



SLOVENSKI STANDARD

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Goriva za motorna vozila - Določanje tipov ogljikovodikovih skupin in izbira ogljikovodikov in kisikovih spojin - Metoda plinske kromatografije z vakuumsko ultravijolično absorpcijsko spektroskopijo (GC-VUV)

Automotive fuels - Determination of hydrocarbon group types and select hydrocarbon and oxygenate compounds - Gas chromatography with vacuum ultraviolet absorption spectroscopy (GC-VUV) method

Kraftstoffe für Kraftfahrzeuge - Bestimmung von Kohlenwasserstoffgruppentypen und Auswahl von Kohlenwasserstoff- und Sauerstoffverbindungen - Gaschromatographie mit Vakuum-Ultraviolett-Absorptionsspektroskopie (GC-VUV)

Carburants pour automobiles - Détermination des types de groupes d'hydrocarbures et sélection des composés d'hydrocarbures et d'oxygénation - Chromatographie gazeuse avec spectroscopie d'absorption ultraviolette sous vide (GC-VUV) méthode

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Automotive fuels - Determination of hydrocarbon group types and select hydrocarbon and oxygenate compounds - Gas chromatography with vacuum ultraviolet absorption spectroscopy (GC-VUV) method

Carburants pour automobiles - Détermination des types de groupes d'hydrocarbures et sélection des composés d'hydrocarbures et d'oxygénation - Chromatographie gazeuse avec spectroscopie d'absorption ultraviolette sous vide (GC-VUV) méthode

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This draft European Standard is submitted to CEN members for enquiry. It has been drawn up by the Technical Committee CEN/TC 19.

If this draft becomes a European Standard, 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.

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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

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Contents	Page
European foreword	3
Introduction	4
1 Scope.....	5
2 Normative references.....	6
3 Terms, definitions and abbreviations	6
3.1 Terms and definitions	6
3.2 Abbreviations.....	7
4 Principle	7
5 Reagents and materials	7
6 Apparatus	10
7 Sampling.....	11
8 Preparation of apparatus.....	11
9 Calibration.....	11
10 Pre-measurement validation.....	13
11 Procedure	14
12 Calculation.....	15
13 Report	20
14 Precision and bias.....	20
Annex A (normative) Generating absorbance spectra from intensity scan data.....	22
A.1 Generating scan intensity data to VUV absorbance spectra.....	22
A.2 Modelling absorbance data	22
Bibliography	23

European foreword

This document (prEN 18015:2023) 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.

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prEN 18015:2023 (E)

Introduction

This document is mainly used for the determination of saturated (paraffinic, isoparaffinic and naphthenic), olefinic, aromatic and oxygenated hydrocarbons in automotive motor gasoline according to European fuel specifications such as EN 228 [1].

The test method described in this document is based on ASTM D8071 [2] with modifications to the gas chromatographic oven temperature profile.

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1 Scope

This test method is a standard procedure for the determination of saturates, olefins, aromatics and oxygenates in unleaded petrol using gas chromatography and vacuum ultraviolet detection (GC-VUV).

Concentrations of compound classes and certain individual compounds are determined by mass fraction % (*m/m*) or volume fraction % (*V/V*). The concentration ranges for which precision has been determined are as given in Table 1.

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

The method is found to be applicable to other oxygenates including isopropanol, iso-butanol, tert-butanol, n-propanol, acetone, tert-pentanol and di-isopropyl ether (DIPE), however precision has not been determined.

Table 1 — Ranges of method applicability

Property	Units	Applicable range
Saturates	% (<i>V/V</i>)	21,48 to 80,87
Olefins	% (<i>V/V</i>)	0,22 to 41,90
Aromatics	% (<i>V/V</i>)	2,35 to 64,55
Benzene	% (<i>V/V</i>)	0,20 to 2,54
Toluene	% (<i>V/V</i>)	0,87 to 30,97
Ethylbenzene	% (<i>V/V</i>)	0,20 to 3,45
Xylenes	% (<i>V/V</i>)	0,49 to 18,59
Methanol	% (<i>V/V</i>)	0,07 to 15,30
Ethanol	% (<i>V/V</i>)	0,08 to 24,96
MTBE	% (<i>V/V</i>)	0,22 to 22,21
ETBE	% (<i>V/V</i>)	0,13 to 23,44
TAME	% (<i>V/V</i>)	0,24 to 21,96
TAEE	% (<i>V/V</i>)	0,24 to 8,60
Oxygen	% (<i>m/m</i>)	0,52 to 12,19

Individual hydrocarbon components are typically not baseline-separated by the procedure described in this test method. The coelutions are resolved at the detector using VUV absorbance spectra (Annex A) and deconvolution algorithms.

While this test method reports by mass fraction % (*m/m*) or volume fraction % (*V/V*) for several specific components that can be present in unleaded petrol, it does not attempt to speciate all possible components that can occur in unleaded petrol. In particular, this test method is not intended as a type of detailed hydrocarbon analysis (DHA).

This test method has been tested for unleaded petrol according EN 228 [1]; the method can apply to petrol blending streams but has not been extensively tested for such applications.

WARNING — The use of this document can 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

prEN 18015:2023 (E)

responsibility of the user of this document to establish appropriate safety and health practices and to 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)*

3 Terms, definitions and abbreviations**3.1 Terms and definitions**

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

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>

3.1.1**integration filter**

mathematical operation performed on an absorbance spectrum for the purpose of converting the spectrum to a single-valued response suitable for representation in a two-dimensional chromatogram plot

3.1.2**library reference spectrum**

absorbance spectrum representation of a molecular species stored in a library database and used for identification of a compound/compound class or deconvolution of multiple coeluting compounds

3.1.3**response area**

response summed over a given time interval having units of absorbance units

Note 1 to entry: Time factor necessary to convert a response area to a true mathematical area cancels out of all critical calculations and is omitted.

3.1.4**relative response factor****RRF**

in vacuum ultraviolet spectroscopy, the relative response factor for a given compound is calculated from the compound's absorption cross section (expressed in cm^2 per molecule) and methane's cross section

Note 1 to entry: The absorption cross section is averaged over the 125 nm to 240 nm wavelength region.

Note 2 to entry: A compound's relative response factor is a function of the type and number of chemical bonds.

Note 3 to entry: A compound's relative response factor is relative to the response of methane, which is taken to have a relative response factor of 1.

3.2 Abbreviations

For the purposes of this document, the following abbreviations apply.

AU	absorbance units
DHA	detailed hydrocarbon analysis
GC	gas chromatograph
GC-VUV	gas chromatography with vacuum ultraviolet spectroscopy detection
RI	retention index
RRF	relative response factor
MTBE	methyl tertiary butyl ether
ETBE	ethyl tertiary butyl ether
TAME	tertiary amyl methyl ether
TAE	tertiary amyl ethyl ether
DIPE	Diisopropyl ether

4 Principle

A sample is introduced to a gas chromatographic (GC) system. After volatilization, the effluent is introduced onto a GC column for separation, and then detected by a vacuum ultraviolet absorption spectroscopy detector¹. The separation is accomplished using a 30 m, nonpolar phase capillary column and a moderately fast temperature ramp (typical operating parameters of this test method are given in Clause 11). Coelutions are resolved by the detector using vacuum ultraviolet absorbance spectra and deconvolution.

The response areas for each sequential time interval over the entire chromatogram is determined. The calculation of the results is based on the deconvoluted response areas of the saturates, olefins, aromatics and oxygenates, in addition to several individual species components. The percent mass concentrations are calculated from the response areas using class-based or compound-specific relative response factors (RRFs). The volume percent concentrations are calculated from the mass concentrations by applying specific component or class and carbon number based density values. The mass and volume percent calculations are software automated, whereby the RRFs and densities are a function of elution time in a static database library¹.

5 Reagents and materials

5.1 Purity of reagents

Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available². Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

¹ The sole source of supply of the apparatus known to the committee at this time is VUV-Analytix, Cedar Park, Texas.

² *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopoeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

prEN 18015:2023 (E)

5.2 Helium carrier gas for gas chromatograph, 99,999 % pure.

NOTE Method performance has not been studied for other carrier gases such as hydrogen or nitrogen.

5.3 Purge or makeup gas, nitrogen, helium or argon, for vacuum ultraviolet detector, 99,999 % pure.

5.4 Methylene chloride or carbon disulfide, reagent grade, used as a solvent test sample and GC rinse solvent. (**Warning** — Toxic material can be combustible at high temperatures.)

5.4.1 Alternate reagent grade solvents may be used provided that autosampler syringe carryover does not interfere with sample analysis and that a suitable baseline (8.6) is achieved.

5.5 Retention time standard consisting of isobutane (iC4), butane (C4), isopentane (iC5), and pentane through pentadecane linear alkanes, approximately 1 % by mass each, in suitable solvent such as methylene chloride, used as retention time markers.

5.6 System validation mixture prepared in compliance with Practice D4307, having the components and approximate concentrations given in Table 2. The actual concentration levels of the prepared system validation mixture in Table 2 are not critical but shall be accurately known.

5.6.1 The components of the system validation mixture may be modified to include linear alkanes or other compounds necessary for determining a retention time marker list (9.1 and 9.2).

5.6.2 The concentrations in Table 2 may be suitably modified to accommodate additional or substituted components. The concentrations shall otherwise be accurately known.

Table 2 — System validation mixture

Component	Concentration % (m/m)	Component	Concentration % (m/m)
Cyclopentane	1,1	Benzene	2,2
n-Pentane	1,1	Toluene	2,2
Cyclohexane	2,1	trans-Decahydronaphthalene	4
2,3-Dimethylbutane	2,1	n-Tetradecane	4,5
n-Hexane	2,1	Ethylbenzene	4,5
1-Hexene	1,5	o-Xylene	4
Methylcyclohexane	4	n-Propylbenzene	5
4-Methyl-1-hexene	1,6	1,2,4-Trimethylbenzene	4,5
n-Heptane	3,5	1,2,3-Trimethylbenzene	5
1,2-Dimethylcyclohexane	5	1,2,4,5-Tetramethylbenzene	5
Isooctane	5	Pentamethylbenzene	5
n-Octane	5	Total Paraffins	32,2
1,2,4-Trimethylcyclohexane	4	Total Isoparaffins	7,1

Component	Concentration % (m/m)	Component	Concentration % (m/m)
n-Nonane	4,5	Total Olefins	3,1
n-Decane	4,5	Total Naphthenes	20,2
n-Undecane	3,5	Total Aromatics	37,4
n-Dodecane	3,5	Total Xylenes	4,0

5.7 Oxygenates mixture consisting of compounds in Table 3. The actual concentration levels of the oxygenates mixture in Table 3 are not critical but shall be accurately known.

Table 3 — Oxygenate mixture

Component	Concentration % (v/v)
Methanol	0,5
Ethanol	5
MTBE	7
ETBE	7
TAME	7
TAAE	7
Isopropanol	1
Isobutanol	1
tert-Butanol	1
Propanol	1
Acetone	1
tert-Pentanol	1
DIPE	1
Toluene	Balance