



SLOVENSKI STANDARD

SIST EN 1601:1998

01-maj-1998

Tekoči naftni proizvodi - Neosvinčeni motorni bencin - Določevanje organskih kisikovih spojin in celotnega organsko vezanega kisika s plinsko kromatografijo (O-FID)

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

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

Produits 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)

Ta slovenski standard je istoveten z: EN 1601:1997

ICS:

75.160.20 Tekoča goriva Liquid fuels

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EUROPEAN STANDARD

EN 1601

NORME EUROPÉENNE

EUROPÄISCHE NORM

June 1997

ICS 75.160.20

Descriptors: petroleum products, liquid fuels, gasoline, chemical analysis, determination of content, organic compounds, oxygen, gas chromatography

English version

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

Produits 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)

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This European Standard was approved by CEN on 1997-02-28. 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.

The European Standards exist 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.

CEN members are the national standards bodies of Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

CEN

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

Central Secretariat: rue de Stassart, 36 B-1050 Brussels

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Foreword

This European Standard has been prepared by Technical Committee CEN/TC 19 "Petroleum products, lubricants and related products", the secretariat of which is held by NNI.

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 December 1997, and conflicting national standards shall be withdrawn at the latest by December 1997.

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

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1 Scope

This European Standard specifies a gas chromatographic method for the quantitative determination of individual organic oxygenate compounds in the range 0,17 % (*m/m*) to 15 % (*m/m*) and total organically bound oxygen up to 3,7 % (*m/m*) in unleaded petrol having a final boiling point not greater than 220 °C.

This European Standard is applicable to the determination of oxygen-containing compounds and total organically bound oxygen in unleaded petrol in line with the relevant EU Directive¹⁾.

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

2 Normative references

This European Standard incorporates, by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

EN ISO 3675	Crude petroleum and liquid petroleum products - Laboratory determination of density or relative density - Hydrometer method
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
EN ISO 12185	Crude petroleum and petroleum products - Determination of density - Oscillating U-tube method
ISO 3170	Petroleum liquids - Manual sampling
ISO 3171	Petroleum liquids - Automatic pipeline sampling

3 Principle

After separation of the sample 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 (O-FID).

1) EU Directive 85/536/EEC, Council Directive on crude-oil savings through the use of substitute fuel components in petrol.

NOTE : Guidance on the oxygen selective detection (O-FID) technique is given in annex B.

4 Reagents and materials

Use only reagents of recognized analytical grade.

4.1 Gases

4.1.1 Carrier gas

Helium, or nitrogen, free of hydrocarbons, oxygen and water as impurities.

Hydrogen shall not be used as a carrier gas because it will interfere with the cracking reaction.

4.1.2 Reactor and detector gases

Hydrogen, and air or oxygen.

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.

4.2 Reagents for the preparation of calibration samples

Reagents shall be not less than 99,0 % (m/m) pure.

Calibration samples may be combinations of the following reagents:

methanol (CH₃OH) (methyl alcohol; MeOH);

ethanol (CH₃CH₂OH) (ethyl alcohol; EtOH);

propan-1-ol (CH₃CH₂CH₂OH) (propyl alcohol; NPA);

propan-2-ol [(CH₃)₂CH OH] (iso-propyl alcohol; IPA);

butan-1-ol (CH₃[CH₂]₃OH) (butyl alcohol; NBA);

butan-2-ol (CH₃CH(OH)CH₂CH₃) (*sec*-butyl alcohol; SBA);

2-methylpropan-2-ol [(CH₃)₃COH] (*tert*-butyl alcohol; TBA);

2-methylpropan-1-ol [(CH₃)₂CH CH₂OH] (iso-butyl alcohol; IBA);

pentan-2-ol [CH₃CH(OH)CH₂CH₂CH₃] (*sec*-amyl alcohol; SAA);

tert-butyl methyl ether [(CH₃)₃CO CH₃] (methyl tertiary butyl ether; MTBE);

methyl *tert*-pentyl ether [(CH₃)₂C(OCH₃)CH₂CH₃] (tertiary amyl methyl ether; TAME);

ethyl *tert*-pentyl ether $[(\text{CH}_3)_2\text{C}(\text{OCH}_2\text{CH}_3)\text{CH}_2\text{CH}_3]$ (ethyl tertiary amyl ether; ETAE);

acetone $[(\text{CH}_3)_2\text{CO}]$;

butanone $(\text{CH}_3\text{CH}_2\text{COCH}_3)$ (methyl ethyl ketone; MEK);

tert-butyl ethyl ether $[(\text{CH}_3)_3\text{COCH}_2\text{CH}_3]$ (ethyl tertiary butyl ether; ETBE).

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 and similar volatility.

4.4 Petrol containing no organic oxygenate compounds

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

5 Apparatus

Usual laboratory apparatus and glassware, together with the following.

5.1 Gas chromatographic assembly

5.1.1 Gas chromatograph, equipped with an oxygen selective flame ionization detection system.

5.1.2 Columns

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

NOTE : Polyethylene glycol and methyl silicone have been found to be suitable.

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 as follows:

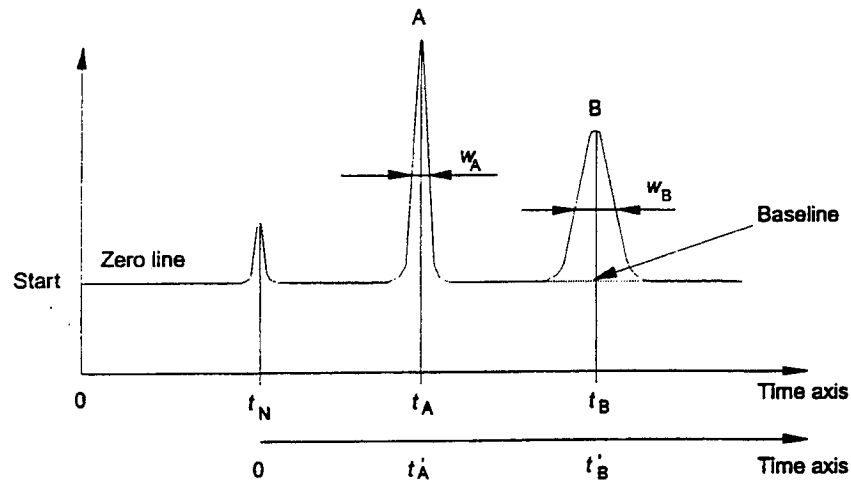
$$R = 1,18 \frac{t'_B - t'_A}{w_A + w_B}$$

where:

t'_A is the retention time of component A;

t'_B is the retention time of component B;

- w_A is the peak width at half-height of component A;
- w_B is the peak width at half-height of component B.



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

NOTE : t_N is the hold-up time zero of the column, i.e. the time taken for an inert component, such as methane, to travel through the column without chromatography taking place.

5.1.3 Devices for the control of the flow of carrier, reactor and detector gases

5.1.4 Recorder and/or integrator

An amplifier and potentiometric recording device, or an integrator or data processor system, giving area values corresponding to the peak area in square millimetres.

5.2 Injection device

5.3 Test sample container, normally with a capacity of between 10 ml and 100 ml, fitted with a self-sealing rubber septum coated with polytetrafluoroethylene (PTFE).

6 Sampling

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

7 Procedure

7.1 Setting up the apparatus

7.1.1 General

Prepare the equipment and set the test conditions in accordance with the manufacturer's instructions.

7.1.2 Carrier gas

Adjust the pressure and flow rate of the carrier gas to levels such that the resolutions are in accordance with 5.1.2.

It is important to minimize oxygen in the carrier gas. To increase specificity and reduce background oxygen it is essential to use oxygen and water filters.

7.2 Calibration

Prepare the calibration sample in accordance with 7.4 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 petrol (4.4).

NOTE : The calibration sample should contain the same oxygenates in similar proportions as present in the sample under test.

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Inject a suitable quantity of the prepared calibration sample into the gas chromatograph. The quantity injected shall be such that the capacity of the column and other components is not exceeded and the linearity of the detector is not impaired.

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 the equation:

$$f_i = \frac{M_i \times A_{st}}{A_i \times M_{st}}$$

where :

M_i is the mass, in grams, of component i in the calibration sample;

A_{st} is the peak area, in square millimetres, of the internal standard.

A_i is the peak area, in square millimetres, of component i ;

M_{st} 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

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/m³.

7.4 Preparation of test sample

Cool the sample to between 5 °C and 10 °C. Weigh, to the nearest 0,1 mg, the test sample container (5.3) and its rubber septum without sealing it.

Transfer a quantity of the internal standard (4.3) to the test sample container and weigh, to the nearest 0,1 mg, the test sample container with contents and septum, without sealing the 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 sample, m_s , but shall not be less than 0,050 g.

Transfer a quantity, normally between 5 ml and 100 ml, of the cooled sample to the test sample container and seal immediately with the septum. Weigh, to the nearest 0,1 mg, the test sample container and contents. Record the mass, m_s , in grams, of the test sample taken, to the nearest 0,1 mg.

Record the amount of internal standard in the prepared test sample as a percentage by mass. Mix the contents of the test sample container by shaking until homogeneous.

7.5 Introduction of test portion

Inject a suitable quantity of the prepared test sample (7.4) into the gas chromatograph. Ensure that the test portion size is such that the capacity of the column and other components of the gas chromatograph is not exceeded and that the linearity of the detector is not impaired.

7.6 Examination of chromatogram

Examine the chromatogram and identify the components of the test portion by means of their retention times (see 7.2).

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 the equation:

$$m_i = \frac{A_i \times f_i \times m_{st}}{A_{st}}$$

where :

A_i is the peak area, in square millimetres, of component i ;

f_i is the calibration factor for component i ;