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Water quality — Determination of selected polycyclic aromatic hydrocarbons (PAH) in whole water samples — Method using solid phase extraction (SPE) with SPE-disks combined with gas chromatography mass spectrometry (GC-MS)

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National foreword

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Water quality - Determination of selected polycyclic aromatic hydrocarbons (PAH) in whole water samples - Method using solid phase extraction (SPE) with SPE-disks combined with gas chromatography mass spectrometry (GC-MS)

Qualité de l'eau - Dosage des hydrocarbures aromatiques polycycliques (HAP) sélectionnés dans des échantillons d'eau totale - Méthode par extraction en phase solide (SPE) avec disques SPE, avec couplage chromatographie en phase gazeuse-spectrométrie de masse (CG-SM)

Wasserbeschaffenheit - Bestimmung von ausgewählten polycyclischen aromatischen Kohlenwasserstoffen (PAK) in Gesamtwasserproben - Verfahren mittels Festphasenextraktion (SPE) mit SPE-Disks in Verbindung mit Gaschromatographie Massenspektrometrie (GC-MS)

This European Standard was approved by CEN on 27 June 2015.

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European foreword

This document (EN 16691:2015) has been prepared by Technical Committee CEN/TC 230 “Water analysis”, the secretariat of which is held by DIN.

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of an identical text or by endorsement, at the latest by March 2016, and conflicting national standards shall be withdrawn at the latest by March 2016.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association.

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Introduction

WARNING — Persons using this European Standard should be familiar with usual laboratory practice. This European Standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted according to this European Standard be carried out by suitably trained staff.

Polycyclic aromatic hydrocarbons (PAH) are priority substances listed in Annex X of the EU Water Framework Directive (WFD, Directive 2000/60/EC) for which environmental quality standards (EQS) have been set at EU level for inland as well as other surface waters to protect the aquatic environment against chemical pollution (Directive 2008/105/EC). With the exception of metals, the EQSs are expressed as total concentrations in the whole water sample. Furthermore, analytical methods used in WFD monitoring need to meet certain requirements as regards the minimum limit of quantification and the maximum tolerable measurement uncertainty (Directive 2009/90/EC). So far, there is no standardized method available for the determination of PAH in whole water samples fulfilling those requirements. Hence, the European Commission mandated CEN to develop or improve standards in support of the implementation of the monitoring requirements of WFD.

Directive 2008/105/EC has been amended by Directive 2013/39/EU, however, this standard has been developed for the analysis of PAH as listed in Annex A of Directive 2008/105/EC.

Organic compounds as specified in the WFD occur in nearly all types of water. These substances are adsorbed on solids (sediments, suspended matter) as well as dissolved in the liquid phase. A large group of these compounds are polycyclic aromatic hydrocarbons (PAH). There are further standards for the analytical determination of PAH in water and waste water:

— EN ISO 17993 describes a method for the determination of 15 PAH by high performance liquid chromatography/UV detection in drinking water, ground water and surface water;

— ISO 7981-1 and ISO 7981-2 describe methods for the determination of 6 PAH by high performance thin layer chromatography or by high performance liquid chromatography in drinking water and ground water;

— ISO 28540 describes a method for at least 16 PAH using gas chromatography with mass spectrometric detection (GC-MS) in drinking water, ground water and surface water;

— ISO/TS 28581 describes a method for the determination of polycyclic hydrocarbons and pesticide residues in drinking water, ground water surface water and waste water.

1 Scope

This European Standard specifies a method for the determination of 7 polycyclic aromatic hydrocarbons (PAH) in whole water samples listed in Table 1. The method uses solid-phase disk extraction with SPE-disks followed by gas chromatography-mass spectrometry (GC-MS). It is applicable to the analysis of PAHs in surface water containing suspended particulate matter (SPM) up to 500 mg/l (whole water samples), drinking water and groundwater.

The lower and upper limit of the working range depends on the matrix, on the specific compound to be analyzed and on the sensitivity of the mass spectrometric detection unit. The limit of quantification (LOQ) determined in the validation is given in Table 1. The upper limit of the working range is approximately 2 000 ng/l.

This method is, with some modifications suitable for the analysis of waste water. This method is applicable to other PAH[1)], provided the method is validated for each PAH.

Table 1 — Polycyclic aromatic hydrocarbons (PAH) determined by this method

Substance	Molecular formula	Molar mass g/mol	EC number[a]	CAS-RN[b]	LOQ[c] ng/l
anthracene	$C_{14}H_{10}$	178,23	204–371–1	120–12–7	0,24
fluoranthene	$C_{16}H_{10}$	202,26	205–912–4	206–44–0	2,1
benzo[*b*]fluoranthene	$C_{20}H_{12}$	252,32	205–911–9	205–99–2	0,56
benzo[*k*]fluoranthene	$C_{20}H_{12}$	252,32	205–916–6	207–08–9	0,44
benzo[*a*]pyrene	$C_{20}H_{12}$	252,32	200–028–5	50–32–8	0,33
benzo[*ghi*]perylene	$C_{22}H_{12}$	276,34	205–883–8	191–24–2	0,44
indeno[*1,2,3-cd*]pyrene	$C_{22}H_{12}$	276,34	205–893–2	193–39–5	0,42

a EC Number: European inventory of existing commercial substances (EINECS) or European list of notified chemical substances (ELINCS).

b CAS-RN: Chemical Abstracts Service Registry Number.

c For the determination of the LOQ the procedure given in NEN 7777+C1:2012 [12] was used.

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

EN ISO 3696, *Water for analytical laboratory use - Specification and test methods (ISO 3696)*

EN ISO 5667-1, *Water quality - Sampling - Part 1: Guidance on the design of sampling programmes and sampling techniques (ISO 5667-1)*

1) During the inter-laboratory validation trial the method was tested for all 16 EPA PAH (see Annex B).

EN ISO 5667-3, *Water quality - Sampling - Part 3: Preservation and handling of water samples (ISO 5667-3)*

3 Principle

PAH (see Table 1) present in the whole water sample are extracted by liquid-solid extraction using an adsorption disk. An internal standard mixture is added to the sample prior to extraction. The extract is concentrated by evaporation, and the residue is dissolved in a solvent appropriate for clean-up or GC-analysis. The extract is analyzed by gas chromatography separation with a low resolution mass spectrometry detection using electron impact (EI) ionization mode (6.4). The concentration of the component is calculated using calibration lines (see Clause 9) and internal standards added before extraction with a correction for recovery, final volume and detector response.

If necessary, extracts (of surface water samples) can be cleaned by column chromatography prior to analysis. (see Annex D). Prior to injection, an injection standard is added to each extract, and an aliquot of the extract is injected into the gas chromatograph.

PAH are separated on a suitable fused silica capillary column (6.5) with an efficient separation e. g. coated with a film of cross-linked non-polar polysiloxane or slightly polar modified polysiloxane. The column shall be suitable for separating benzo[*a*]pyrene and benzo[*e*]pyrene. Identification and quantification is performed by means of mass spectrometry using electron impact ionization (EI) (6.4).

4 Interferences

4.1 Interferences with sampling, extraction and concentration

Use sampling containers of materials (6.1) that do not affect the analyte content during the contact time, preferably of stainless steel or glass. Avoid plastics and organic materials other than polytetrafluoroethene (PTFE) during sampling, sample storage at (3 ± 2)°C or extraction.

If automatic samplers are used, avoid the use of silicone or rubber material for the tubes. If these materials are present, ensure that the contact time is minimized. Rinse the sampling line with the water to be sampled before taking the test sample. EN ISO 5667-1 and EN ISO 5667-3 provide guidance. Storage temperature is at (3 ± 2)°C. For sampling and sample preservation see Clause 7. During storage of the test samples, losses of components may occur due to adsorption on the walls of the containers. The extent of the losses may depend on the storage time.

Commercially available solid-phase extraction disks (SPE-disks) differ frequently in quality. Variations in the selectivity of the materials also frequently occur from batch to batch, thus possibly causing significant deviations in extraction yield. This does not basically impair their suitability, apart from a resulting higher detection limit for individual substances. To ensure that the measuring results show high trueness and precision, use materials of one batch for both measurement and calibration. Avoid major fluctuations in the extraction times and elution procedures within one sample sequence when analysing the samples.

4.2 Interferences with GC

Substances with similar retention times and masses as the target PAH may lead to interferences and overlapping or incompletely resolved peaks in the chromatogram. Depending on their intensity those co-eluents can affect the trueness of the analysis.

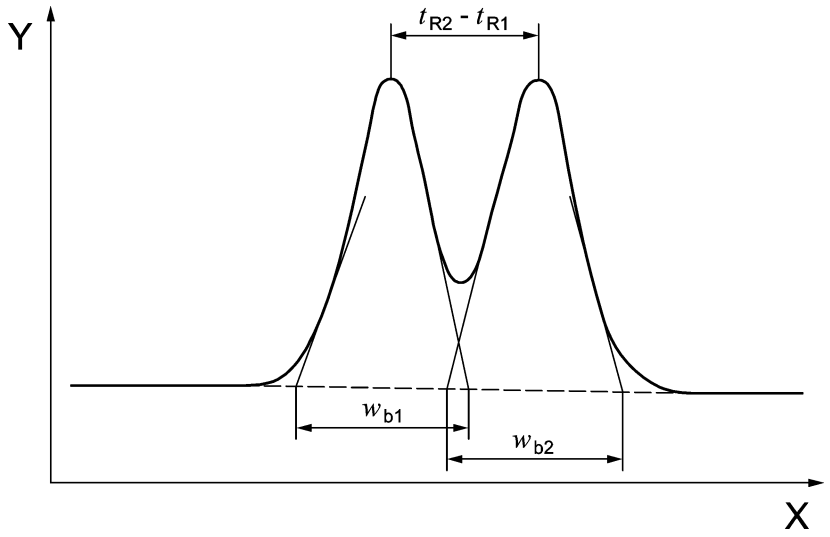
A chromatographic resolution of $R > 0{,}8$ is required for anthracene and phenanthrene (m/z 178) and benzo[*a*]pyrene and benzo[*e*]pyrene (m/z 252) . If the criterion cannot be reached, a suitable capillary column shall be chosen, capable to meet the required resolution.

A chromatographic resolution of $R > 0{,}8$ is required for benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene (*m/z* 252). If the criterion cannot be reached for benzo[*j*]fluoranthene, the sum of the co-eluting PAH shall be given in the test report.

Co-eluting mass fragments of dibenzo[*a,h*]anthracene und dibenzo[*a,c*]anthracene (*m/z* 276) may lead to interferences with indeno[1,2,3-*cd*]pyrene.

The resolution shall be assessed if adjustments in the chromatographic system have been made which may affect the resolution, e. g. shortening of the separation column, installation of a new column.

The chromatographic resolution is calculated according to Figure 1 and Formula (1).



Key:

X	time
Y	intensity
t_{R1}, t_{R2}	retention time of eluting substances 1 and 2 in seconds (s)
w_{b1}, w_{b2}	peak width at the base of each peak in seconds (s)

Figure 1 — Resolution of chromatographic peaks

$$R = 2\frac{(t_{R2} - t_{R1})}{w_{b1} + w_{b2}} \quad (1)$$

where

R	is the resolution;
t_{R1}, t_{R2}	Retention time of eluting substances 1 and 2 in seconds (s);
w_{b1}, w_{b2}	peak width at the base of each peak in seconds (s).

5 Reagents

The reagents shall be free from impurities possibly interfering with the GC-MS analysis.

Use solvents and reagents of sufficient purity, i.e. with negligibly low impurities compared with the concentration of analytes to be determined. As reagents use, as far as available, “residual grade”, “picograde” or better in order to obtain clean blanks. Check blanks regularly and establish proper charge control. If necessary, apply additional cleaning steps.

5.1 Water, complying to grade 1 according to EN ISO 3696, or equivalent.

5.2 Operating gases for the gas chromatography mass spectrometry, of high purity and according to the manufacturer's specifications.

5.3 Nitrogen of high purity, i.e. minimum 99,996 % by volume, for concentration by evaporation.

5.4 Solvents for extraction, chromatography and preparation of reference solutions.

A variety of solvents may be used depending on the procedural step and the availability of commercial stock solutions, e. g.

- acetone, C_3H_6O, (boiling point: 56 °C);
- dichloromethane, CH_2Cl_2, (boiling point: 39,7 °C);
- toluene, C_7H_8, (boiling point: 111 °C);
- *iso*-hexane, C_6H_{14}, (boiling point: 60 °C).

5.5 Sodium sulfate, Na_2SO_4, anhydrous, pre-cleaned by heating to 500 °C for 4 h or free of interfering compounds. Store the dried sodium sulfate in an Erlenmeyer with a glass stopper (6.12) in the desiccator (6.11). The shelf life is 6 months.

5.6 Silica, average particle size approximately 40 µm, heated at 450 °C for 3 h and stored in a desiccator to ensure maximum activity.

5.7 Stock solutions:

For the shelf life of the stock solutions see analysis certificate of the stock solution.

5.7.1 Stock solution of internal standards (deuterated PAH standards), see Table 2[2)].

^{13}C-isotopically labelled PAH standards may also be used as internal standards.

5.7.2 Stock solution of the 7 target substances (native reference PAH standards), see Table 2.

5.7.3 Stock solution injection standard

1,2,3,4-Tetrachloronaphthalene (CAS-RN 20020-02-4) or any other suitable standard: 1 000 mg/l in e. g. dichloromethane.

Some of the stock solutions may crystallize if they are stored for a long period of time in the freezer. In this case bring the solution, before use, to room temperature and place it in an ultrasonic bath for approximately 10 min.

2) PAH stock solutions are commercially available. Examples are for instance CIL ES-2528 d-PAH cocktail: 100 mg/l in benzene-d6 and NIST SRM 1647e: 1 mg/l to 20 mg/l in acetonitrile. These examples are given only as information for the users of this European Standard and do not constitute an endorsement by CEN of these products.

5.8 Standards:

5.8.1 Native reference substances and deuterated internal standards (see Table 2):

For all 7 PAH deuterated internal standards are used. The deuterated internal standards are added to the sample to be extracted and are therefore dissolved in a water soluble solvent e. g. acetone (5.4).

Table 2 — Native and deuterated PAH

Native reference substances	Deuterated internal standard substances	CAS-RN (deuterated substances)
anthracene	anthracene-d10	1719–06–8
fluoranthene	fluoranthene-d10	93951–69–0
benzo[*b*]fluoranthene	benzo[*b*]fluoranthene-d12	93951–98–5
benzo[*k*]fluoranthene	benzo[*k*]fluoranthene-d12	93952–01–3
benzo[*a*]pyrene	benzo[*a*]pyrene-d12	63466–71–7
indeno[1,2,3-*cd*]pyrene	indeno[1,2,3-*cd*]pyrene-d12	203578–33–0
benzo[*g,h,i*]perylene	benzo[*g,h,i*]perylene-d12	93951–66–7

5.8.2 Internal standard

Prepare a solution of deuterated PAH internal standards by diluting the stock solution (5.7.1) in an appropriate solvent with a final mass concentration of 5 µg/ml (see Annex C, Table C.1).

5.8.3 Injection standard

Prepare a solution of 1,2,3,4-tetrachloronapthalene by diluting the stock solution (5.7.3) in toluene (5.4) with a final mass concentration of 10 µg/ml (see Annex C, Table C.2).

This standard is added to a sample before injection into the GC-MS apparatus, to monitor variability of instrument response and to calculate internal standard recovery

5.8.4 Calibration standard

Prepare calibration standard solutions for at least five concentration levels (e. g. CS1 to CS5 as given in Annex C) by diluting the deuterated PAH internal standard solution (5.8.2), the native PAH solution (5.7.2) and the injection standard 1,2,3,4-tetrachloronaphthalene (5.7.3) in toluene (5.4) with final mass concentrations of native PAH from 1 ng/ml to 2 000 ng/ml (see Annex C). These calibration standards are also used for the determination of retention times of the native and deuterated PAH, the Relative Response Factors (*RRF*) and the recovery of the internal standards.

6 Apparatus

Equipment or parts of it which have contact with the water sample or its extract shall be free from residues causing interferences. It is recommended to clean all glassware, for example, by rinsing with detergent and hot water, and drying for about 15 min to 30 min at about 120 °C. After cooling the glassware can be rinsed with acetone (5.4), sealed and stored in a clean environment.

It is preferable not to re-use glassware that has been in contact with samples with high concentration of PAH. Glassware can be re-used as long as an effective method of cleaning has been demonstrated.

6.1 Sample containers, preferably of stainless steel or brown/green glass narrow-necked, flat-bottomed, 1 000 ml, with PTFE cap liner. Avoid plastics and organic materials other than polytetrafluoroethene (PTFE).

6.2 Microlitre syringes, e. g. 10 µl, 100 µl and 1 000 µl.

6.3 Glass autosampler vials, brown glass, capacity e. g. 2 ml, with inert cap and PTFE-coated septum.

6.4 Capillary gas chromatograph with mass spectrometric detector (GC-MS), using EI-ionization mode, gas supply in accordance with the respective manufacturer's instructions.

6.5 Capillary column, high resolution, low bleeding, for gas chromatography (see 4.2 for requirements and Annex A for an example).

6.6 One-mark volumetric flasks, according to EN ISO 1042, class A.

6.7 Pasteur pipettes.

6.8 Molecular sieve beads, pore diameter 0,4 nm.

6.9 Vacuum device for solid-phase extraction, extraction box or automated workstation for solid-phase extraction.

6.10 Solid-phase extraction disk, inner diameter between 40 mm and 60 mm packed with an appropriate reversed phase adsorbent material (see Annex E for examples).

6.11 Desiccator.

6.12 Erlenmeyer with glass stopper.

6.13 Equipment for concentrating the eluates by evaporation, e. g. rotary evaporator, adjustable for constant vacuum and with a temperature-controlled water bath, or stripping equipment using nitrogen gas.

6.14 Glass bottles, brown/green glass, narrow-necked, flat-bottomed, 1 000 ml, with PTFE cap liner.

6.15 Balance, with an accuracy of ± 0,1 g.

6.16 Glass wool, rinsed with *iso*-hexane (5.4).

7 Sampling

For sampling, use thoroughly cleaned, flat bottomed sample containers (6.1).

Preservation and handing of the sample can be found in EN ISO 5667-3 Store the sample at (3 ± 2)°C, protected from light, until the extraction is carried out.

Ensure that the extraction is carried out within the maximum preservation time, as specified in EN ISO 5667-3, to avoid losses. It is generally recommended to carry out the extraction as soon as practicable to minimize potential adsorption to the glass wall which could be a potential interference if glassware is re-used.

8 Procedure

8.1 Sample preparation and extraction

8.1.1 Sample preparation

In general samples are examined without pre-treatment, with a pH between 6 and 8 and suspended particulate matter is not removed prior to analysis. Do not filter the sample.

Large particles (e. g. leaves, little branches) should be removed using a sieve (screening gap 1 mm).

Transfer 950 ml sample into a glass-bottle or use the transfer bottle. Add a precisely defined amount of the internal standards (5.8.2) e. g. a volume containing 100 ng, dissolved in an appropriate water soluble solvent.

8.1.2 Conditioning of SPE-disk

Put the disk (6.10) on the vacuum device extraction apparatus (6.9) and add 20 ml of dichloromethane (5.4) and soak 1 min. Elute the dichloromethane and let it pass through the disk in about 20 s, e.g. using a vacuum device. Ensure that the adsorbent does not run dry.

Repeat this step once with 10 ml of acetone (5.4).

Add 20 ml of water (5.1) and let it pass through the disk in about 20 s, e. g. using the vacuum device. Ensure that the adsorbent does not run dry.

8.1.3 Extraction and elution

Weigh the sample bottle with the sample and note the weight to an accuracy of ± 0,1 g. Pass the sample through the conditioned adsorbent at a flow rate of about 25 ml/min. Rinse the sample reservoir (e.g. the sample bottle) with 4 ml of water (5.1) and pass it through the adsorbent as described above. Dry the adsorbent in a stream of nitrogen (5.3) not longer than 5 min.

NOTE If the adsorbent is dried for more than 10 min, volatile PAH may be lost.

Elute the disk as follows.

Add 5 ml of acetone (5.4) allowing 2 min for the solvent to soak. Collect the eluate by passing it through the disk (6.10) in about 20 s.

Add 10 ml of dichloromethane (5.4) allowing 2 min for the solvent to soak. Collect the eluate by passing it through the disk (6.10) in about 40 s.

Add 5 ml of dichloromethane (5.4) allowing 1 min for the solvent to soak. Collect the eluate by passing it through the disk (6.10) in about 20 s;

Repeat the last step four times.

Rinse the glass bottle (6.14) and the sampling bottle both with 15 ml of dichloromethane (5.4) and pass through the disk.

Collect the combined eluates in a glass vessel and dry it by passing it through a funnel filled with about 50 g of conditioned Na_2SO_4 (5.5).To prevent loss of Na_2SO_4 put a plug of glass wool (6.16) in the narrow part of the funnel. Collect the dried eluate in a vessel.

Alternative drying methods may be applied provided that they can show that they dry as effectively.

Allow the sample bottle to drain well, then weigh the sample bottle and note the weight to an accuracy of ± 0,1 g.

8.1.4 Solvent concentrating

Concentrate the dried solvent extract (e.g. in a gentle stream of nitrogen or with a rotary evaporator (6.13), at a temperature of 45 °C, slowly lowering the pressure to 55 kPa).

Do not evaporate the extracts to dryness, as losses of the 3-ring compound may occur.

Dissolve the extract in approximately 0,5 ml of solvent (5.4). Be sure that any residues that may be deposited on the glass wall are dissolved by shaking the extract using the shaking apparatus. If no clean-up or solvent change is necessary add 10 µl of injection standard (5.8.3) and transfer the enriched sample into a glass autosampler vial (6.3). Keep the extract in a cool and dark place at (3 ± 2) °C until the analysis is carried out. Otherwise proceed with cleaning of the extracts (see Annex D) or solvent change (see 8.1.5).

Use an aliquot for the GC-MS determination.

Clean extracts of samples of unknown origin using silica clean-up (see Annex D) or if the chromatogram shows interferences that hamper the quantification.

8.1.5 Solvent change

Evaporate the extract to almost dry under a gentle stream of nitrogen (5.3) at room temperature. Re-dissolve the extract in toluene by adding 2 ml of toluene (5.4) and evaporate with nitrogen (5.3) to a volume less than 0,5 ml.

Fill the extract up to a (known) volume (e. g. 0,5 ml) add 100 ng of injection standard (5.8.3) and transfer the enriched sample into a glass autosampler vial (6.3). Keep the extract in a cool and dark place at (3 ± 2 °C) until the analysis is carried out.

Use an aliquot for the GC-MS determination.

8.2 Gas chromatographic conditions

Operate the GC-MS (6.4) according to the manufacturer's instructions.

Select a capillary column (6.5) and chromatographic conditions where efficient separation is achieved (see Annex A for examples).

In case of peak tailing the pre-column or capillary column (6.5) shall be replaced.

Analyze calibration solutions, blank solutions and samples in the same conditions. After adding the injection standard (5.8.3) to the calibration standards and extracts, mix thoroughly and inject in the GC.

8.3 Blank measurement

Perform blank determinations using water (5.1) prior to and during series of analyses, at least one per series. This water should be free of detectable PAH. Blank measurements shall include all steps of the analytical procedure from the sample arrival at the laboratory to the evaluation of the gas chromatogram. If blank values are unusually high, review every step in the procedure and determine the cause by systematic checks so as to be able to eliminate the contamination source. Try to reduce the blank values as much as possible by applying various measures, such as avoiding contamination by ambient air and using suitable solvents (5.4) as well as checking the analytical instrumentation.

9 Calibration

9.1 General

The PAHs are quantified on the basis of Relative Response Factors (*RRF*) determined from calibration standards (5.8.4), and the internal standards (5.8.2) which are added to the samples.

9.2 Calibration by internal standard

Labelled internal standard calibration (5.8.2) is used for all the PAH samples.

For the initial calibration, analyze the calibration standards (5.8.4). Determine the response factor (*RF*) of each PAH relative to its labelled analogue, using the area responses of diagnostic ion 1. Plot the *RF* versus concentration in calibration solutions or compute using a linear regression. For acceptable linearity the regression line of each PAH standard curve should be greater than 0,99.

The Relative Response Factor (*RRF*) is determined using the calibration standard solutions according to Formula (2):

$$RRF = \frac{A_{\mathrm{n}}}{A_{\mathrm{is}}} \cdot \frac{C_{\mathrm{is}}}{C_{\mathrm{n}}} \tag{2}$$

where

A_{n} peak area of diagnostic ion 1 for component n in the calibration standard;

A_{is} peak area of diagnostic ion 1 for the internal standard in the calibration standard;

C_{is} concentration of internal standard in the calibration standard in nanograms per millilitre (ng/ml);

C_{n} concentration of component n in the calibration standard in nanograms per millilitre (ng/ml).

Calculate the mean *RRF* using the following Formula (3):

$$\overline{RRF} = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{A_n}{A_{is}} \times \frac{C_{is}}{C_n}\right)_i \tag{3}$$

where

$\overline{RRF}$ is the mean of the *RRF* values from the calibration solutions (5.8.4);

n is the number of calibration points.

Calculate the relative standard deviations (*RSD*) of the replicate *RRF* values using Formula (4):

$$RSD = \frac{SD}{RRF} \times 100 \tag{4}$$

where

SD the standard deviation of the replicate *RRF* values used to calculate the mean *RRF*.

The relative standard deviation (*RSD*) should be less than 30 % for all PAHs.

If an acceptable initial calibration is not achieved the cause shall be identified. After this corrective active action is performed and the initial calibration is repeated.

For the daily check of the calibration (recalibration), inject at least two calibration standards, e. g. at concentrations of (20 ± 10) % and (80 ± 10) % of the linear range. Compare the calculated response factor with those obtained in the previous batch of samples. They should not differ more than 20 %.

10 Measurement of samples

10.1 Mass spectrometric (MS) conditions

The GC-MS (6.4) with electron impact (EI) ionization method is adjusted in accordance with the manufacturer's instructions. Chromatograms are recorded in selected ion monitoring/recording mode (SIM/SIR).

Adjust the scan rate of the mass spectrometer to a velocity allowing one gas chromatographic peak to be described by at least 7 data points.

A list of the diagnostic ions is given in Table 3.

10.2 Sample measurement

Equilibrate the measuring system before measuring samples and adjust the mass spectrometer (6.4) according to the manufacturer's instructions.

For the measurement, the following conditions shall apply:

— Ionization method: electron impact (EI) ionization mode;

— Mass range of the spectrum: 46 u to 300 u, where u is a unified atomic mass unit, at least 10 u above the highest mass of the substances to be determined. With interferences, e. g. due to CO_2, the spectrum may be started at 46 u;

— Cycle duration: so that at least 7 spectra can be taken per substance peak.

If only single masses are registered in order to increase sensitivity, register the base peak and at least two more ions. All these shall have the same cycle duration so that at least 7 spectra can be taken per substance peak.

To set up one or more instrumental analyses a sequence file can be created. The preferred order of analysis is that samples with expected low levels are analyzed before the samples with high levels to prevent “carry-over” or “memory” effects. With regard to the contamination of the system it may also be useful to put the most clean extracts before the more contaminated extracts.

The quantification is based on integration of mass chromatograms of the MS. The integration results (peak areas) are processed in a spread sheet.

11 Identification of individual compounds by means of GC-MS (SIM)

Components are identified on the basis of the retention time and the response of the diagnostic ions. The retention times and the response of the diagnostic ions are determined on the basis of the calibration standard. For the components present in the calibration standard the diagnostic ions are given in Table 3; for approximate retention times see Annex A, Figure A.1 and A.2.

A component is positively identified if:

— the relative retention time of a substance in the total ion current chromatogram of the sample does not differ by more than ± 0,2 % if the absolute retention time is > 500 s and < 5 000 s;

— the relative intensity of the recorded diagnostic ions in the mass spectrum of the sample acquired under identical conditions does not differ by more than $\pm (0{,}1 \times I + 10)$ % from those of the corresponding substances in the reference substance (where I is the relative intensity recorded from the characteristic ions in the mass spectrum of the reference solution).

In order to allow for a correct peak quantification of a peak in the chromatogram it is necessary to satisfy he following conditions:

— the peak of a component should be at least 7 data points, if less the peak is not sufficiently defined by the determined a peak area;

— the recoveries of the internal standards should be at least 70 % and with a maximum of 110 %;

— if the quantity of a polycyclic aromatic hydrocarbon in the extract is higher than the upper limit of the measuring range, then the extract shall be diluted and re-analyzed.

NOTE Further guidance on identification is given in EN ISO 22892 [3] and the SANCO/12571/2013 guideline [17].

Table 3 — Characteristic masses of polycyclic aromatic hydrocarbons

Compound	Diagnostic ion		
	1 *m/z*	**2** *m/z*	**3** *m/z*
anthracene	178 (100)	176 (18)	76 *(3)*
anthracene-d10	188 (100)	184 (14)	
fluoranthene	202 (100)	200 (20)	100 *(3)*
fluoranthene-d10	212 (100)	208 (17)	
benzo[*a*]pyrene	252 (100)	250 (24)	113 (11)
benzo[*a*]pyrene-d12	264 (100)	260 (20)	
benzo[*k*]fluoranthene	252 (100)	250 (22)	126 (5)
benzo[*k*]fluoranthene-d12	264 (100)	260 (19)	
benzo[*b*]fluoranthene	252 (100)	250 (20)	126 (5)
benzo[*b*]fluoranthene-d12	264 (100)	260 (23)	
indeno[1,2,3-*cd*]pyrene	276 (100)	274 (22)	*138 (12)*
indeno[1,2,3-*cd*]pyrene-d12	288 (100)	284 (19)	
benzo[*g,h,i*]perylene	276 (100)	274 (22)	*138 (12)*
benzo[*g,h,i*]perylene-d12	288 (100)	284 (19)	

NOTE Figures in parentheses are the relative intensities of the fragment ion; Figures in italics indicate fragments that are often not present.

12 Calculation

12.1 Recovery of internal standards

The recovery of the internal standards (η_{is}) is determined on the basis of the calibration standard, which is corrected for the injection system, according to Formula (5):

$$\eta_{is} = \frac{A_{is,m}}{A_{is,std}} \cdot \frac{A_{inj,std}}{A_{inj,m}} \cdot \frac{C_{is,std}}{C_{is,m}} \cdot \frac{C_{inj,m}}{C_{inj,std}} \cdot 100 \quad (5)$$

where

η_{is} is the recovery of the internal standard in percent (%);

$A_{is,m}$ is the peak area of internal standard in the sample;

$A_{is,std}$ is the peak area of internal standard in the calibration standard;

$A_{inj,m}$ is the peak area of injection standard in the sample;

$A_{inj,std}$ is the peak area of injection standard in the calibration standard;

$C_{is,m}$ is the concentration of internal standard in the sample, e. g. in nanograms per millilitre (ng/ml);

$C_{is,std}$ is the concentration of internal standard in the calibration standard, e. g. in nanograms per millilitre (ng/ml);

$C_{inj,m}$ is the concentration of injection standard in the sample, e. g. in nanograms per millilitre (ng/ml);

$C_{inj,std}$ is the concentration of injection standard in the calibration standard, e. g. in nanograms per millilitre (ng/ml).

The recoveries of the internal standard should be at least 70 % and not exceed 110 %. If the recovery of any of the internal standards in the diluted sample is outside this range (accounting for the dilution), the calibration solutions (5.8.4) shall be analyzed and the calibration shall be verified. For each compound, confirm that the result of the verification analysis is within 20 % of the nominal concentration. If, however, any compound falls outside its respective limit, the measurement system is not performing properly for that compound. In this case, prepare a fresh calibration standard or correct the problem causing the failure and repeat the tuning of the GC-MS (6.4) and verification test or recalibrate (see 10.2).

If the internal standard recovery is outside these ranges, a diluted sample should be analyzed.

12.2 Concentration in the sample

The concentration of PAH in a water sample is calculated according to Formula (6):

$$C_n = \frac{A_n}{A_{is}} \cdot \frac{C_{is} \cdot V_{is}}{RRF} \cdot \frac{1}{V_w} \quad (6)$$

where

C_n is the concentration of a PAH, *n*, in the sample in nanograms per litre (ng/l);

A_n is the peak area of a PAH, *n*, in the sample extract;

A_{is} is the peak area of the internal standard in the sample extract;

RRF is the relative response factor of a PAH according to Formula (2);

C_{is} is the concentration of internal standard solution in nanograms per millilitre (ng/ml);

V_{is} is the added volume of internal standard solution in millilitres (ml);

V_w is the volume of the original sample in litres (l).

13 Expression of results

The mass concentration, in nanograms per litre (ng/l), of the individual compounds listed in Table 1 shall be reported to two significant figures.

EXAMPLES	anthracene	11 ng/l
	fluoranthene	1,2 ng/l
	benzo[*k*]fluoranthene	0,14 ng/l

14 Test report

The test report shall contain at least the following information:

a) the test method used, together with a reference to this European Standard (EN 16691);

b) complete identification of the sample;

c) sample preparation and extraction;

d) expression of the results, according to Clause 13;

e) any details not specified in this European Standard or which are optional, as well as any factor which may have affected the test results.

Annex A
(informative)

Suitable gas chromatographic conditions and example chromatograms — GC-conditions

GC equipment:	Agilent 7890A[3)] (or similar)
Injector:	Agilent 7693[3)] autoinjector (or similar)

For **dichloromethane** extracts applies:

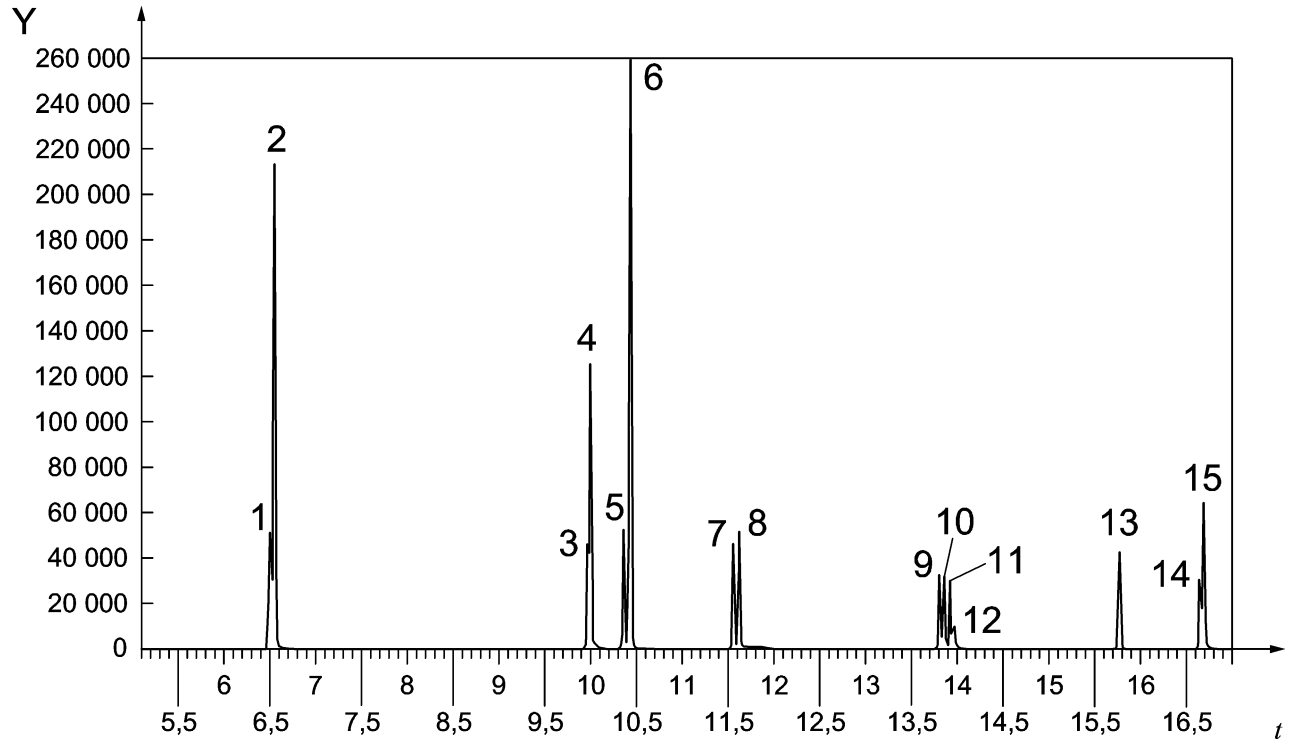
Injection:	pulsed splitless, 290 °C
Capillary column:	HP-5MS[3)], 30 m × 0,25 mm (inner diameter), film thickness 0,25 µm (or similar)
Injection volume	2 µl
Transfer line	280 °C
Carrier gas:	helium, 1,2 ml/min
Temperature programme 1:	60 °C (1 min) with 10 °C/min to 100 °C, with 20 °C/min to 320 °C (6 min)

If **toluene** is used as solvent then the above settings are used with the following modifications:

Temperature programme 2:	90 °C (2 min) with 10 °C/min to 300 °C (8 min)

Mass spectrometer:	HP5975C GC-MS Single Quad[3)] (or similar)
Ionization:	EI, 70 eV
Source:	300 °C
Solvent delay:	6,5 min (for toluene 5,8 min)
Acquisition:	SIM
GAIN:	10
SIM program:	See Table 3.

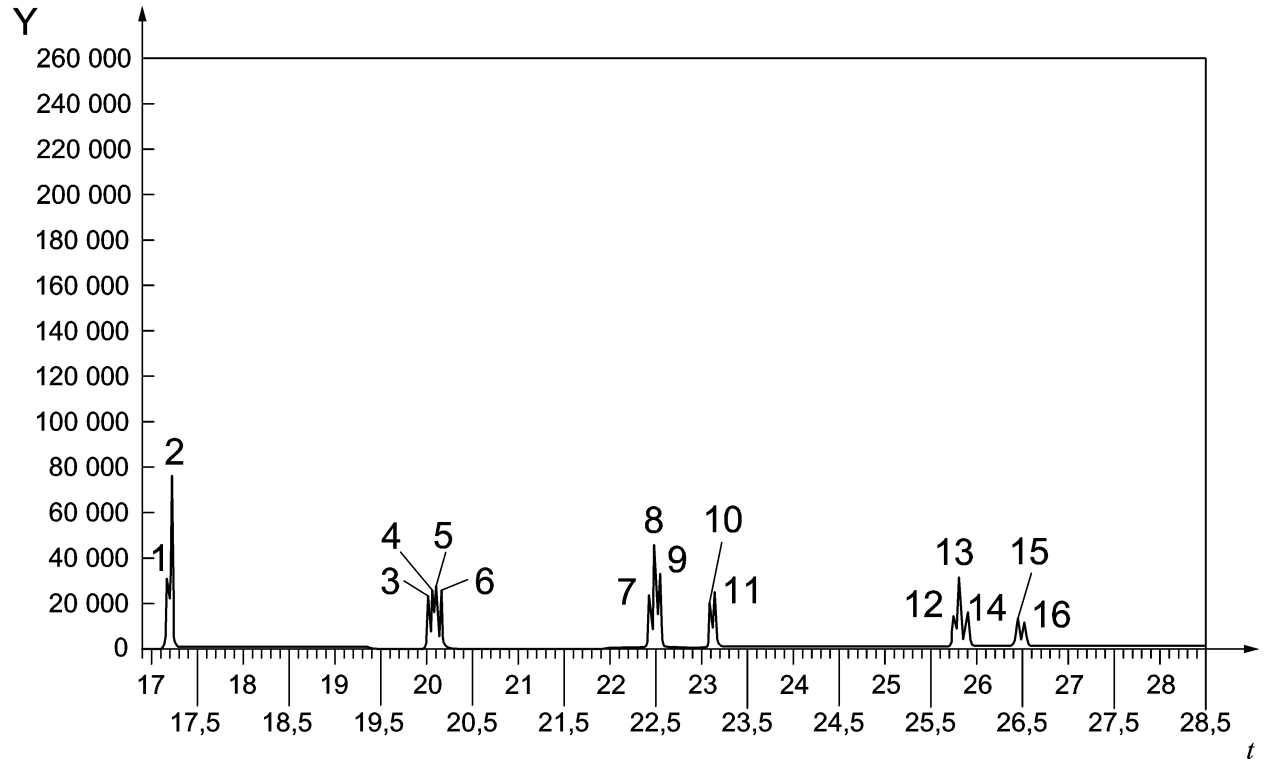
3) Agilent 7890A, Agilent 7693, HP-5MS and HP5975C GC/MS Single Quad are examples of suitable products which are commercially available. These examples are given only as information for the users of this European Standard and do not constitute an endorsement by CEN of these products.



Key

t	time in minutes (min)		
Y	abundance, signal intensity		
1	naphthalene-d	9	phenanthrene-d
2	naphthalene	10	phenanthrene
3	acenaphthylene-d	11	anthracene-d
4	acenaphthylene	12	anthracene
5	acenaphthene-d	13	1,2,3,4-tetrachloronaphthalene
6	acenaphthene	14	fluoranthene-d
7	fluorene-d	15	fluoranthene
8	fluorene		

Figure A.1 — Example chromatogram



Key

t	time in minutes (min)		
Y	abundance, signal intensity		
1	pyrene-d	9	benzo[*k*]fluoranthene
2	pyrene	10	benzo[*a*]pyrene-d
3	benzo[*a*]anthracene-d	11	benzo[*a*]pyrene
4	benzo[*a*]anthracene	12	indeno[1,2,3-*cd*]pyrene-d
5	chrysene-d	13	indeno[1,2,3-*cd*]pyrene, Dibenzo[*a,h*]anthracene-d
6	chrysene	14	dibenzo[*a,h*]anthracene
7	benzo[*b*]fluoranthene-d	15	benzo[*g,h,i*]perylene-d
8	benzo[*b*]fluoranthene, benzo[*k*]fluoranthene-d	16	benzo[*g,h,i*]perylene

Figure A.2 — Example chromatogram

Annex B
(informative)

Repeatability and reproducibility data

The performance data on repeatability and reproducibility given in Tables B.1, B.2 and B.3 were determined in a European inter laboratory trial for validation carried out in June 2014 on spiked natural mineral water.

- sample 1 and sample 2 were spiked with different amounts of suspended particulate matter (SPM) containing PAH;
- sample 1 was spiked with SPM derived from ERM-CZ100 at 20 mg/l;
- sample 2 was spiked with a synthetic PAH-containing SPM derived from the PAH model SPM [18], [19];
- sample 3 was spiked with PAH according to Table B.3.

Evaluation process of data was carried out according to ISO 5725-2.

The physico-chemical interactions taking place when adding model SPM to pre-filled water bottles are not known in detail. Therefore all concentrations in the final water samples based on slurry addition are estimated.

Table B.1 —Performance data for PAH mineral water, additionally spiked with 20 mg/l of suspended particulate matter (SPM), sample 1

Compound	l	n	o %	X ng/l	$\overline{\overline{x}}$ ng/l	η %	s_R ng/l	$C_{V,R}$ %	s_r ng/l	$C_{V,r}$ %
anthracene	10	20	0,0	5,66	3,44	60,89	1,67	48,4	1,15	33,4
fluoranthene	13	26	0,0	94,3	51,2	54,26	21,38	41,8	8,82	17,2
benzo[*b*]fluoranthene	11	22	8,3	28,7	33,2	115,69	10,56	31,8	5,18	15,6
benzo[*k*]fluoranthene	11	22	8,3	13,5	17,4	128,65	8,25	47,4	2,77	15,9
benzo[*a*]pyrene	8	16	33,3	14,5	13,5	92,69	2,58	19,1	0,563	4,2
benzo[*g,h,i*]perylene	10	20	16,7	35,6	34,2	96,10	6,50	19,0	6,50	19,0
indeno[1,2,3-*cd*]pyrene	7	14	36,4	21,6	22,5	104,23	1,67	7,4	0,927	4,1
naphthalene	4	8	20,0		7,75		4,01	51,8	1,20	15,5
fluorene	6	12	0,0		3,24		1,50	46,3	0,580	17,9
acenaphthene	4	7	22,2		2,28		2,49	109,5	0,064	2,8
acenaphthylene	8	16	0,0		2,99		2,50	83,6	0,473	15,8
phenanthrene	8	16	0,0	45,0	18,6	41,40	5,96	32,0	1,99	10,7
pyrene	9	18	0,0	92,7	51,5	55,59	19,48	37,8	10,51	20,4
chrysene	8	16	11,1	32,5	30,3	93,15	10,36	34,2	1,45	4,8
benzo[*a*]anthracene	6	12	14,3	18,4	16,6	90,04	2,93	17,7	1,63	9,8
dibenzo[*a,h*]anthracene	7	14	22,2	3,64	4,09	112,25	1,29	31,6	1,09	26,7

l number of laboratories after outlier rejection
n number of individual test results after outlier rejection
o percentage of outliers
X assigned value
$\overline{\overline{x}}$ overall mean of results (without outliers)
η recovery rate
s_R reproducibility standard deviation
$C_{V,R}$ coefficient of variation of reproducibility
s_r repeatability standard deviation
$C_{V,r}$ coefficient of variation of repeatability

Table B.2 — Performance data for PAH mineral water, additionally spiked with 200 mg/l of suspended particulate matter (SPM), sample 2

Compound	l	n	o	X	$\overline{\overline{x}}$	η	s_R	$C_{V,R}$	s_r	$C_{V,r}$
			%	ng/l	ng/l	%	ng/l	%	ng/l	%
anthracene	11	20	0,0	27,2	22,6	82,9	10,83	48,0	2,77	12,3
fluoranthene	13	24	0,0	476,3	223	46,9	80,39	36,0	18,41	8,2
benzo[*b*]fluoranthene	12	23	0,0	159,8	190	118,9	40,11	21,1	20,25	10,7
benzo[*k*]fluoranthene	10	19	17,4	118,8	77,9	65,5	13,57	17,4	8,99	11,5
benzo[*a*]pyrene	13	25	0,0	122,8	108	87,9	24,27	22,5	8,19	7,6
benzo[*g,h,i*]perylene	12	23	0,0	156,9	145	92,4	30,25	20,9	12,73	8,8
indeno[1,2,3-*cd*]pyrene	10	19	9,5	135,1	144	106,9	16,65	11,5	4,93	3,4
naphthalene	6	12	0,0	65,8	29,3	44,5	11,38	38,9	6,61	22,6
fluorene	6	12	0,0		9,45		2,91	30,8	0,852	9,0
acenaphthene	7	13	0,0		5,24		3,57	68,1	0,415	7,9
acenaphthylene	8	15	0,0		43,3		22,70	52,4	9,91	22,9
phenanthrene	8	16	0,0		153		48,81	31,8	10,95	7,1
pyrene	9	17	0,0		213		60,88	28,6	14,19	6,7
chrysene	8	16	11,1		159		46,78	29,4	20,88	13,1
benzo[*a*]anthracene	5	10	28,6		128		14,74	11,5	2,54	2,0
dibenzo[*a,h*]anthracene	9	18	0,0		29,6		5,06	17,1	2,46	8,3

NOTE Explanation of symbols see Table B.1.

Table B.3 — Performance data for PAH spiked mineral water, sample 3

Compound	l	n	o	X	$\overline{\overline{x}}$	η	s_R	$C_{V,R}$	s_r	$C_{V,r}$
			%	ng/l	ng/l	%	ng/l	%	ng/l	%
anthracene	10	20	0,0	100	103,7	103,7	19,34	18,6	9,95	9,6
fluoranthene	11	22	0,0	100	100,9	100,9	14,57	14,4	5,78	5,7
benzo[*b*]fluoranthene	10	20	9,1	30	27,7	92,2	3,02	10,9	1,47	5,3
benzo[*k*]fluoranthene	10	20	9,1	30	28,5	95,0	2,68	9,4	0,951	3,3
benzo[*a*]pyrene	11	22	0,0	50	50,0	99,9	5,10	10,2	2,93	5,9
benzo[*g,h,i*]perylene	10	20	9,1	20	19,0	95,1	2,86	15,0	1,30	6,8
indeno[1,2,3-cd]pyrene	9	18	10,0	20	19,8	98,9	2,23	11,3	1,35	6,8
naphthalene	6	12	0,0	100	99,8	99,8	10,77	10,8	5,41	5,4
fluorene	5	10	16,7	50	50,7	101,4	2,19	4,3	1,22	2,4
acenaphthene	7	14	0,0	100	107,5	107,5	14,70	13,7	6,78	6,3
acenaphthylene	8	16	0,0	100	106,5	106,5	19,48	18,3	10,70	10,0
phenanthrene	7	14	0,0	50	50,1	100,1	6,69	13,4	1,81	3,6
pyrene	8	16	0,0	50	52,0	104,0	5,97	11,5	1,02	2,0
chrysene	8	16	11,1	30	27,8	92,7	6,55	23,5	1,36	4,9
benzo[*a*]anthracene	7	14	0,0	30	29,3	97,6	4,17	14,2	2,29	7,8
dibenzo[*a,h*]anthracene	8	16	0,0	20	20,8	104,2	3,60	17,3	2,31	11,1

NOTE Explanation of symbols see Table B.1.

Annex C
(informative)

Dilution Schedules for standards

Table C.1 — Dilution schedule deuterated internal standard (5.8.2)

	Stock/ampoule µg/ml	**Microlitre syringes** µl	**Graduated flask** ml	**Concentration each d-PAH** µg/ml
CIL ES-2528 d-PAH Cocktail	100	500	10	5

Table C.2 — Dilution schedule injection standard (5.8.3)

	Stock/ampoule µg/ml	**Microlitre syringes** µl	**Graduated flask** ml	**Concentration** µg/ml
1,2,3,4-tetrachloronapthalene	1000	100	10	10

Table C.3 — Dilution schedule calibration standard (5.8.4)

Analyte		CS1	CS2	CS3	CS4	CS5
	ACN stock concentration					
	µg/l	ng/ml	ng/ml	ng/ml	ng/ml	ng/ml
anthracene	0,79	0,79	3,95	19,75	98,75	197,5
fluoranthene	7,58	7,58	37,9	189,5	947,5	1895
benzo[*b*]fluoranthene	4,19	4,19	20,95	104,75	523,75	1047,5
benzo[*k*]fluoranthene	4,69	4,69	23,45	117,25	586,25	1172,5
benzo[*a*]pyrene	4,87	4,87	24,35	121,75	608,75	1217,5
indeno[1,2,3-*cd*]pyrene	4,27	4,27	21,35	106,75	533,75	1067,5
benzo[*g,h,i*]perylene	3,67	3,67	18,35	91,75	458,75	917,5
	toluene stock concentration					
1,2,3,4-tetrachloronaphthalene	10	100	100	100	100	100
	benzene-d6 stock concentration					
anthracene-d10	5	100	100	100	100	100
fluoranthene-d10	5	100	100	100	100	100
benzo[*b*]fluoranthene-d12	5	100	100	100	100	100
benzo[*k*]fluoranthene-d12	5	100	100	100	100	100
benzo[*a*]pyrene-d12	5	100	100	100	100	100
indeno[1,2,3-*cd*]pyrene-d12	5	100	100	100	100	100
benzo[*g,h,i*]perylene-d12	5	100	100	100	100	100

Annex D
(informative)

Silica clean-up

Dry the solvents used for cleaning the extract by applying molecular sieve beads (6.8). The silica should have its maximum activity.

For clean-up of the extract use columns containing at least 3 g of silica (5.6). Add a layer of sodium sulfate (5.5) on top of the column. Clean the silica in the column with five bed volumes of a mixture of dichloromethane/*iso*-hexane (5.4) (1+1), followed by conditioning with the same volume of iso-hexane.

Concentrate the enriched extract by blowing with a gentle stream of nitrogen (5.3) so that a volume of 500 µl remains and add 500 µl of *iso*-hexane (5.4).

Transfer the concentrated extract using a Pasteur pipette (6.7) onto the iso-hexane covered silica and allow to soak almost completely into the silica. Collect the eluate in a autosampler (6.3).

Rinse the reduction flask with 500 µl of *iso*-hexane (5.4), and add this solution onto the column and allow to soak almost completely into the silica.

Elute the PAH with 12 ml of a mixture of dichloromethane/*iso*-hexane (5.4) (1+1).

Enrich to approximately 1 000 µl by a stream of nitrogen (5.3) and proceed with Solvent Change (8.1.5).

Annex E
(informative)

Examples of suitable solid-phase extraction disks (SPE-disks)

Table E.1 lists some examples of solid-phase extraction disk (SPE-disk) that have been tested and which have proved to be suitable for the purpose. Other disks can be used as well if their suitability has been established in preliminary tests.

Table E.1 — Examples of suitable SPE-disks

Sorbent (disk type)	Product name (supplier)
styrene-divinyl benzene copolymer (cartridge type, 47 mm)	BAKERBOND [4)] Speedisk H_2O-philic DVB 8072–06 low capacity, (J.T.Baker)
styrene-divinyl benzene copolymer (cartridge type, 47 mm)	BAKERBOND [5)] Speedisk H_2O-philic DVB 8072–07 high capacity, (J.T.Baker)

4) BAKERBOND Speedisk are examples of suitable products which are commercially available. These examples are given only as information for the users of this European Standard and do not constitute an endorsement by CEN of these products.

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