SLOVENSKI STANDARD
SIST EN 1601:2017

01-oktober-2017

Nadomešča:

SIST EN 1601:2014

SIST EN 1601:2014/AC:2014

Tekoči naftni proizvodi - Določevanje organskih kisikovih spojin in celotnega organsko vezanega kisika v neosvinčenem motornem bencinu - Metoda s plinsko kromatografijo (O-FID)

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

Flüssige Mineralölerzeugnisse - Bestimmung sauerstoff-haltiger organischer Verbindungen und des Gesamtgehalts an organisch gebundenem Sauerstoff in Unverbleitem Ottokraftstoff - Methode mittels Gaschromatographie (O-FID)

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

Ta slovenski standard je istoveten z: EN 1601:2017

ICS:

71.040.50	Fizikalnokemijske analitske metode	Physicochemical methods of analysis
75.160.20	Tekoča goriva	Liquid fuels

SIST EN 1601:2017 **en,fr,de**

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 1601

August 2017

ICS 75.160.20

Supersedes EN 1601:2014

English Version

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

Produits pétroliers liquides - Détermination des composés oxygénés organiques et de la teneur totale en oxygène organiquement lié dans l'essence sans plomb - Méthode par chromatographie en phase gazeuse (O-FID)

Flüssige Mineralölerzeugnisse - Bestimmung sauerstoffhaltiger organischer Verbindungen und des Gesamtgehalts an organisch gebundenem Sauerstoff in unverbleitem Ottokraftstoff - Methode mittels Gaschromatographie (O-FID)

This European Standard was approved by CEN on 19 May 2017.

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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 CEN-CENELEC Management Centre has the same status as the official versions.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Ref. No. EN 1601:2017 E

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European foreword

This document (EN 1601:2017) 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 February 2018, and conflicting national standards shall be withdrawn at the latest by February 2018.

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

This document supersedes EN 1601:2014.

Significant changes between this document and EN 1601:2014 include:

— Improved description of the carrier gases, equipment and procedure for cooling the samples;

— Expansion of Table 1 on the oxygenate compounds data, a.o. the addition of ETBE and TAEE;

— Editorial changes in order to clarify the test procedure.

According to the CEN-CENELEC Internal Regulations, the national standards organisations 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, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

Introduction

This European Standard is an update of the first edition (EN 1601:1997).

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]. The previous precision data for an individual oxygenate compound content in the range of 0,17 % (*V/V*) to 15 % (*V/V*) has not been updated or extended above 15 % (*V/V*).

A dilution procedure to measure an oxygenate compound content higher than 15 % (*m/m*) is included in the standard. 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.

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 The conversion from percent mass to percent volume is done using the calculation mentioned in 8.3 and 9.5.3.

NOTE 2 Precision data are not available for an oxygenate compound content higher than 15 % (*m/m*); see Introduction.

NOTE 3 For the purposes of this European Standard, the terms "% (*m/m*)" and "% (*V/V*)" are used to represent respectively the mass fraction, μ, respectively the volume fraction, φ.

WARNING —The use of this European Standard can 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 users of this European Standard to take appropriate measures to ensure the safety and health of personnel prior to application of the standard, and fulfil statutory and regulatory requirements for this purpose.

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.

Hydrogen shall be dosed exactly and mixed properly to the carrier gas to ensure a stable operation of the cracking reactor (see Figure A.1 and the recommendation in A.2).

It is important to minimize the oxygen content of 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

4.2.1 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:

4.2.2 methanol (MeOH);

4.2.3 ethanol (EtOH);

4.2.4 propan-1-ol [*n*-propyl alcohol (NPA)];

4.2.5 propan-2-ol [*iso*-propyl alcohol (IPA)];

4.2.6 butan-1-ol [*n*-butyl alcohol (NBA)];

4.2.7 butan-2-ol [*s*-butyl alcohol (SBA)];

4.2.8 2-methylpropan-2-ol [tert-butyl alcohol (TBA)];

4.2.9 2-methylpropan-1-ol [*iso*-butyl alcohol (IBA)];

4.2.10 2-pentanol (SAA);

4.2.11 2-methoxy-2-methylpropane [Methyl *tert*-butyl ether (MTBE)];

4.2.12 2-methoxy-2-methylbutane [tert-Amyl methyl ether (TAME)];

4.2.13 2-Isopropoxypropane [Diisopropyl ether (DIPE)];

4.2.14 2-Ethoxy-2-methyl-propane [Ethyl *tert*-butyl ether (ETBE)];

4.2.15 2-Ethoxy-2-methylbutane [tert-Amyl ethyl ether (TAEE)];

4.2.16 butan-2-one [methyl-ethyl ketone (MEK)];

4.2.17 acetone [dimethyl ketone (DMK)].

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 oxygenate compounds detectable by this test method.

Cool the oxygenate free petrol to between 0 °C and 5 °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 A.1.

5.1.2 Columns, the separation column shall consist of a capillary column, coated with a suitable phase for achieving the required resolution. Polyethylene glycol and polydimethylsiloxane are suitable phases.

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

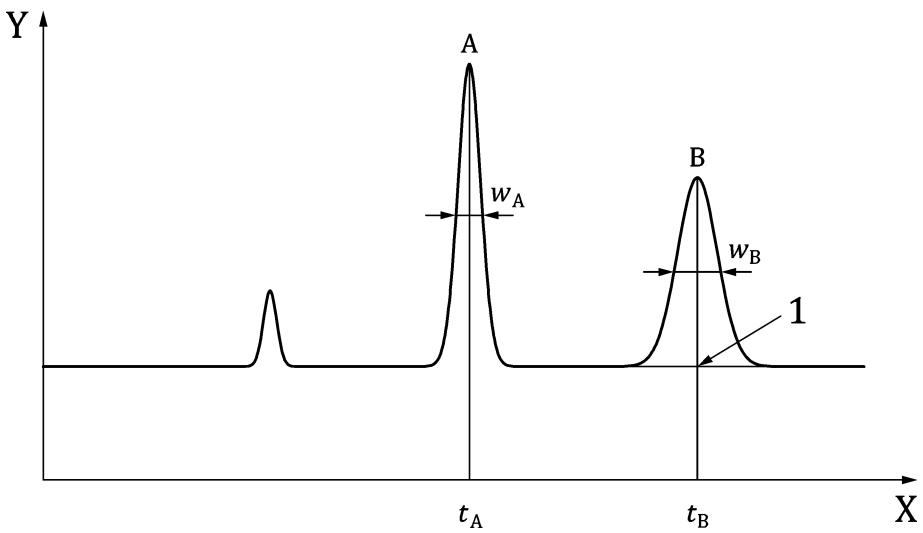
$$CR = 1{,}18 \frac{t_B - t_A}{W_A + W_B} \tag{1}$$

5.2 Other equipment

5.2.1 Balance, capable of weighing to the nearest 1 mg or less.

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).



Key

X retention time

Y instrument response

1 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

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. After sampling and until the preparation of test samples, to prevent loss by evaporation, cool the samples to a temperature between 0 °C and 5 °C

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 of the sample under test.

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 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.

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).

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

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/m³.

7.4 Preparation of the 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.