



SLOVENSKI STANDARD
SIST EN 12916:2000

01-julij-2000

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

iTeh STANDARD PREVIEW

Produits pétroliers - Détermination (standards.iteh.ai) des familles d'hydrocarbures dans les distillats moyens - Méthode par chromatographie liquide a haute performance avec détection par réfractométrie différentielle

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ICS:

75.080 Naftni proizvodi na splošno Petroleum products in general

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EUROPEAN STANDARD

EN 12916

NORME EUROPÉENNE

EUROPÄISCHE NORM

April 2000

ICS 75.080

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

This European Standard was approved by CEN on 22 March 2000.

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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, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.



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

Central Secretariat: rue de Stassart, 36 B-1050 Brussels

Foreword

This European Standard has been prepared by Technical Committee CEN/TC 19 "Petroleum products, lubricants and related products", the secretariat of which is held by NNI.

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of an identical text or by endorsement, at the latest by October 2000, and conflicting national standards shall be withdrawn at the latest by October 2000.

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

In this standard annex A is informative.

1 Scope

This European Standard specifies a method for the determination of the content of mono-aromatic, di-aromatic and tri+-aromatic hydrocarbons in diesel fuels and petroleum distillates boiling in the range of 150 °C to 400 °C. The total content of aromatic compounds is calculated from the sum of the corresponding individual 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.

NOTE 1 For the purpose of this European Standard, the term "% (m/m)" is used to represent the mass fraction.

NOTE 2 The precision of the method has been established for diesel fuels and their blending components containing 4 % (m/m) to 40 % (m/m) mono-aromatic hydrocarbons, 0 % (m/m) to 20 % (m/m) di-aromatic hydrocarbons, 0 % (m/m) to 6 % (m/m) tri+-aromatic hydrocarbons, 0 to 26 % (m/m) polycyclic aromatic hydrocarbons, and 4 % (m/m) to 65 % (m/m) total aromatic hydrocarbons.

NOTE 3 By convention, this standard defines the aromatic hydrocarbon types on the basis of their elution characteristics from the specified liquid chromatography column relative to model aromatic compounds. Quantification is by external calibration using a single aromatic compound, which may or may not be representative of the aromatics in the sample, for each aromatic hydrocarbon type. Alternative techniques and methods may classify and quantify individual aromatic hydrocarbon types differently.

NOTE 4 Fatty Acid Methyl Esters (FAME), if present, interfere with tri+-aromatic hydrocarbons. If this method is used for diesel containing FAME, the amount of tri+-aromatics will be over estimated.

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.

2 Normative References

This European Standard incorporates, by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are cited hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

ISO 1042, *Laboratory glassware - One-mark volumetric flasks.*

EN ISO 3170, *Petroleum liquids - Manual sampling (ISO 3170, including Amendment 1:1998).*

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

3 Definitions

For the purposes of this standard, the following definitions apply.

3.1

non-aromatic hydrocarbons

compounds having a shorter retention time on the specified polar column than the majority of mono-aromatic hydrocarbons

3.2

mono-aromatic hydrocarbons

(MAH)

compounds 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 hydrocarbons

(DAH)

compounds 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 hydrocarbons

(T+AH)

compounds having a longer retention time on the specified polar column than the majority of di-aromatic hydrocarbons

3.5

polycyclic aromatic hydrocarbons

(POLY-AH)

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

3.6

total aromatic hydrocarbons

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

NOTE The elution characteristics of aromatic and non-aromatic compounds on the specified polar column have not been determined specifically for this standard. Published and unpublished data indicate 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.

4 Principle

A known mass of sample is diluted with mobile phase (heptane). A fixed volume of this solution is injected into a high performance liquid chromatograph fitted with a polar column. This column has little affinity for non-aromatic hydrocarbons, whilst exhibiting a pronounced 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. At a predetermined time, after the elution of the DAHs, the column is backflushed to elute the T+AHs as a single sharp band.

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 monitored continually by a data processor. The amplitudes of the signals from the aromatics in the sample are compared with those obtained from previously measured calibration standards, in order to calculate the percentage by mass of MAHs, DAHs and T+AHs in the sample. The sum of the percentages by mass of the DAHs and T+AHs is reported as the percentage by mass of POLY-AH in the sample, and the sum of the percentages by mass of MAHs, DAHs and T+AHs is reported as the percentage by mass of aromatic compounds in the sample.

5 Reagents and materials

WARNING Protective gloves should be worn when handling aromatic compounds.

NOTE The highest purity reagents and materials available should be used; those required to be of "HPLC" grade (gold label) are available commercially from major suppliers.

5.1 Cyclohexane, of > 99 % purity.

NOTE Cyclohexane may contain benzene as an impurity.

5.2 Heptane, high performance liquid chromatography (HPLC) grade, as the mobile phase.

NOTE 1 Batch to batch variation of the solvent quality in terms of water content, viscosity, refractive index, and purity could cause unpredictable column behaviour. Drying and filtering the mobile phase could help to reduce the effect of the trace impurities 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 *o*-Xylene (1,2-dimethylbenzene), of > 98 % purity.

5.4 1-Methylnaphthalene, of > 98 % purity.

5.5 Phenanthrene, of > 98 % purity.

5.6 Dibenzothiophene, of > 95 % purity.

5.7 9-Methylanthracene, of > 95 % purity.

6 Apparatus

6.1 Liquid chromatograph, consisting of a high performance instrument capable of pumping the mobile phase at flow rates of between 0,5 ml/min and 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 injecting 10 μ l (nominal) of sample solution with a repeatability of 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), when used correctly, can meet these repeatability requirements. When using the partial filling mode, it is recommended that the injection volume should be 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 μ l (typically in the range 3 μ l to 20 μ l) may be used provided they meet these requirements for injection repeatability, refractive index sensitivity and linearity (see 9.4), and column resolution (see 8.6).

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

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

6.5 Temperature control, consisting of either a block heating, 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 to within ± 1 °C in the range 20 °C to 40 °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 Backflush valve, consisting of a manual, or air or electrically actuated automatic, flow-switching valve designed for use in HPLC systems, capable of operating at pressures up to 2×10^4 kPa.

6.7 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 has a facility for independent temperature control, it is recommended to set it at the same temperature as the column oven.

6.8 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 measurement. It shall also have minimum facilities 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.

6.9 Volumetric flasks, 10 ml and 100 ml capacity, conforming to ISO 1042, grade B or better.

6.10 Analytical balance, capable of weighing to the nearest $\pm 0,0001$ 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 chromatograph (6.1), injection system (6.2), column (6.4), backflush valve (6.6), refractive index detector (6.7) and computing integrator (6.8) in accordance with the manufacturers' manuals. If a column oven (6.5) is used, install the HPLC column in the column oven. Insert the backflush valve so the detector is always connected independently of the direction of flow through the column (see figure 1). Maintain the sample injection valve at the same temperature as the sample solution; in most cases this will be at room temperature.

NOTE1 It is recommended to install the backflush valve in the column oven and to install the apparatus away from draughts (i.e. not near adjacent to an air-conditioning unit or fume cupboard). Pipework and/or valving which is not temperature controlled should be insulated.

NOTE 2 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.

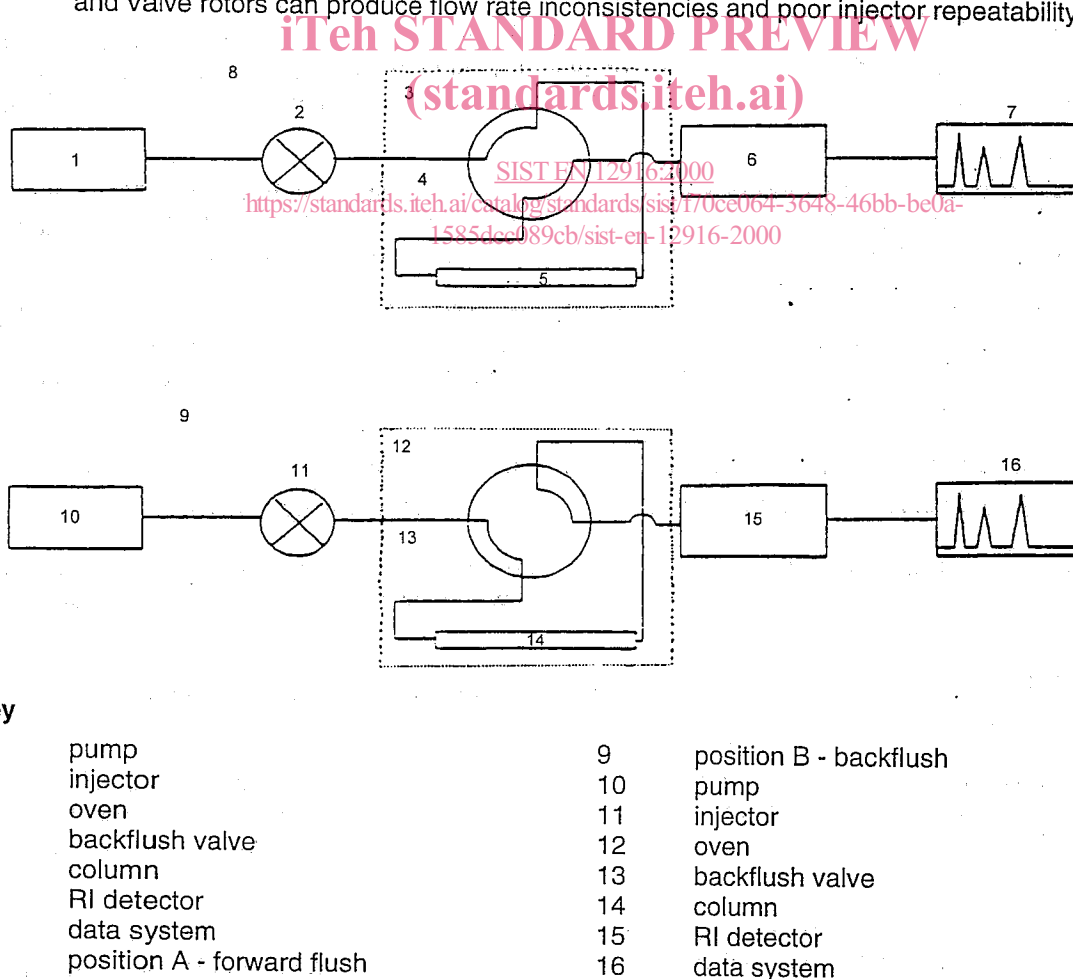


Figure 1 - Schematic representation of liquid chromatograph

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 this is equipped with temperature control, to stabilize.

NOTE 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 reference and analysis cell mis-match due to drying-out and temperature or pressure gradients are minimized; typically, this can be accomplished with a mobile phase flow through the reference cell of one tenth of that through the analysis cell.

8.3 Prepare a system calibration standard (SCS) by weighing 1,0 g \pm 0,1 g cyclohexane (5.1), 0,5 g \pm 0,05 g *o*-xylene (5.3), 0,05 g \pm 0,005 g dibenzothiophene (5.6) and 0,05 g \pm 0,005 g 9-methylanthracene (5.7) into a 100 ml volumetric flask and making up to the mark with heptane (5.2). Ensure that the dibenzothiophene and 9-methylanthracene are dissolved in the *o*-xylene/cyclohexane mixture, e.g. by using an ultrasonic bath, before adding the heptane.

NOTE The SCS may be kept for at least 1 year if stored in a tightly stoppered bottle in a cool dark place.

8.4 When operating conditions are steady, as indicated by a stable horizontal baseline, inject 10 μ l of the SCS (8.3). Ensure the baseline drift over the period of the HPLC analysis run is less than 0,5 % of the peak height for cyclohexane. A period of up to 1 hour could be required before the liquid chromatograph reaches steady state conditions.

NOTE A baseline drift greater than 0,5 % of the peak height for cyclohexane may indicate problems with the temperature control of the column/refractive index detector and/or material eluting from the column.

8.5 Ensure that baseline separation is obtained between all four components of the SCS (see figure 2).

8.6 Ensure that the resolution (see 11.1) between cyclohexane and *o*-xylene is not less than 5,0.

8.7 Measure the retention times of the dibenzothiophene and 9-methylanthracene peaks using the data system. Calculate the backflush time using the equation given in 11.2. The backflush time is the time at which the backflush valve will be actuated during the calibration procedure (see clause 9) and the analysis of samples (see clause 10).