



SLOVENSKI STANDARD

SIST EN 12916:2006

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SIST EN 12916:2000

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Petroleum products - Determination of aromatic hydrocarbon types in middle distillates - High performance liquid chromatography method with refractive index detection

Mineralölerzeugnisse - Bestimmung von aromatischen Kohlenwasserstoffgruppen in Mitteldestillaten - HPLC-Verfahren mit Brechzahl-Detektor

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Produits pétroliers - Détermination des familles d'hydrocarbures aromatiques dans les distillats moyens - Méthode par chromatographie liquide a haute performance avec détection par réfractométrie différentielle

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English Version

Petroleum products - Determination of aromatic hydrocarbon
types in middle distillates - High performance liquid
chromatography method with refractive index detection

Produits pétroliers - Détermination des familles
d'hydrocarbures aromatiques dans les distillats moyens -
Méthode par chromatographie liquide à haute performance
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Mineralölerzeugnisse - Bestimmung von aromatischen
Kohlenwasserstoffgruppen in Mitteldestillaten - HPLC-
Verfahren mit Brechzahl-Detektor

This European Standard was approved by CEN on 20 April 2006.

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, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.



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Foreword

This document (EN 12916:2006) 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 November 2006, and conflicting national standards shall be withdrawn at the latest by November 2006.

This document supersedes EN 12916:2000.

The method has been updated and improved in the sense that:

- a method without back-flush is prescribed resulting in simplicity of the instrument;
- the integration of aromatic hydrocarbon types has been better defined (definition of cut times);
- fluorene is used as calibrant for the determination of aromatic hydrocarbons content instead of 1-methylnaphthalene in order to minimize the bias on the di-aromatic hydrocarbons content between the former method and this version;
- diesel fuels containing FAME up to 5 % (V/V) are included in the scope of the method and the interferences between FAME and tri+-aromatic hydrocarbons do not exist any more;
- The precision of the method has been re-calculated using data from a new inter-laboratory test programme. The precision statement for % (m/m) PAHs, as defined by EN 590: 2004 [1], is now included.

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

1 Scope

This European Standard specifies a test method for the determination of the content of mono-aromatic, di-aromatic and tri+-aromatic hydrocarbons in diesel fuels that may contain fatty acid methyl esters (FAME) up to 5 % (V/V) and petroleum distillates in the boiling range from 150 °C to 400 °C. The polycyclic aromatic hydrocarbons content is calculated from the sum of di-aromatic and tri+-aromatic hydrocarbons and the total content of aromatic compounds is calculated from the sum of the individual aromatic hydrocarbon types.

Compounds containing sulfur, nitrogen and oxygen may interfere in the determination; mono-alkenes do not interfere, but conjugated di-alkenes and polyalkenes, if present, may do so.

The precision statement of the test method has been established for diesel fuels with and without FAME blending components, with a mono-aromatic content in the range from 6 % (m/m) to 30 % (m/m), a di-aromatic content from 1 % (m/m) to 10 % (m/m), a tri+-aromatic content from 0 % (m/m) to 2 % (m/m), a polycyclic aromatic content from 1 % (m/m) to 12 % (m/m), and a total aromatic content from 7 % (m/m) to 42 % (m/m).

NOTE 1 For the purpose of this European Standard, the terms “% (m/m)” and “% (V/V)” are used to represent the mass fraction, and the volume fraction of a material respectively.

NOTE 2 By convention, the aromatic hydrocarbon types are defined on the basis of their elution characteristics from the specified liquid chromatography column relative to model aromatic compounds. Their quantification is performed using an external calibration with a single aromatic compound for each of them, which may or may not be representative of the aromatics present in the sample. Alternative techniques and test methods may classify and quantify individual aromatic hydrocarbon types differently.

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 to determine the applicability of regulatory limitations prior to use.

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2 Normative references

The following referenced documents are indispensable for the application 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 14214, *Automotive fuels – Fatty acid methyl esters (FAME) for diesel engines – Requirements and test methods*

EN ISO 1042, *Laboratory glassware – One-mark volumetric flasks (ISO 1042:1998)*

EN ISO 3170, *Petroleum liquids – Manual sampling (ISO 3170:2004)*

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

3 Terms and definitions

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

3.1 non-aromatic hydrocarbon
compound having a shorter retention time on the specified polar column than the majority of mono-aromatic hydrocarbons

3.2**mono-aromatic hydrocarbon****MAH**

compound having a longer retention time on the specified polar column than the majority of non-aromatic hydrocarbons, but a shorter retention time than the majority of di-aromatic hydrocarbons

3.3**di-aromatic hydrocarbon****DAH**

compound having a longer retention time on the specified polar column than the majority of mono-aromatic hydrocarbons, but a shorter retention time than the majority of tri+-aromatic hydrocarbons

3.4**tri+-aromatic hydrocarbon****T+AH**

compound having a longer retention time on the specified polar column than the majority of di-aromatic hydrocarbons, but a shorter retention time than chrysene

3.5**polycyclic aromatic hydrocarbon****POLY-AH**

sum of the di-aromatic hydrocarbons and tri+-aromatic hydrocarbons

3.6**total aromatic hydrocarbon**

sum of the mono-aromatic hydrocarbons, di-aromatic hydrocarbons and tri+-aromatic hydrocarbons

NOTE Published and unpublished data indicate that the major constituents for each hydrocarbon type may include:

- a) non-aromatic hydrocarbons: acyclic and cyclic alkanes (paraffins and naphthenes), mono-alkenes (if present),
- b) MAHs: benzenes, tetralins, indanes and higher naphthenobenzenes (e.g. octahydrophenanthrenes), thiophenes, styrenes, conjugated polyalkenes,
- c) DAHs: naphthalenes, biphenyls, indenenes, fluorenes, acenaphthenes, benzothiophenes and dibenzothiophenes,
- d) T+AHs: phenanthrenes, pyrenes, fluoranthenes, chrysenes, triphenylenes, benzanthracenes.

3.7**fatty acid methyl ester****FAME**

mixture of fatty acid methyl esters as specified in EN 14214

4 Principle

A known mass of sample is diluted with heptane and a fixed volume of this solution injected into a high performance liquid chromatograph fitted with a polar column. This column has little affinity for non-aromatic hydrocarbons, whilst exhibiting a strong selectivity for aromatic hydrocarbons. As a result of this selectivity, the aromatic hydrocarbons are separated from the non-aromatic hydrocarbons and into distinct bands according to their ring structure, i.e. MAH, DAH and T+AH compounds.

The column is connected to a refractive index detector which detects the components as they elute from the column. The electronic signal from the detector is continually monitored by a data processor. The amplitudes of the signals from the aromatics in the sample are compared with those obtained from calibration standards in order to calculate the mass fraction of MAHs, DAHs and T+AHs in the sample. The sum of the DAHs and T+AHs mass fractions is reported as the mass fraction of POLY-AH, and the sum of the MAHs, DAHs and T+AHs mass fractions is reported as the mass fraction of total aromatic hydrocarbons.

5 Reagents and materials

NOTE The highest purity reagents and materials available should be used; those required to be of high performance liquid chromatography (HPLC) grade are commercially available from major suppliers.

5.1 Cyclohexane, of 99 % (*m/m*) minimum purity

NOTE Cyclohexane may contain benzene as an impurity.

5.2 Heptane, HPLC analytical grade, as the mobile phase

NOTE 1 Batch to batch variation of the solvent water content, viscosity, refractive index, and purity may cause unpredictable column behaviour. Drying (for example, by standing over activated molecular sieve type 5A) and filtering the mobile phase may help reducing the effect of trace impurities present in the solvent.

NOTE 2 It is recommended practice to de-gas the mobile phase before use; this can be done conveniently on-line or off-line by helium sparging, vacuum degassing or ultrasonic agitation. A failure to de-gas the mobile phase may lead to negative peaks.

5.3 1-Phenyldodecane, of 98 % (*m/m*) minimum purity

5.4 1,2-Dimethylbenzene (*o*-xylene), of 98 % (*m/m*) minimum purity

5.5 Hexamethylbenzene, of 98 % (*m/m*) minimum purity

5.6 Naphthalene, of 98 % (*m/m*) minimum purity

5.7 Fluorene, of 98 % (*m/m*) minimum purity

5.8 Phenanthrene, of 98 % (*m/m*) minimum purity

5.9 Dibenzothiophene, of 95 % (*m/m*) minimum purity

5.10 9-Methylanthracene, of 95 % (*m/m*) minimum purity

5.11 Chrysene, of 95 % (*m/m*) minimum purity

5.12 FAME (see 3.7)

WARNING — Protective gloves should be worn when handling aromatic compounds.

6 Apparatus

6.1 Liquid chromatograph, consisting of a high performance instrument capable of pumping the mobile phase at flow rates from 0,5 ml/min to 1,5 ml/min, with a precision better than 0,5 % and a pulsation of < 1 % full scale deflection under the test conditions described in Clause 8.

6.2 Sample injection system, capable of nominally injecting 10 µl of sample solution with a repeatability better than 1 %.

NOTE 1 Equal and constant volumes of the calibration and sample solutions are injected into the chromatograph. Both manual and automatic sample injection systems, using either complete or partial filling of the sample loop, can meet these repeatability requirements when used correctly. When using the partial filling mode, it is recommended that the injection volume is less than half the total loop volume. For complete filling of the loop, best results are obtained by overfilling the loop at least six times.

The repeatability of the injection system may be checked by comparing peak areas from at least four injections of the system calibration standard (see 8.3).

NOTE 2 Sample and calibration injection volumes different from 10 μl (typically in the range 3 μl to 20 μl) may be used provided they meet the requirements for injection repeatability, refractive index sensitivity and linearity (see 9.4), and column resolution (see 8.9).

6.3 Sample filter, if required (see 10.1), consisting of a microfilter of porosity 0,45 μm or less, chemically inert towards hydrocarbon solvents, for the removal of particulate matter from the sample solutions.

NOTE PTFE filters have been found to be suitable.

6.4 Column system, consisting of a stainless steel HPLC column(s) packed with a commercial 3 μm , 5 μm or 10 μm amino-bonded (or amino/cyano-bonded) silica stationary phase meeting the resolution requirements given in 8.6, 8.7 and 8.9. See Annex A for guidance on the selection and use of suitable column systems.

6.5 Temperature control, consisting of either a heating block, or an air-circulating HPLC column oven or an alternative form of temperature control, such as a temperature-controlled laboratory, capable of maintaining a constant temperature in the range 20 $^{\circ}\text{C} \pm 1$ $^{\circ}\text{C}$ to 40 $^{\circ}\text{C} \pm 1$ $^{\circ}\text{C}$.

NOTE The refractive index detector is sensitive to both sudden and gradual changes in the temperature of the eluent. All necessary precautions should be taken to establish constant temperature conditions throughout the liquid chromatograph system. The temperature should be optimised depending on the stationary phase.

6.6 Refractive index detector, capable of being operated over the refractive index range 1,3 to 1,6 and giving a linear response over the calibration range with a suitable output signal for the data system.

NOTE If the detector is equipped with a device for independent temperature control, it is recommended that it is set at the same temperature as the column oven.

6.7 Computer or computing integrator, compatible with the refractive index detector, having a minimum sampling rate of 1 Hz and capable of peak area and retention time measurements. It shall also have minimum capabilities for post-analysis data processing such as baseline correction and re-integration.

NOTE The ability to perform automatic peak detection and identification and to calculate sample concentrations from peak area measurements is recommended, but is not essential.

6.8 Volumetric flasks, 10 ml and 100 ml capacity, conforming to grade A of EN ISO 1042.

6.9 Analytical balance, capable of weighing to the nearest 0,000 1 g.

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 the product under test.

8 Apparatus preparation

8.1 Set up the liquid chromatograph (6.1), sample injection system (6.2), column (6.4), refractive index detector (6.6) and computing integrator (6.7) in accordance with the manufacturer's manuals. If a column oven is used (6.5), install the HPLC column in the column oven. Maintain the sample injection system at the same temperature as the sample solution; in most cases this should be at room temperature.

NOTE Regular maintenance of the liquid chromatograph and its components is important to ensure consistent performance. Leakages and partial blockage of filters, frits, injector needles and valve rotors can produce flow rate inconsistencies and poor injector repeatability.