SLOVENSKI STANDARD
oSIST prEN 12177:2022

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Tekoči naftni proizvodi - Neosvinčeni motorni bencini - Določevanje benzena s plinsko kromatografijo

Liquid petroleum products - Unleaded petrol - Determination of benzene content by gas chromatography

Flüssige Mineralölerzeugnisse - Unverbleite Ottokraftstoffe - Bestimmung des Benzolgehaltes mittels Gaschromatographie

Produits pétroliers liquides - Essence sans plomb - Détermination de la teneur en benzène par chromatographie en phase gazeuse

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75.160.20	Tekoča goriva	Liquid fuels

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English Version

Liquid petroleum products - Unleaded petrol - Determination of benzene content by gas chromatography

Produits pétroliers liquides - Essence sans plomb - Détermination de la teneur en benzène par chromatographie en phase gazeuse

Flüssige Mineralölerzeugnisse - Unverbleite Ottokraftstoffe - Bestimmung des Benzolgehaltes mittels Gaschromatographie

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Recipients of this draft are invited to submit, with their comments, notification of any relevant patent rights of which they are aware and to provide supporting documentation.

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

CEN-CENELEC Management Centre: Rue de la Science 23, B-1040 Brussels

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European foreword

This document (prEN 12177:2022) 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 document is currently submitted to the CEN Enquiry.

This document will supersede EN 12177:1998.

At the time of the development of the test method the ethanol content of gasoline was limited to 5 % (*V/V*) which was reflected in the scope of the test method. Since several years, fuels containing up to 10 % of ethanol (3,7 % (*m/m*)) are common in the European market. This revision is meant to extend the scope of the test methods to those fuels, thus reflecting market needs.

1 Scope

This document specifies a column switching gas chromatographic method for the quantitative determination of benzene content in the range 0,05 % (*V/V)* to 6 % (*V/V*) in unleaded petrol having a final boiling point not greater than 220 °C.

The method described in this document is suitable for determining benzene in petrol, including petrol containing oxygenates up to E10 (up to 3,7 % (*m/m*) oxygen content), in line with the relevant EC Directives [3].

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

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

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 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 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at https://www.electropedia.org/
- ISO Online browsing platform: available at https://www.iso.org/obp

4 Principle

The benzene-containing fraction is isolated from the sample using a capillary column and, in a second capillary column, the benzene is separated and detected using a flame ionization detector.

NOTE 1 Some oxygenates are known to interfere with the determination of benzene using a single column gas chromatographic method.

NOTE 2 Guidance on the column switching technique is given in Annex A.

5 Reagents and materials

Use only chemicals and reagents of recognized analytical grade.

5.1 Carrier gas

5.2 Carrier gas, helium, nitrogen or hydrogen, of at least 99,999 % (*V/V*) purity. Any oxygen present is removed by a chemical resin filter.

5.3 Hydrogen, grade suitable for flame ionization detectors

5.4 Compressed air regulated for flame ionization detectors.

WARNING — Hydrogen is explosive in mixtures with air at concentrations of hydrogen 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.

5.5 Reagents for the preparation of calibration samples

NOTE Calibration samples will normally be combinations of benzene, solvent and an internal standard.

5.5.1 Benzene, not less than 99,0 % (*m/m*) pure.

WARNING — Benzene is toxic and carcinogenic.

5.5.2 Solvent, not containing benzene or internal standard, e.g. heptane.

5.6 Internal standard, reagent for which it has been established that it is not present in the sample.

NOTE Isobutyl methyl ketone is preferred as the internal standard.

6 Apparatus

Usual laboratory apparatus and glassware, together with the following:

6.1 Gas chromatographic assembly

6.1.1. 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, a split injector and two flame ionization detectors (FID). See Annex A for typical operating conditions.

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 oxygenates which can give rise to corrosion and changes of retention times in systems constructed partly using metals.

6.1.2 Two capillary columns, of appropriate dimensions, each internally coated with a substance of different polarity, such that the resolution between the benzene peak and the matrix is at least 1 after elution from the second column.

The resolution, *R*, between peaks A and 8 (see Figure 1) is calculated using Formula 1:

$$R = 1{,}18\frac{t'_A - t'_8}{w_A + w_B} \quad (1)$$

where:

t'_A is the reduced retention time of component A;

t'_8 is the reduced 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 8.

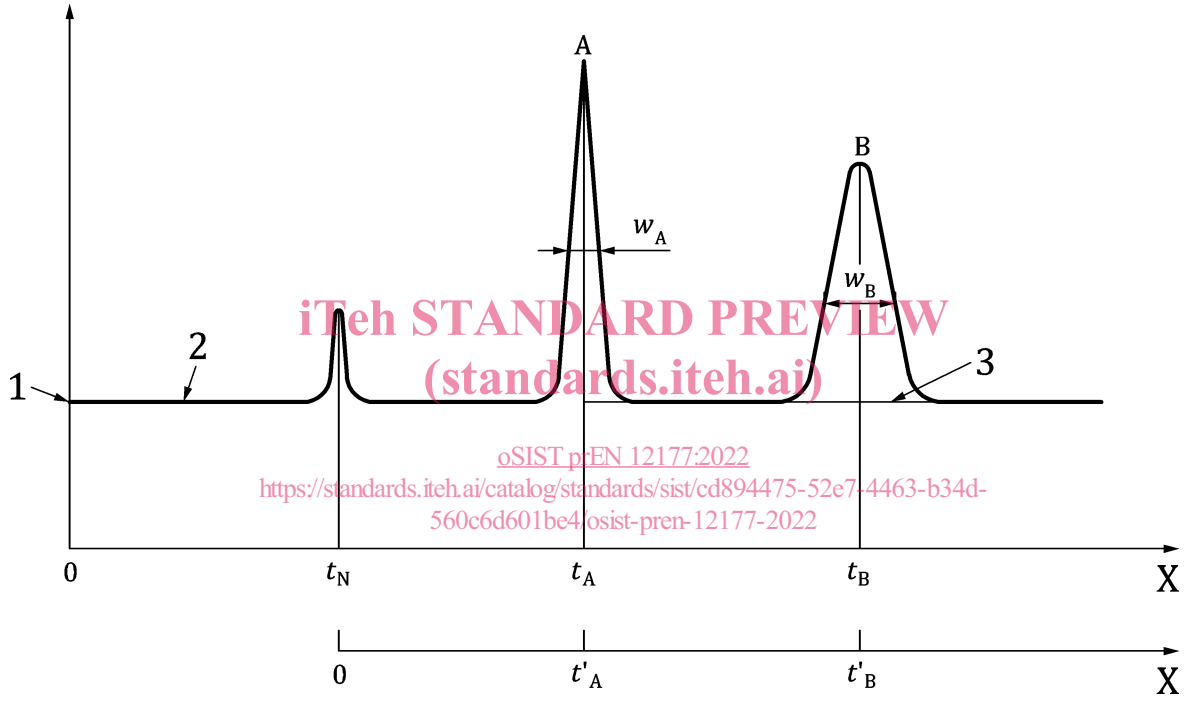

Figure 1 — Calculation of the resolution between peaks A and B

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.

6.1.3 Device for the control of the flow of carrier gas, the chromatograph shall be able to deliver a constant carrier gas flow over the whole range of the analysis

6.2 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).

7 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.

8 Procedure

8.1 Setup of the apparatus

8.1.1 General

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

8.1.2 Carrier gas

Adjust the pressure and flow rate of the carrier gas to levels such that the resolution is in accordance with 6.1.2.

8.2 Calibration

Prepare the calibration sample by combining known masses of benzene (5.5.1) and internal standard (5.6) in a suitable solvent (5.5.2).

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 for benzene and for the internal standard. Calculate the calibration factor, *f,* for benzene using the following Formula (2):

$$f = \frac{m_1 \times A_2}{A_1 \times m_2} \qquad (2)$$

where:

m_1 is the mass of benzene in the calibration sample, in g;

A_2 is the peak area of the internal standard, in mm^2;

A_1 is the peak area of benzene, in mm^2;

m_2 is the mass of the internal standard in the calibration sample, in g.

8.3 Determination of density

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

8.4 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 (6.2) and its rubber septum without sealing it.

Transfer a quantity of the internal standard (5.6) 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 g, 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 g, of the test sample taken, to the nearest 0,1 mg.

Record the amount of internal standard in the prepared test sample in % (*m/m*). Homogenize the content of the test sample container by shaking vigorously.

8.5 Introduction of test portion

Inject a suitable quantity of the test sample (8.4) into the gas chromatograph. Ensure that the test portion size does not exceed the capacity of the columns and other components of the gas chromatograph and that the linearity of the detector is not impaired.

8.6 Examination of the chromatogram

Examine the chromatogram and identify the benzene and the internal standard by means of their retention times (see 8.2).

9 Calculation

9.1 Calculation of mass of benzene in the test sample

Calculate the mass, $m_{3,}$ in g, of benzene in the test sample using Formula (3):

$$m_3 = \frac{f \times A_3 \times m_4}{A_4} \tag{3}$$

where:

f is the calibration factor for benzene;

A_3 is the peak area of benzene, in mm^2;

m_4 is the mass of the internal standard in the test sample {see 8.4), in g;

A_4 is the peak area of the internal standard, in mm^2.

9.2 Calculation of volume of benzene in the test sample

Calculate the volume, V_1, in ml, of benzene in the test sample using Formula (4):

$$V_1 = \frac{m_3 \times 1\,000}{\rho_{t,}} \tag{4}$$

where:

m_3 is the mass of benzene in the test sample {see 9.1), in g;

$\rho_{t,}$ is the density of benzene at 15 °C, i.e. 884,3 kg/m^3.

9.3 Calculation of volume of test sample

Calculate the volume, $V_{2,}$ in ml, of the test sample using Formula (5):

$$V_2 = \frac{m_s \times 1\,000}{\rho_s} \tag{5}$$

where:

m_s is the mass of the test sample {see 8.4), in g;

ρ_s is the density at 15 °C of the sample, in kg/m^3.