SLOVENSKI STANDARD
SIST EN 13132:2000

01-julij-2000

Tekoči naftni proizvodi - Neosvinčeni motorni bencin - Določevanje organskih kisikovih spojin in celotnega organsko vezanega kisika s plinsko kromatografijo s preklopom kolon

Liquid petroleum products - Unleaded petrol - Determination of organic oxygenate compounds and total organically bound oxygen content by gas chromatography using column switching

Flüssige Mineralölerzeugnisse - Unverbleite Ottokraftstoffe - Bestimmung sauerstoffhaltiger organischer Verbindungen und des Gesamtgehaltes an organisch gebundenem Sauerstoff mittels Gaschromatographie mit Säulenschaltung

Produits pétroliers liquides - Essence sans plomb - Détermination des composés oxygénés organiques et de la teneur totale en oxygene organique par chromatographie en phase gazeuse avec commutation de colonnes

Ta slovenski standard je istoveten z: **EN 13132:2000**

ICS:

75.160.20	Tekoča goriva	Liquid fuels

SIST EN 13132:2000 **en**

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 13132

March 2000

ICS 75.160.20

English version

Liquid petroleum products - Unleaded petrol - Determination of organic oxygenate compounds and total organically bound oxygen content by gas chromatography using column switching

Produits pétroliers liquides - Essence sans plomb - Détermination des composés oxygénés organiques et de la teneur totale en oxygène organique par chromatographie en phase gazeuse avec commutation de colonnes

This European Standard was approved by CEN on 14 February 2000.

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.

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.

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

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

Ref. No. EN 13132:2000 E

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 September 2000, and conflicting national standards shall be withdrawn at the latest by September 2000.

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.

In this standard, annex A is normative and annex B is informative.

1 Scope

This European Standard specifies a gas chromatographic method using column switching 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 3,7 % (*m/m*) in unleaded petrol having a final boiling point not greater than 220 °C.

NOTE 1 The final boiling point can be measured by using prEN ISO 3405:1998 [1)].

NOTE 2 Fur 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.

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 Directives[2)].

WARNING The use of this Standard can 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 standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

EN ISO 3170, *Petroleum liquids - Manual sampling (ISO 3170:1988, including Amendment 1:1998).*

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

EN ISO 3675, *Crude petroleum and liquid petroleum products - Laboratory determination of density - Hydrometer method (ISO 3675:1998).*

EN ISO 3696, *Water for analytical laboratory use - Specification and test methods (ISO 3696:1987).*

---

1) prEN ISO 34051998: Petroleum products - Determination of distillation characteristics at atmosphere pressure (ISO/DIS 3405:1998).

2) EU Directive 85/210/EEC, Council Directive on the approximation of the laws of the Member States concerning the lead content of petrol. EU Directive 85/536/EEC, Council Directive on crude-oil savings through the use of substitute fuel components in petrol.

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 3838:1983).*

EN ISO 12185, *Crude petroleum and petroleum products - Determination of density - Oscillating U-tube method (ISO 12185:1996).*

3 Principle

Oxygen containing organic compounds are isolated from the sample using a first capillary column. In a second capillary column the oxygen containing organic compounds are separated, and detected individually using a flame ionisation detector.

NOTE Guidance on the column switching technique is given in annex B.

4 Reagents and materials

Use only reagents of recognized analytical grade and water conforming to grade 3 of EN ISO 3696.

4.1 Carrier gas

Hydrogen, helium, or nitrogen, free of hydrocarbons.

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	CH_3OH	methyl alcohol; MEOH;
ethanol	CH_3CH_2OH	ethyl alcohol; ETOH;
propan-1-ol	$CH_3CH_2CH_2OH$	propyl alcohol; NPA;
propan-2-ol	$(CH_3)_2CHOH$	iso-propyl alcohol; IPA;
butan-1-ol	$CH_3[CH_2]_3OH$	butyl alcohol; NBA;
butan-2-ol	$CH_3CH(OH)CH_2CH_3$	*sec*-butyl alcohol; SBA;
2-methylpropan-2-ol	$(CH_3)_3COH$	*tert*-butyl alcohol; TBA;
2-methylpropan-1-ol	$(CH_3)_2CHCH_2OH$	iso-butyl alcohol; IBA;
pentan-2-ol	$CH_3CH(OH)CH_2CH_2CH_3$	*sec*-amyl alcohol; SAA;
tert-butyl methyl ether	$(CH_3)_3CO\ CH_3$	methyl tertiary butyl ether; MTBE;
methyl *tert*-pentyl ether	$(CH_3)_2C(OCH_3)CH_2CH_3$	tertiary amyl methyl ether; TAME;
ethyl *tert*-pentyl ether	$(CH_3)_2C(OCH_2CH_3)CH_2CH_3$	ethyl tertiary amyl ether; ETAE;
acetone	$(CH_3)_2CO$	
butanone	$CH_3CH_2COCH_3$	methyl ethyl ketone; MEK
tert-butyl ethyl ether	$(CH_3)_3CO\ CH_2CH_3$	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, or n-heptane

Petrol which has been examined to ensure that it contains no organic oxygenate compounds detectable by this method, or n-heptane.

5 Apparatus

Usual laboratory apparatus and glassware, together with the following:

5.1 Gas chromatographic assembly

5.1.1 Gas chromatograph, provided with a means for column switching, equipped with a programmable oven temperature controller, or controllers in the case of dual oven gas chromatographs, and a flame ionisation detector (FID).

NOTE It is recommended that a system constructed entirely of glass from the sample injection port up to the detector system is used since petrol may contain organic oxygenate compounds which can give rise to corrosion and changes of retention times in systems constructed using metals.

5.1.2 Two capillary columns

NOTE Recommended columns are described in annex B.

The columns shall be coated with a suitable phase so that the required resolution between the components and between the components and the matrix to be determined, shall be at least 1 after elution from the second column.

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:

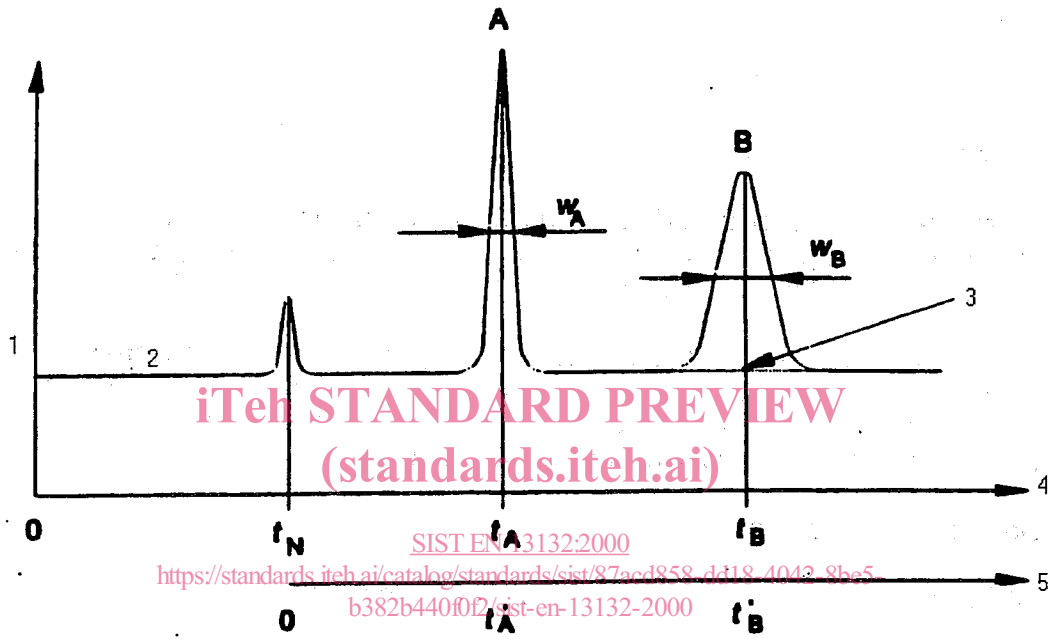
t'_A is the retention time of component A in s;

t'_B is the retention time of component B in s;

w_A is the peak width at half-height of component A in s;

w_B is the peak width at half-height of component B in s;

1,18 is a factor originating from a peak resolution equation.



Key

1 Start
2 Zero line
3 Baseline
4 Time axis
5 Time axis

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.

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

5.1.3 Device for the control of the flow of carrier gas

5.1.4 Recorder and/or integrator

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

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 in accordance with EN ISO 3170 or EN 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.

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 petrol or n-heptane (4.4).

> NOTE The calibration sample should contain the same organic oxygenate compounds in similar proportions as present in the sample under test.

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

Determine and record the retention times, 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 microvoltseconds or in square millimetres, of the internal standard;

A_i is the peak area, in microvoltseconds or 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/m^3.

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 columns 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 microvoltseconds or insquare millimetres, of component i;

f_i is the calibration factor for component i;

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

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

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

Calculate as a percentage by mass, ω_i, each component i in the sample using the equation:

$$\omega_i = \frac{m_i}{m_s} \times 100$$

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 the equation:

$$\phi_i = \frac{V_i}{V_s} \times 100$$

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 annex A and the density of the sample (7.3), using the general equation:

$$\text{volume} = \frac{\text{mass}}{\text{density}}$$

For component, i, this becomes

$$V_i = \frac{m_i \times 1000}{\rho_i}$$

where:

ρ_i is the density in kilograms per cubic metre at 15 °C of component i.