
Naftni proizvodi - Določevanje benzo(a)pirena (BaP) in izbranih policikličnih aromatskih ogljikovodikov (PAO) v polnilnih oljih - Postopek uporabe dvojnega LC-čiščenja in analize GC/MS

Petroleum products - Determination of content of Benzo(a)pyrene (BaP) and selected polycyclic aromatic hydrocarbons (PAH) in extender oils - Procedure using double LC cleaning and GC/MS analysis

Mineralölerzeugnisse - Bestimmung des Gehaltes an Benzo(a)pyren (BaP) und ausgewählten polycyclischen Kohlenwasserstoffen (PAH) in Extenderölen - Verfahren mittels doppelter LC-Vorreinigung und GC/MS-Analyse

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Produits petroliers - Détermination de la teneur en Benzo(a)pyrene (BaP) et polycyclic hydrocarbons aromatique selective en huiles extender - Méthodes par spectrométrie d'absorption atomique (SAA)

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EUROPEAN STANDARD

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Petroleum products - Determination of content of
Benzo(a)pyrene (BaP) and selected polycyclic aromatic
hydrocarbons (PAH) in extender oils - Procedure using double
LC cleaning and GC/MS analysis

Produits pétroliers - Détermination de la teneur en
Benzo(a)pyrène (BaP) et en certains hydrocarbures
aromatiques polycycliques (HAP) dans les huiles de
dilution - Méthode par double purification
chromatographique en phase liquide et par GC/MS

Mineralölerzeugnisse - Bestimmung des Gehaltes an
Benzo(a)pyren (BaP) und ausgewählten polycyclischen
Kohlenwasserstoffen (PAKs) in Extenderölen - Verfahren
mittels doppelter LC-Vorreinigung und GC/MS-Analyse

This European Standard was approved by CEN on 14 December 2012.

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Foreword

This document (EN 16143:2013) 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of an identical text or by endorsement, at the latest by August 2013, and conflicting national standards shall be withdrawn at the latest by August 2013.

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Introduction

This document has been prepared under a mandate given to CEN by the European Commission (EC) [1] and the European Free Trade Association (EFTA). EU Directive 2005/69/EC [2] sets restrictions on the marketing and use of polycyclic aromatic hydrocarbons (PAHs) in extender oils and tyres. Tyres are produced using extender oils that may contain PAHs not added intentionally. Due to the fact that PAHs can be incorporated during the production process into the rubber matrix, they can be present in various amounts in the final products. The presence of PAHs can be detected qualitatively and quantitatively using benzo[a]pyrene (BaP) as marker. BaP and PAHs are dangerous substances classified according to the Directive 67/548/EEC [3] as carcinogenic, mutagenic and toxic for reproduction.

Precision data for each analyte have been developed in CEN/TC 19 inter-laboratory studies according to EN ISO 4259 [4]. These studies recognised the difficulties of this type of very complex trace analysis, which are not only due to the fact that suitable samples are very rare and almost impossible to find. Insufficient purity for some charges of the used internal standards as reported by some participating laboratories, as well as an overlap of triphenylene and Chrysene peaks on some systems, were matters that led to a test method standard being produced with less precision than was desirable. Although the "2R" rule for limit setting for BaP is not fully met for the limits targeted by the EU Directive, the results (in terms of reproducibility) from the CEN/TC 19 Round Robin Test are much better than those resulting from comparable exercises with alternate methods.

The complexity of the sample preparation steps and subsequent GC-MS analysis showed that laboratories need sufficient expertise to properly perform the analyses described in this document. Therefore, only a limited number of laboratories were able to participate in and contribute to the Round Robin test conducted by CEN/TC 19. In consideration of the progression of the standardization project, no additional time or resources were left e.g. to conduct additional Round Robin Tests, and the test method therefore is produced in its actual form. Further experience in the future may lead to improved precision and a more comprehensive scope.

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1 Scope

This European Standard specifies a procedure for the determination of the content of benzo[a]pyrene (BaP) in extender oils which are commonly used in the rubber industry for the production of tyres or parts of tyres. The method also yields the sum of the eight individual polycyclic aromatic hydrocarbons (PAHs) listed in Table 1.

The procedure has been tested and verified for the PAHs listed in Table 1 (those required by the European Commission [1]) and additional PAHs as listed in Table A.2.

Analysis of other PAHs is possible in principle, but sufficient quality assurance performed by the user is necessary to secure the analysis.

The application range for this method is from approximately 4 mg/kg to approximately 15 mg/kg for the eight individual PAHs and from approximately 0,5 mg/kg to approximately 2 mg/kg for BaP.

NOTE 1 The intended working range for this method is in the 0,1 mg/kg to 15 mg/kg range. For the lower levels precision has not yet been established.

NOTE 2 For the purposes of this European Standard, the term “% (m/m)” is used to represent the mass fraction (ω).

Table 1 — List of individual PAHs in extender oils

Name of PAH	Abbreviation	CAS Registry number
benzo(a)pyrene	BaP	50-32-8
benzo(e)pyrene	BeP	192-97-2
benzo(a)anthracene	BaA	56-55-3
chrysene	CHR	218-01-9
benzo(b)fluoranthene	BbFA	205-99-2
benzo(j)fluoranthene	BjFA	205-82-3
benzo(k)fluoranthene	BkFA	207-08-9
dibenzo(a,h)anthracene	DBahA	53-70-3
See Table A.1 for additional data on some PAH.		

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 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.

EN 16143:2013 (E)**3.1****polycyclic aromatic hydrocarbons**

PAHs

hydrocarbon molecules that consist of three or more condensed aromatic rings

3.2**extender oil**

specific oil fraction which is used in the rubber industry for the production of rubber parts, especially tyres

4 Principle

The product under investigation is submitted to a double cleaning step using column chromatography (LC). The polycyclic aromatic hydrocarbons and components of interest (see Clause 1) are separated by gas chromatography (GC). Identification and quantification is performed by mass spectroscopic (MS) detection in Selected Ion Monitoring (SIM) mode.

5 Reagents and materials**5.1 Solvents.**

In this context, the requirement "free from PAH" means that in the analysis of a blank sample, no peaks from the PAH compounds of interest larger than the signal-to noise-ratio of the chromatogram should be found.

5.1.1 Acetone, free from PAH, for chromatography, CAS Registry number 67-64-1.

5.1.2 Cyclohexane, free from PAH, for chromatography, CAS Registry number 110-82-7.

5.1.3 n-Pentane, free from PAH, for chromatography, CAS Registry number 109-66-0.

5.1.4 Propanol-2, free from PAH, for chromatography, CAS Registry number 67-63-0.

5.2 LC separation phase materials.

5.2.1 Silica gel, of high purity grade, for example TYPE ICN 02747.

5.2.2 Sephadex® LH20¹⁾ of high purity grade.

5.3 Standards.

The standards shall be chosen so that they behave in the same way as the corresponding analytes and that they can be readily quantified. Suitable compounds that can be used as standards are listed in Table A.1.

5.3.1. Internal standards, deuterated or C13 marked PAH, with >98% purity (see also Table A.1).

5.3.2 Injection standards, 4,4',5,5',6,6'-Decafluorobiphenyl or deuterated/C13 marked PAH, typically blended at 50×10^{-3} g/l concentration.

5.3.3 Master standard, a commercially available standard solution containing certified concentrations of the PAHs of interest.

1) Sephadex® is the trade name of a product supplied by GE Healthcare Bio-Sciences AB, SE-751 84 Uppsala. This information is given for the convenience of users of this European Standard 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.

- 5.4 Carrier gas**, Helium > 99,996 purity.
- 5.5 UV-light source**, with radiation predominantly at 366 nm.
- 5.6 Pasteur pipette**.
- 5.7 LC Chromatography glass column**, consisting of:
- 5.7.1 Column a**: ID 10mm, length 160 mm.
- 5.7.2 Column b**: ID 23mm, length 100 mm.
- 5.8 Syringes**, for injection, blending of solutions and internal standards syringes with the following capacities: 1 µl, 5 µl, 10 µl, 25 µl, 50 µl, 100 µl and 250 µl.
- 5.9 Volumetric flasks**, capacity 1 ml, 5 ml and 100 ml.
- 5.10 Conical bottom flasks**, capacity 10 ml.
- 5.11 Pipettes**, class A, capacity 2 ml.

6 Apparatus

6.1 Gas chromatograph with mass spectrometer.

The analysis system consists of a commercial GC system connected with an MS detector and data station. The system shall be used with direct or split analysis on capillary column and shall allow operation using the chromatography parameters given in Table 2.

NOTE The mass-spectrometer is run in the "Selected Ion" (SIM) mode under 70 eV ionisation.

When a high resolution type mass spectrometer is used, the second step of the cleaning procedure (see 8.3) can be by-passed if the desired detection limits can be met.

6.2 Gas chromatographic columns.

Fused silica type capillary columns with dimensions are listed in Table 2. A commonly used liquid phase is 5 % phenyl-methylpolysiloxane of 0,25 µm film thickness. Other columns of comparable or improved performance can also be used, such as a strongly recommended DB-5ms column (5 % phenyl-methylpolysiloxane).

Table 2 — Typical gas chromatographic parameters

Parameter	Value
GC-column	30 m x 0,25 mm x 0,25 µm
Stationary phase	5 % phenyl-methylpolysiloxane
Oven initial temperature	60 °C
Initial time	2 min
Temperature program	5 °C/min to 300 °C, hold for 12 min
Injection	according to Grob, splitless
Injection temperature	275 °C to 300 °C
Temperature transfer line	275 °C to 300 °C
MS Detector temperature	according to the instrument manufacturer
Injection volume	1 µl to 3 µl
Carrier gas	Helium, with a linear velocity of 40 cm/sec

Depending on chromatographic conditions (e.g. column length), it can happen that the different benzofluoranthene isomers co-elute. In these cases, determining the sum of the three isomers rather than reporting each isomer separately should be considered. Another alternative would be to use longer GC-columns (60 m instead of 30 m). See B.2 for further advice on the peak overlap of the isomers.

Ferrules used shall not contain more than 40 % graphite (a suitable ferrule is made of 60 % polyimide and 40 % graphite) to decrease the risk that PAHs are absorbed.

6.3 Sample concentrator, typically a rotary evaporator or similar digital evaporator device.

7 Sampling and sample handling

7.1 General sampling procedure

Samples shall be taken according to EN ISO 3170 or EN ISO 3171, as well as in accordance with the requirements of national standards or regulations for the sampling of the product under test.

If samples are not tested immediately, they shall be stored tightly sealed and in a cool and dark place.

It shall be secured that glassware is thoroughly cleaned and that all new materials that may come into contact with the sample are checked by blank analysis that they give no interference.

NOTE Interferences which can affect the results can occur due to contaminations from glassware, solvents and other materials that can come into contact with the sample. Such interferences will form an artefact or will increase the detector baseline. Interferences can also come from components in samples that co-elute with the specific PAHs of interest.

7.2 Preparation of a sample solution

Approximately 70 mg of the sample is introduced to the nearest 0,1 mg into a 5 ml volumetric flask (5.9) and dissolved in 2 ml n-pentane (5.1.3). Before the sample clean-up, the sample solution is spiked with internal standard. The concentration of internal standard shall be adjusted such that it is in the same range as the expected PAHs in the sample.

8 Clean-up procedure

8.1 General

Since the extender oils under investigation have a complex matrix which can hide the PAHs of interest, samples shall be submitted to a clean-up procedure before GC separation (see 6.1).

The first cleaning step is done with Silica gel (5.2.1).

For quantification a second cleaning step shall be performed on Sephadex LH20 (5.2.2) or equivalent.

These procedures are strongly recommended in order to make sure the samples are cleaned thoroughly before analysing them by GC-MS.

8.2 First clean-up step using silica column

8.2.1 Preparation of the silica column

Before use, the silica gel (5.2.1) is deactivated over 24 h by stirring with 7 % (m/m) water which does not contain PAHs. Of the deactivated silica, 5 g is mixed with n-pentane (5.1.3) and then transferred into a glass column (5.7.1). Vibrate or knock mildly on the column to ensure that the silica is evenly and sufficiently packed without voids.

8.2.2 Chromatography on silica column

Run 10 ml of n-pentane (5.1.3) through the column and discard the eluted volume. Apply the sample just before the last free n-pentane is about to vanish from the silica surface. Apply the sample in portions with a suitable Pasteur pipette (5.6).

After the applied sample volume has vanished from the surface, apply an additional 2 ml portion of n-pentane to assure that whole sample is applied in the column. Just before the last n-pentane has vanished from the silica surface, apply 25 ml n-pentane in several portions. All volume eluted with n-pentane shall be discarded.

Apply 75 ml cyclohexane (5.1.2) in several portions and collect the eluted volume in a clean 100 ml volumetric flask. Concentrate the collected cyclohexane fraction using the sample concentrator (6.3) to less than 1 ml, ensuring that the temperature does not exceed 35 °C. If the second clean-up step is applied for quantitative results, this concentrate is to be submitted to further processing in the Sephadex clean-up step (8.3.2)

If the Sephadex clean-up step is **not** used, transfer the concentrate to a 1 ml volumetric flask, add the injection standard to it and adjust the sample solution volume to 1ml with Cyclohexane by filling up to the mark. This 1 ml sample is used to inject test portions for GC separation.

8.3 Second clean-up step using Sephadex-LH 20 column

8.3.1 Preparation of the Sephadex-LH20 column

Prepare a slurry of 5 g of dry Sephadex-LH20 (5.2.2) and propanol-2 (5.1.4), using a 3:1 (m/m) proportion for the solvent/Sephadex mixture. Let the slurry stand overnight for deactivation.

Fill a glass column (5.7.2) with 5 g of the deactivated slurry and drain the column from any free propanol-2, then close the bottom valve.

When a fresh Sephadex-LH20 quality batch is used, it shall be tested with a solution of approximately 100 mg/l fluoranthene in propanol-2, so that it has an elution volume between 24 ml and 32 ml propanol-2 and that a straight level zone can be seen under UV-light (366 nm).