
Naftni proizvodi - Določevanje aromatskih ogljikovodikov v srednjih destilatih - Metoda tekočinske kromatografije visoke ločljivosti z detekcijo lomnega količnika

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 - Hochleistungsflüssigkeitschromatographie-Verfahren mit Brechzahl-Detektion

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

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European foreword

This document (prEN 12916:2023) 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.

The document is currently submitted to the CEN Enquiry.

This document will supersede EN 12916:2019+A1:2022.

Major change compared to the previous version EN 12916:2019+A1:2022 of edition EN 12916:2019 is the addition of an Annex C with instructions on determination of tri+-aromatics and additional sampling requirements. This should improve lab precision when testing paraffinic diesel products. Next, the practical instructions for these type of samples in Annex B have been improved and exemplary chromatograms have been introduced. The instructions on storage precautions after sampling have been restricted to paraffinic diesel products only.

The addition of a calibration procedure with reference material ensures better results for all products. Furthermore, a study executed in 2021 has delivered confirmation of the published precision for PAH and DAH for concentration range from (6 – 10) % (*m/m*).

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prEN 12916:2023 (E)

1 Scope

This document specifies a test method for the determination of the content of mono-aromatic, di-aromatic and tri+-aromatic hydrocarbons in diesel fuels, paraffinic diesel fuels and petroleum distillates.

This document defines two procedures, A and B.

Procedure A is applicable to diesel fuels that may contain fatty acid methyl esters (FAME) up to 30 % (V/V) (as in [1], [2] or [3]) and petroleum distillates in the boiling range from 150 °C to 400 °C (as in [4]).

Procedure B is applicable to paraffinic diesel fuels with up to 7 % (V/V) FAME. This procedure does not contain a dilution of the sample in order to determine the low levels of aromatic components in these fuels.

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 can interfere in the determination; mono-alkenes do not interfere, but conjugated di-alkenes and poly-alkenes, if present, can do so. The measurement ranges that apply to this method are given in Table 2 and Table 3.

NOTE 1 For the purpose of this document, the terms “% (m/m)” and “% (V/V)” are used to represent the mass fraction, μ , and the volume fraction, φ , 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 can be representative of the aromatics present in the sample. Alternative techniques and test methods can classify and quantify individual aromatic hydrocarbon types differently.

NOTE 3 Backflush is part of laboratory-internal maintenance.

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 responsibility of users of this document 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 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 14214, *Liquid petroleum products — Fatty acid methyl esters (FAME) for use in diesel engines and heating applications — Requirements and test methods*

EN ISO 1042, *Laboratory glassware — One-mark volumetric flasks (ISO 1042)*

EN ISO 3170, *Petroleum liquids — Manual sampling (ISO 3170)*

EN ISO 3171, *Petroleum liquids — Automatic pipeline sampling (ISO 3171)*

3 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 <http://www.electropedia.org/>
- ISO Online browsing platform: available at <http://www.iso.org/obp>

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 including 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 1 to entry: Published and unpublished data indicate that the major constituents for each hydrocarbon type include:

- a) non-aromatic hydrocarbons: cyclic and acyclic 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, benzantracenes.

prEN 12916:2023 (E)**3.7****fatty acid methyl ester****FAME**

mixture of fatty acid methyl esters derived from vegetable oil or animal fats and complying to the specification defined in EN 14214

4 Principle

A known mass of sample is taken and a fixed volume of this sample is injected into a high performance liquid chromatograph fitted with a polar column. Diesel fuels with a concentration of FAME up to 30 % (V/V) and petroleum distillates need to be diluted with heptane (Procedure A). Paraffinic diesel fuels are injected neat (Procedure B).

This column has little affinity for non-aromatic hydrocarbons, while 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.

When following Procedure A, the column may be backflushed after the aromatics have eluted from the column to allow any remaining components such as FAME to elute in a backflush peak. This will allow for a better cleaning of the column but care should be taken as it can affect the lifetime of the column.

5 Reagents and materials

WARNING — Aromatic compounds can be volatile and flammable, their vapours can form explosive mixtures with the air, and they can cause acute or chronic harm when inhaled or in case of contact with the skin. In addition, they can be water polluting.

5.1 General

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.

5.2 Cyclohexane, of 99 % (*m/m*) minimum purity (CAS registry number 110-82-7).

NOTE Cyclohexane can contain benzene as an impurity.

5.3 Heptane, HPLC analytical grade, as the mobile phase (CAS registry number 142-82-5).

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

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

5.4 1-Phenyldodecane, of 98 % (*m/m*) minimum purity (CAS registry number 123-01-3).

- 5.5 **1,2-Dimethylbenzene (*o*-xylene)**, of 98 % (*m/m*) minimum purity (CAS registry number 95-47-6).
- 5.6 **Hexamethylbenzene**, of 98 % (*m/m*) minimum purity (CAS registry number 87-85-4).
- 5.7 **Naphthalene**, of 98 % (*m/m*) minimum purity (CAS registry number 91-20-3).
- 5.8 **Fluorene**, of 98 % (*m/m*) minimum purity (CAS registry number 86-73-7).
- 5.9 **Phenanthrene**, of 98 % (*m/m*) minimum purity (CAS registry number 85-01-8).
- 5.10 **Dibenzothiophene**, of 95 % (*m/m*) minimum purity (CAS registry number 132-65-0).
- 5.11 **9-Methylanthracene**, of 95 % (*m/m*) minimum purity (CAS registry number 779-02-2).
- 5.12 **Chrysene**, of 95 % (*m/m*) minimum purity (CAS registry number 218-01-9).
- 5.13 **FAME**, compliant to EN 14214.
- 5.14 **Reference Material (RM)**, samples used as reference, and which contain aromatic hydrocarbons at concentration levels comparable to those of the test sample.

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. Make sure that the equipment for handling or testing the sample is not sensitive to FAME. Recommended materials are Polytetrafluoroethylene, Viton®¹ and Nylon.

6.2 **Sample injection system**, capable of nominally injecting 10 µl of sample solution with a repeatability better than 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 can be checked by comparing peak areas from at least four injections of the system calibration standard (see 8.4).

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 8.10).

¹ Viton® is the trademark of a fluoroelastomer supplied by the Chemours Company, Wilmington, Delaware 19899 (USA). This information is given for the convenience of users of this document and does not constitute an endorsement by CEN of the product named. Equivalent products may be used if they can be shown to lead to the same results.

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6.3 Sample filter, if required (see 10.1 and 10.2), 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 Polytetrafluorethylene (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 8.7, 8.8, 8.10 and 8.12. See Annex A for guidance on the selection and use of suitable column systems.

6.5 Temperature controls, for different parts of the apparatus (column, sample injection system, solvent, refractive index detector). Maintain the sample injection system at the same temperature as the sample solution, for the column a heating block or an air-circulating HPLC column oven may be used. Also, a temperature-controlled laboratory, capable of maintaining a constant temperature in the range $(20 \pm 1) ^\circ\text{C}$ to $(40 \pm 1) ^\circ\text{C}$ may be used.

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 optimized 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 ranges with a suitable output signal for the data system.

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.

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 0,1 mg.

7 Sampling

7.1 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.

7.2 Paraffinic diesel fuel samples analysed according to Procedure B require additional storage conditions, as follows.

A storage temperature of $19 ^\circ\text{C} \pm 5 ^\circ\text{C}$ shall be maintained. If for some reason, the samples have been exposed to temperatures above $25 ^\circ\text{C}$ for a long period during storage or in custody (that you are aware of), this shall be reported.

At least 24 h before a test the blend shall be placed at ambient temperature.

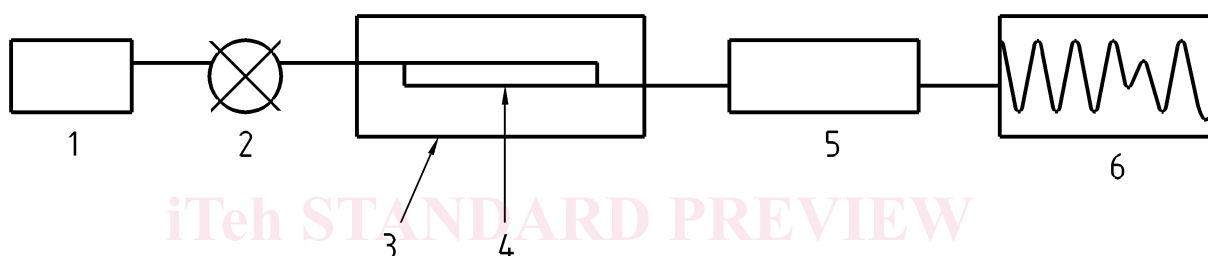
After finishing the tests completely, replace the air by nitrogen or any noble gas before closing the container tightly.

8 Apparatus preparation

8.1 Ensure that the equipment and any sample distribution system is clean and dry before use.

8.2 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) as in Figure 1 and 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.

Regular maintenance of the liquid chromatograph and its components is important and thus recommended 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.



Key

1	pump	4	column
2	injection device	5	refractive index detector
3	oven	6	data acquisition system

Figure 1 — Diagrammatic representation of a liquid chromatograph

8.3 Adjust the flow rate of the mobile phase to a constant between 0,8 ml/min and 1,2 ml/min. Allow the temperature of the column and of the refractive index detector, if it is equipped with temperature control, to stabilize.

In order to minimize instrument drift, the reference cell of the detector should be filled with mobile phase, either by flushing mobile phase through the reference cell immediately prior to the analysis, and then isolating the reference cell to prevent evaporation, or by compensating for evaporation by supplying a steady flow of mobile phase through the reference cell. The flow should be optimized so that cell mismatch due to drying-out (reference cell) or temperature or pressure gradients (reference or analysis cells, depending the type of detector) are minimized; with some detectors this can be accomplished using a mobile phase flow through the reference cell of one tenth of that through the analysis cell.

8.4 Prepare into a 100 ml volumetric flask (6.8) a system calibration standard 1 (SCS1) by weighing to the nearest 0,000 1 g:

- (1,0 ± 0,1) g cyclohexane (5.2),
- (0,1 ± 0,01) g 1-phenyldodecane (5.4),
- (0,5 ± 0,05) g 1,2-dimethylbenzene (5.5),