National Standards Authority of Ireland

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PETROLEUM PRODUCTS - DETERMINATION OF AROMATIC HYDROCARBON TYPES IN MIDDLE DISTILLATES - HIGH PERFORMANCE LIQUID CHROMATOGRAPHY METHOD WITH REFRACTIVE INDEX DETECTION

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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 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.

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

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of an identical text or by endorsement, at the latest by October 2000, and conflicting national standards shall be withdrawn at the latest by October 2000.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

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