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BSI Standards Publication

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

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National foreword

This British Standard is the UK implementation of EN 12916:2016. It supersedes BS EN 12916:2006 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee PTI/15, Natural Gas and Gas Analysis.

A list of organizations represented on this committee can be obtained on request to its secretary.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

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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 dans les distillats moyens - Méthode par chromatographie liquide à haute performance avec détection par réfractométrie différentielle

Mineralölerzeugnisse - Bestimmung von aromatischen Kohlenwasserstoffgruppen in Mitteldestillaten - Hochleistungsflüssigkeitschromatographie-Verfahren mit Brechzahl-Detektion

This European Standard was approved by CEN on 13 December 2015.

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European foreword

This document (EN 12916:2016) 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of an identical text or by endorsement, at the latest by August 2016, and conflicting national standards shall be withdrawn at the latest by August 2016.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document supersedes EN 12916:2006.

The third version of the method has been updated to extend the scope of the method beyond the common diesel products to middle distillates with FAME contents up to 30 % (V/V) on the basis of the results of a study performed on B5, B10, and B30 samples. As the procedure remains unchanged, the precision statement from the previous version is still valid.

Additionally the method allows the use of a backflush to clean the column once the tri+-aromatics have been eluted.

According to the CEN-CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the 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 30 % *(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 can interfere in the determination; mono-alkenes do not interfere, but conjugated di-alkenes and poly-alkenes, 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 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 users of this standard 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, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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.

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 1 to entry: 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, indenes, 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 derived from vegetable oil or animal fats and complying to the specification defined 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, 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.

After the aromatics have eluted from the column it may be backflushed 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

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 RN 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 may 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 RN 123-01-3)

5.5 1,2-Dimethylbenzene (*o*-xylene), of 98 % *(m/m)* minimum purity (CAS RN 95-47-6)

5.6 Hexamethylbenzene, of 98 % *(m/m)* minimum purity (CAS RN 87-85-4)

5.7 Naphthalene, of 98 % *(m/m)* minimum purity (CAS RN 91-20-3)

5.8 Fluorene, of 98 % *(m/m)* minimum purity (CAS RN 86-73-7)

5.9 Phenanthrene, of 98 % *(m/m)* minimum purity (CAS RN 85-01-8)

5.10 Dibenzothiophene, of 95 % *(m/m)* minimum purity (CAS RN 132-65-0)

5.11 9-Methylanthracene, of 95 % *(m/m)* minimum purity (CAS RN 779-02-2)

5.12 Chrysene, of 95 % *(m/m)* minimum purity (CAS RN 218-01-9)

5.13 FAME, compliant to EN 14214

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 %.

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).

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 polytetrafluorethyleen (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, 8.9 and 8.11 . 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 can be used. Also, a temperature-controlled laboratory, capable of maintaining a constant temperature in the range (20 ± 1)°C to (40 ± 1)°C can 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 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 ranges 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, with an accuracy of ± 0,000 1 g.

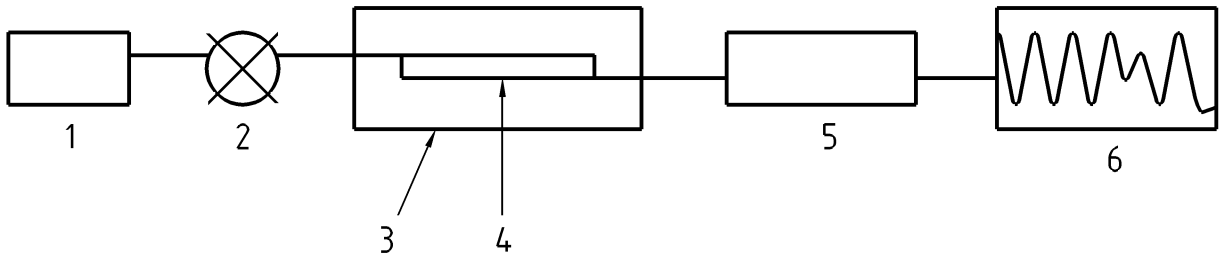
7 Sampling

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.



Key

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

Figure 1 — Diagrammatic representation of a liquid chromatograph

8.2 Adjust the flow rate of the mobile phase to a constant between 0,8 ml/min and 1,2 ml/min and ensure the reference cell of the refractive index detector is full of mobile phase. 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.

8.3 Prepare into a 100 ml volumetric flask a system calibration standard 1 (SCS1) by weighing, to the nearest 0,001 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),

— (0,1 ± 0,01) g hexamethylbenzene (5.6),

— (0,1 ± 0,01) g naphthalene (5.7),

— (0,05 ± 0,005) g dibenzothiophene (5.10), and

— (0,05 ± 0,005) g 9-methylanthracene (5.11).

Place the flask and its contents into an ultrasonic bath until a visual examination shows that all the components have dissolved into the 1,2 dimethylbenzene/cyclohexane mixture. Remove from the ultrasonic bath and make up to the mark with heptane.

The SCS1 may be kept for at least one year if stored in a tightly stoppered bottle in a cool dark place (for example in a refrigerator).

8.4 Prepare into a 100 ml volumetric flask a system calibration standard 2 (SCS2) by weighing, to the nearest 0,001 g, (0,4 ± 0,1) g FAME (5.13) and (0,04 ± 0,01) g chrysene (5.12) and making up to the mark with heptane (5.3). Keep the solution into an ultrasonic bath at 35 °C.

Ensure the appearance is homogeneous without deposits of chrysene on the bottom.

NOTE 25 min has been found to be a suitable time for all the components to become dissolved.

The SCS2 may be kept for at least one year if stored in a tightly stoppered bottle in a cool dark place (for example in a refrigerator).

8.5 When operating conditions are steady, as indicated by a stable horizontal baseline, inject 10 µl of the SCS1 (8.3). Ensure the baseline drift over the period of the HPLC analysis run is less than 1 % of the peak height for cyclohexane.

NOTE A baseline drift greater than this indicates problems with the temperature control of the column/refractive index detector and/or material eluting from the column.

8.6 Ensure the components of the SCS1 are eluted in the order: cyclohexane, phenyldodecane, 1,2 dimethylbenzene, hexamethylbenzene, naphthalene, dibenzothiophene and 9-methylanthracene.

8.7 Ensure that baseline separation is obtained between all components of the SCS1 (see Figure 2).

8.8 Measure the retention times of the cyclohexane, phenyldodecane, 1,2 dimethylbenzene, hexamethylbenzene, dibenzothiophene and 9-methylanthracene peaks using the data system.

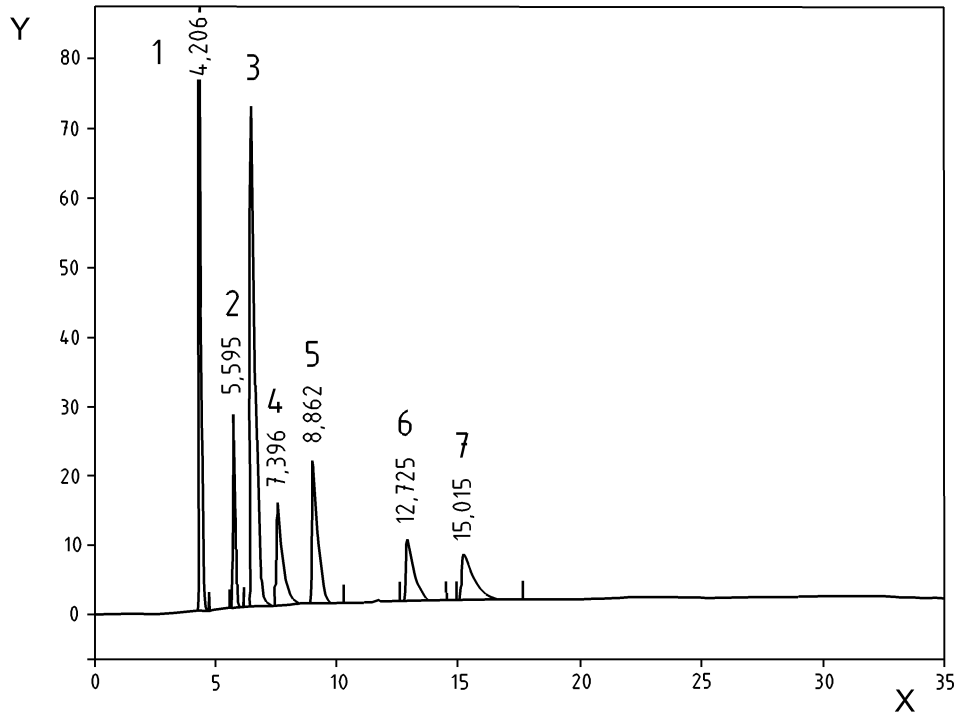
8.9 Ensure that the resolution between cyclohexane and 1,2 dimethylbenzene is between 5,7 and 10 (see 11.2).

8.10 Calculate the cut times using the equations given in 11.3.

8.11 Ensure the appearance of SCS2 is homogeneous (8.4) and then, inject 10 µl of the SCS2 and check the chrysene peak elutes just before or together with the first peak of FAME.

Ensure the retention time of chrysene peak be higher than the retention time of 9-methylanthracene peak.

Test the column with the SCS2 to verify its performances when starting the method with a new column, after a period of time of inactivity or when samples with FAME should be run.



Key

1	cyclohexane	5	naphthalene
2	phenyldodecane	6	dibenzothiophene
3	1,2 dimethylbenzene	7	9-methylanthracene
4	hexamethylbenzene		
x-axis	time (min)		
y-axis	signal (mV)		

Figure 2 — Chromatogram of the system calibration standard SCS1

9 Calibration

9.1 Prepare four calibration standards referenced A, B, C and D at the approximate (but accurately known) concentrations given in Table 1, by weighing the appropriate materials to the nearest 0,000 1 g into 100 ml volumetric flasks and making up to the mark with heptane (5.3).

NOTE The calibration standards are viable for at least six months if stored in tightly stoppered containers (e.g. 100 ml volumetric flasks) in a cool dark place (for example, in a refrigerator).

9.2 When operating conditions are steady (see 8.5), inject 10 µl of calibration standard A. Record the chromatogram and measure the peak areas for each aromatic standard (see Figure 3).

Table 1 — Concentrations of calibration standard components

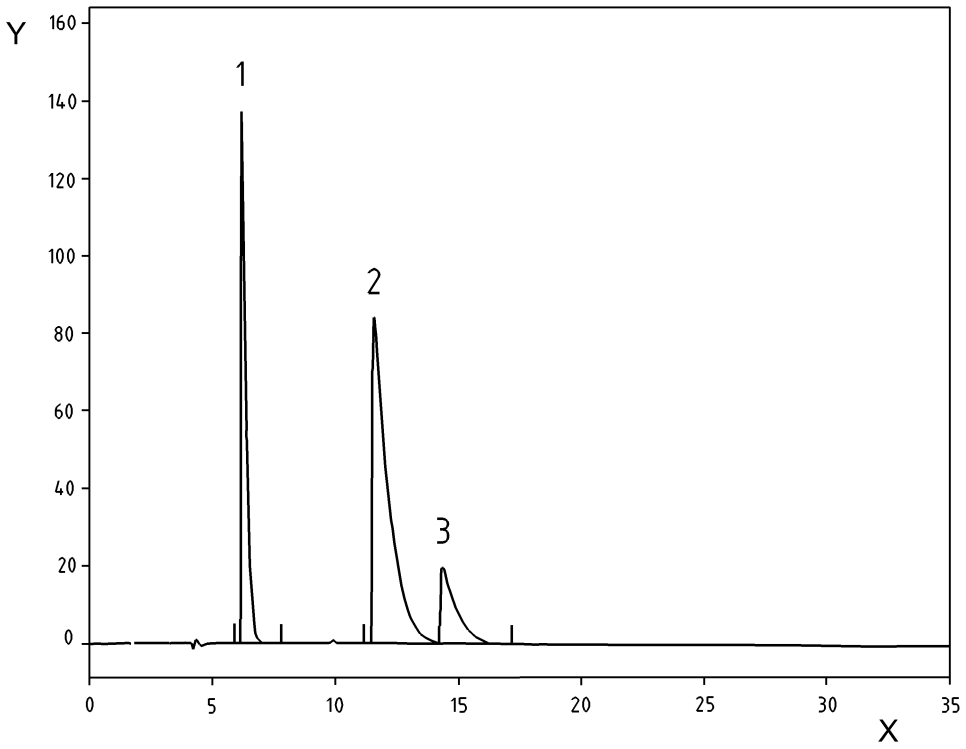
Calibration standard	**1,2 Dimethylbenzene** g/100 ml	**Fluorene** g/100 ml	**Phenanthrene** g/100 ml
A	4,0	2,0	0,4
B	1,0	1,0	0,2
C	0,25	0,25	0,05
D	0,05	0,02	0,01

9.3 Repeat 9.2 for each of the other calibration standards B, C and D.

If the peak area for phenanthrene in calibration standard D is too small to be accurately measured, prepare a new calibration standard, D^+, with a higher concentration of phenanthrene, e.g. 0,02 g/100 ml, and repeat 9.2.

9.4 Plot concentrations in g/100 ml against area counts for each aromatic standard, i.e. 1,2 dimethylbenzene, fluorene and phenanthrene.

The calibration functions shall be regarded as correct only if the correlation coefficient is greater than 0,999 and the intercept is between ± 0,01 g/100 ml. A computer or data system may be used to perform these calibrations.



Key

1	1,2 dimethylbenzene	x-axis	time (min)
2	fluorene	y-axis	signal (mV)
3	phenanthrene		

Figure 3 — Chromatogram of calibration standard

10 Procedure

10.1 Weigh between 0,9 g and 1,1 g of sample to the nearest 0,001 g into a 10 ml volumetric flask and make up to the mark with heptane (5.3). Shake thoroughly to mix. Allow the solution to stand for 10 min and, if necessary, use a filter to remove insoluble material (6.3).

For samples where the concentration of one or more aromatic hydrocarbon types falls outside the calibration range, prepare a more concentrated (2 g/10 ml) or more dilute (0,5 g/10 ml) sample solution, as appropriate.

NOTE If another dilution factor than the one suggested is used, it can modify the retention time and the amount calculated.

10.2 When operating conditions are steady (see 8.5) and identical to those used for obtaining the calibration data (Clause 9), inject 10 µl of the sample solution (10.1) and start data collection.

10.3 Identify correctly the MAHs, DAHs and T+AHs:

— MAH are compounds having a retention time between t_b and t_c (see 11.3);

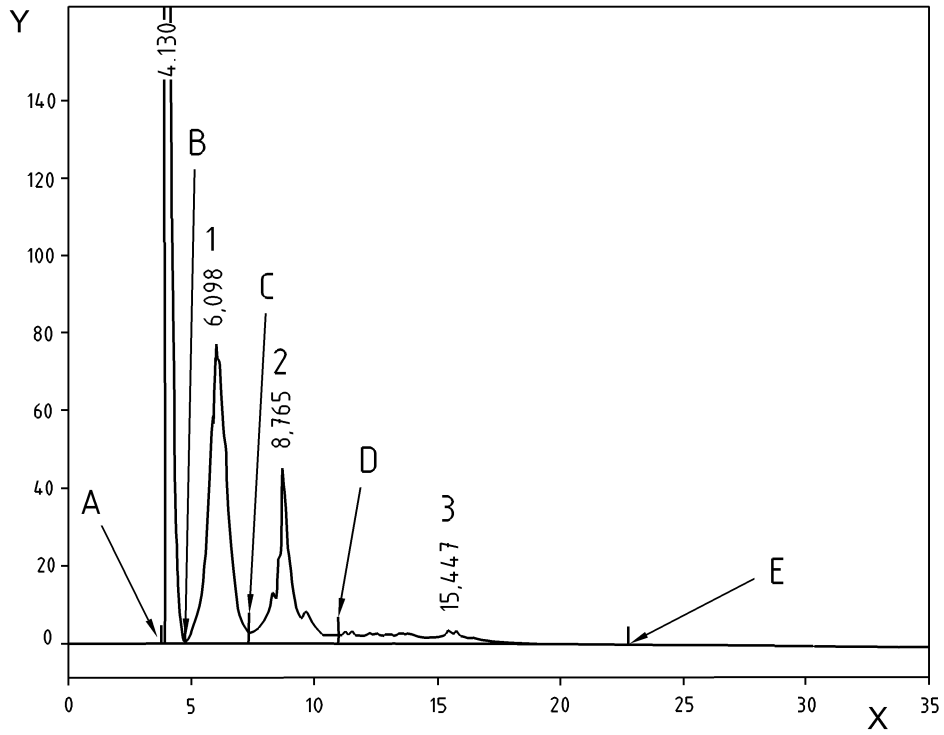
— DAH are compounds having a retention time between t_c and t_d (see 11.3);

— T+AH are compounds having a retention time between t_d and t_e (see 11.3).

10.4 After the aromatics have eluted from the column it may be backflushed to allow any remaining components such as FAME to elute in a backflush peak.

Backflushing allows for a better cleaning of the column but care should be taken as it can affect the lifetime of the column.

10.5 Draw a line from just before the beginning of the non-aromatics peak (point A, t_a, in Figure 4) to a point on the chromatogram immediately after the T+AHs (point E, t_e, in Figure 4), where the signal has returned to its baseline value (i.e. the signal at point A after allowance has been made for any baseline drift, 8.5).



Key

1	mono-aromatic hydrocarbons (MAH)	x-axis	time (min)
2	di-aromatic hydrocarbons (DAH)	y-axis	signal (mV)
3	tri+-aromatic hydrocarbons (T+AH)	A	start of non-aromatic fraction, t_a
B	start of MAH fraction, t_b	C	valley between MAH and DAH, t_c
D	valley between DAH and T+AH, t_d	E	End of integration area, t_e

Figure 4 — Chromatogram with the peaks identified and showing the integration

If DAHs and/or T+AHs are not present in the sample then point E shall be selected at an earlier retention time provided the signal has returned to its baseline value (i.e. the signal at point A after allowance has been made for any baseline drift, 8.5).

10.6 Drop a vertical line from the valley between the non-aromatics and MAHs (point B, t_b, in Figure 4) to the baseline (10.5). If several valleys are present, use the nearest-one from the time t_b (see 11.3).

10.7 Drop a vertical line from the valley between the MAHs and DAHs (point C, t_c in Figure 4) to the baseline (10.5). If several valleys are present, use the nearest-one from the time t_c (see 11.3).

10.8 Drop a vertical line from the valley between the DAHs and T+AHs (point D,t_d, in Figure 4) to the baseline (10.5). If several valleys are present, use the nearest-one from the time t_d (see 11.3). If no valley is present, use t_d.

10.9 Integrate the area due to MAHs from points B to C.

10.10 Integrate the area due to DAHs from points C to D.

10.11 Integrate the area due to T+AHs from points D to E.

10.12 If the chromatographic data have been processed automatically, check visually that the integration parameters have correctly identified and integrated the peaks.

11 Calculation

11.1 Retention times

Retention times to be measured from the chromatogram of SCS1 (8.8) are:

— the retention time of cyclohexane (t_1), in seconds;

— the retention time of 1-phenyldodecane (t_2), in seconds;

— the retention time of 1,2 dimethylbenzene (t_3), in seconds;

— the retention time of hexamethylbenzene (t_4), in seconds;

— the retention time of dibenzothiophene (t_6), in seconds;

— the retention time of 9-methylanthracene (t_7), in seconds.

11.2 Column resolution

Calculate the resolution, *CR*, between cyclohexane and 1,2 dimethylbenzene using the following formula.

$$CR = \frac{2\left(t_3 - t_1\right)}{1{,}699\left(y_1 + y_3\right)} \quad (1)$$

where

y_1 is the width at half-height of the cyclohexane peak, in seconds;

y_3 is the width at half-height of the 1,2 dimethylbenzene peak, in seconds.

11.3 Cut times

Determine the cut times, t_a, t_b,, t_c, t_d, and t_e, in seconds, using the following:

t_a is a point on the baseline just before the non-aromatic peak;

t_b is $0{,}5\left(t_1 + t_2\right)$;

t_c is t_4;

t_d is $t_6 + 0{,}4(t_7 - t_6)$;

t_e is a point on the baseline when all T+AHs have been eluted.

NOTE For samples that contain FAME, t_e is a point on the baseline just before the first peak of FAME.

11.4 Aromatic hydrocarbons type content

Determine the content, C, as mass fraction, of MAHs, DAHs and T+AHs, either directly from the data system, or calculated using the following formula:

$$C = \frac{\left[\left(A \times S\right) + I\right] \times V}{M} \qquad (2)$$

where

A is the MAH or DAH or T+AH peak area of the sample;

S is the slope of the MAH or DAH or T+AH calibration plot (concentration in g/100 ml versus peak area);

I is the intercept of the MAH or DAH or T+AH calibration plot;

M is the mass of sample taken, in grams (10.1);

V is the volume of sample solution, in millilitres (10.1).

11.5 Polycyclic and total aromatic hydrocarbons content

Calculate the polycyclic aromatic hydrocarbons content of the sample, as a mass fraction, from the sum of the di and tri+-hydrocarbons types contents (i.e. DAHs and T+AHs), and the total aromatic hydrocarbons content of the sample, as a mass fraction, from the sum of the individual hydrocarbons types (i.e. MAHs, DAHs and T+AHs).

12 Expression of results

Report the MAH, DAH, T+AH, POLY-AH and total aromatic hydrocarbons content to the nearest 0,1 % (*m/m*).

13 Precision

13.1 General

The precision as determined by statistical examination of inter-laboratory test results in accordance with EN ISO 4259 [2] is given in 13.2 and 13.3.

13.2 Repeatability *r*

The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, in the normal and correct operation of the test method, would in the long run exceed the values given in Table 2 only in one case in twenty.

13.3 Reproducibility *R*

The difference between two single and independent results, obtained by different operators working in different laboratories on nominally identical test material, in the normal and correct operation of the test method, would in the long run exceed the values given in Table 2 only in one case in twenty.

Table 2 — Precision values

Aromatic type	**Measurement Range** % (*m/m*)	**Repeatability** % (*m/m*)	**Reproducibility** % (*m/m*)
Mono-aromatic hydrocarbons (MAH)	6 - 30	0,032 *X* – 0,161	0,144 *X* – 0,344
Di-aromatic hydrocarbons (DAH)	1 - 10	0,151 *X* – 0,036	0,363 *X* – 0,087
Tri+- aromatic hydrocarbons (T+AH)	0 - 2	0,092 *X* + 0,098	0,442 *X* + 0,471
Polycyclic aromatic hydrocarbons (POLY-AH)	1 - 12	0,074 *X* + 0,186	0,185 *X* + 0,465
Total aromatic hydrocarbons	7 - 42	0,040 *X* – 0,070	0,172 *X* – 1,094
NOTE *X* is the mean of two results being compared.			

14 Test report

The test report shall include at least the following information:

a) type and identification of the product under test;

b) reference to this European Standard, i.e. EN 12916;

c) results of the test (see Clause 12);

d) any deviation, by agreement or otherwise, from the procedure specified;

e) date of the test.

Annex A
(informative)
Column selection and use

Column lengths of 150 mm to 300 mm with an internal diameter of 4 mm to 5 mm have been found to be satisfactory. It is good practice to protect the analytical column by using a guard column (e.g. 30 mm by 4,6 mm ID packed with amino-silica) and replacing it regularly.

Batch to batch variations, in terms of resolution and aromatic hydrocarbon type selectivity, have been noted for some commercial stationary phases. Laboratories are advised to test individual columns prior to purchase to ensure they meet the resolution and selectivity requirements of this standard.

New columns will typically be shipped in a solvent different from the mobile phase used in this standard and should be conditioned by purging the column with the mobile phase (heptane). A minimum of two hours conditioning at 1 ml/min is recommended but longer periods of up to two days are sometimes necessary. Alternatively, a reduced flow rate (e.g. 0,25 ml/min) for a minimum of 12 h (e.g. overnight) may be used.

Most of the columns used in the round robin precision study have exhibited long-term stability and column lifetimes may be two or more years. However, small changes in column performance can go undetected by an operator in the absence of appropriate quality control measures. Laboratories are advised to record, on a regular basis, the column head pressure and calibrant retention times as a simple diagnostic tool for monitoring system and column performance. Participation in inter-laboratory precision monitoring schemes and the regular use of validated and/or internal reference gas oils as part of the test procedure and column evaluation are strongly recommended.

Used columns, which do not meet the requirements of this standard, may be regenerated by flushing the column in backflush mode with a polar solvent (e.g. dichloromethane, 1 ml/min for two hours) and then re-conditioning as for a new column. Before discarding a used column, it is recommended to carefully check all other system components for leaks, dead volumes and/or partial blockage of filters, column frits, tubing, injector needles/seals and valve rotors which can also contribute to poor column performance.

Bibliography

[1] EN 590, *Automotive fuels - Diesel - Requirements and test methods*

[2] EN ISO 4259, *Petroleum products - Determination and application of precision data in relation to methods of test (ISO 4259)*

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