoms in the group;

H_{aw} = atomic mass of hydrogen, 1,008;

H_n = 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 mass fraction, μ_{PG} , in % (m/m) is calculated according to equation (2).

$$\mu_{PG} = 100 \times Area_{PG} \times RRF_{PG} / \sum (Area_{PG} \times RRF_{PG}) \quad (2)$$

where

$Area_{PG}$ is the total, corrected signal area for partial Group PG.