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# Ambient air — Method for the measurement of benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene

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# Ambient air - Method for the measurement of benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene

Air ambiant - Méthode pour la mesure de benz[a]anthracène, benzo[b]fluoranthène, benzo[j]fluoranthène, benzo[k]fluoranthène, dibenz[a,h]anthracène, indeno[1,2,3-cd]pyrène et benzo[ghi]perylène

Außenluft - Verfahren zur Messung von Benz[a]anthracen, Benzo[b]fluoranthen, Benzo[j]fluoranthen, Benzo[k]fluoranthen, Dibenz[a,h]anthracen, Indeno[1,2,3-cd]pyren und Benzo[ghi]perylen

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**CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels**

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# Foreword

This document (CEN/TS 16645:2014) has been prepared by Technical Committee CEN/TC 264 “Air quality”, the secretariat of which is held by DIN.

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# Introduction

The measurement methods specified in this document are based on methods that were worked out during the laboratory and field validation tests for the European Standards EN 15549 [5] (determination of BaP in ambient air) and EN 15980 [6] (determination of the deposition of several particle bound PAH compounds). Many data on the performance of the extraction and analysis of benz[*a*]anthracene (BaA), benzo[*b*]fluoranthene (BbF), benzo[*j*]fluoranthene (BjF), benzo[*k*]fluoranthene (BkF), dibenz[*a,h*]anthracene (DBahA), indeno[1,2,3-*cd*]pyrene (INP) and benzo[*ghi*]perylene (BghiP) in deposition or PM10 samples were gathered. These data do not cover the complete measurement procedure including sampling and consequently enable publication of a Technical Specification instead of a European Standard.

It is the long-term goal to combine this document with EN 15549 [5], once adequate progress has been made in the development of reliably working oxidant denuders.

# 1 Scope

This Technical Specification specifies a measurement method for the determination of the particle bound polycyclic aromatic hydrocarbon (PAH) compounds benz[*a*]anthracene (BaA), benzo[*b*]fluoranthene (BbF), benzo[*j*]fluoranthene (BjF), benzo[*k*]fluoranthene (BkF), dibenz[*a,h*]anthracene (DBahA), indeno[1,2,3-*cd*]pyrene (INP) and benzo[*ghi*]perylene (BghiP) in ambient air, which can be used in the framework of Council Directive 2008/50/EC [10] and Directive 2004/107/EC [11]. This document specifies performance characteristics and performance criteria for this measurement method. The performance characteristics of the measurement method are based on a sampling period of 24 h.

This Technical Specification describes a measurement method which comprises sampling of the selected PAH compounds as part of the PM10 particles, sample extraction and analysis by high performance liquid chromatography (HPLC) with fluorescence detector (FLD) or by gas chromatography with mass spectrometric detection (GC-MS). The method is applicable for the measurement of the PAH compounds in the concentration range from approx. 0,04 ng/m$^3$ to approximately 20 ng/m$^3$ for BaA, BbF, BjF, BkF, BaP, INP and BghiP and 0,02 ng/m$^3$ to approximately 2 ng/m$^3$ for DBahA. Table 1 shows examples for concentrations of the compounds (annual mean values) for sampling sites with different characteristics.

**Table 1 — Examples of annual mean values of PAH compounds in PM10 at sampling sites with different characteristics (in ng/m$^3$)**

| Compound | Industrial [a] | Urban background [b] | Traffic [c] | Rural background [d] |
|---|---|---|---|---|
| BaA | 0,85 | 0,24 | 0,24 | 0,06 |
| BbF | 2,44 | 0,62 | 0,48 [e] | 0,16 [e] |
| BjF | 0,89 | 0,27 | | |
| BkF | 0,89 | 0,24 | 0,17 | 0,15 |
| BaP | 1,15 | 0,29 | 0,27 | 0,13 |
| BghiP | 1,31 [f] | 0,20 [g] | 0,34 | 0,09 |
| DBahA | 0,20 | 0,10 | 0,05 [f] | 0,07 [h] |
| INP | 1,60 | 0,43 | 0,23 | 0,08 |

[a] Bottrop (Germany, 2010), HPLC/FLD.

[b] Mülheim-Styrum (Germany, 2010), HPLC/FLD.

[c] London Crystal Palace Parade (UK, 2010), GC-MS.

[d] Harwell (UK, 2010), GC-MS.

[e] (Bbf+BjF).

[f] Wijk aan Zee (The Netherlands, 2011), GC-MS.

[g] Rotterdam (The Netherlands, 2011), GC-MS.

[h] (DBacA+DBahA).

The lower limit of the applicable range depends on the noise level of the detector and the variability of the laboratory filter blank.

## 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 12341, *Ambient air — Standard gravimetric measurement method for the determination of the PM10 or PM2,5 mass concentration of suspended particulate matter*

ENV 13005, *Guide to the expression of uncertainty in measurement*

EN ISO 20988, *Air quality — Guidelines for estimating measurement uncertainty (ISO 20988)*

EN ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories (ISO/IEC 17025)*

ISO/IEC Guide 98-3:2008, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

ISO 7870-2, *Control charts — Part 2: Shewhart control charts*

## 3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

**3.1**
**calibration solution**
solution used for calibration of the analytical instrument, containing the analyte of interest at a suitable concentration, prepared by dilution of the stock standard solution

[SOURCE: EN 15549:2008 [5]]

**3.2**
**certified reference material**
CRM
reference material, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures

[SOURCE: JGCM 200:2012 [12]]

**3.3**
**external standard solution**
solution of compounds of known concentrations which are analysed separately from the unknown sample under identical conditions

**3.4**
**field blank filter**
filter that is taken through the same procedure as a sample, except that no air is drawn through it

[SOURCE: EN 15549:2008 [5]]

**3.5**
**internal standard solution**
solution of known compounds of known concentrations, added to the sample before chromatographic analysis

**3.6**
**laboratory blank filter**
unused filter that does not leave the laboratory and is taken through the same analytical procedure as the sample

[SOURCE: EN 15549:2008 [5]]

**3.7**
**PM10**
particulate matter suspended in air which is small enough to pass through a size-selective inlet with a 50 % efficiency cut-off at 10 µm aerodynamic diameter

Note 1 to entry: By convention, the size-selective standard inlet designs prescribed in this Technical Specification – used at the prescribed flow rates – possess the required characteristics to sample the relevant PM fraction suspended in ambient air.

Note 2 to entry: The efficiency of the size selectiveness of other inlets used may have a significant effect on the fraction of PM surrounding the cut-off, and, consequently on the particle bound PAH compounds determined.

[SOURCE: EN 12341:2014, modified — the very end of Note 2 to entry has been modified.]

**3.8**
**reagent blank solution**
solution that contains all the reagents used during analysis of the sample, but without the sample and filter matrix

[SOURCE: EN 14902:2005 [4]]

**3.9**
**stock standard solution**
solution used for preparing calibration solutions, containing the analyte of interest at a concentration traceable to national or international standards

[SOURCE: EN 15549:2008 [5]]

**3.10**
**surrogate standard solution**
solution of a compound added to the test material, the chemical and physical behaviour of which is taken to be representative of the native analyte

Note 1 to entry: This solution is used to spike filters before extraction in order to check the recovery efficiency.

**3.11**
**uncertainty (of measurement)**
parameter associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand

[SOURCE: ISO/IEC Guide 98-3:2008]

# 4 Symbols and abbreviations

## 4.1 Symbols

$a$ is the slope of linear calibration function

$A_C$ is the peak area or peak height of a PAH compound or of its characteristic ion in the chromatogram of the calibration solution

$A_E$ is the peak area or peak height of a PAH compound or of its characteristic ion in the chromatogram of the sample extract

$A_{IS}$ is the peak area or peak height of the internal standard or of its characteristic ion in the chromatogram of the calibration solution

$A_{ISE}$ is the peak area or peak height of the internal standard or of its characteristic ion in the chromatogram of the sample extract

$b$ is the intercept of the linear calibration function

$C$ is the concentration of the PAH compound in ambient air, in ng/m$^3$

$D_C$ is the detection limit, in ng/m$^3$

$D_M$ is the absolute detection limit in the sample, in ng

$f$ is the response factor of the PAH compound

$\bar{m}_b$ is the mean of laboratory filter blanks, in ng

$m_C$ is the mass of the PAH compound in the calibration solution, in ng

$m_{CRM}$ is the certified mass in the CRM, in ng

$m_E$ is the mass of the PAH compound in the sample extract, in ng

$m_F$ is the mass of the PAH compound on the filter sample, in ng

$m_i$ is the individual filter blank, in ng

$m_{IS}$ is the mass of the internal standard in the calibration solution, in ng

$m_{ISE}$ is the mass of the internal standard in the sample extract, in ng

$m_{reg}$ is the mass of the PAH compound calculated from the regression formula at the level of the calibration standard, in ng

$m_{SSE}$ is the mass of the surrogate standard in the sample extract, in ng

$m_{SSF}$ is the mass of the surrogate standard added to the filter, in ng

$m/z$ is the mass-to-charge ratio;

$n$ is the number of analysed filters;

$R$ is the recovery efficiency of the PAH compound, in %;

$R_s$ is the peak resolution

$S_{lfb}$ is the standard deviation of laboratory filter blanks, in ng

$s(m_E)$ is the standard deviation of the replicate measurement results of the mass determined, in ng

$t$ is the sampling time, in h

$t_{n-1;0,95}$ is the Student factor for n measurements and a 95 % confidence interval

$t_{R1}$ is the retention time for peak 1, in min

$t_{R2}$ is the retention time for peak 2, in min

$V_E$ is the volume of the extract, in ml

$V$ is the volume of air sampled in, $m^3$

$V_n$ is the nominal daily sampling volume, in $m^3$

$w_1$ is the peak width of peak 1, in min

$w_2$ is the peak width of peak 2, in min

$X_a$ is the measured mass fraction of the PAH compound, in mg/kg

$X_{ca}$ is the certified mass fraction of the PAH compound, in mg/kg

### 4.2 Abbreviations

| | |
|---|---|
| BaA | Benz[*a*]anthracene |
| BaP | Benzo[*a*]pyrene |
| BbF | Benzo[*b*]fluoranthene |
| BghiP | Benzo[*ghi*]perylene |
| BjF | Benzo[*j*]fluoranthene |
| BkF | Benzo[*k*]fluoranthene |
| CRM | Certified reference material |
| DAD | Diode array detection |
| DBahA | Dibenz[*a,h*]anthracene |
| FLD | Fluorescence detection |
| GC | Gas chromatography |
| HPLC | High performance liquid chromatography |
| INP | Indeno[1,2,3-*cd*]pyrene |
| MS | Mass spectrometry |
| PAH | Polycyclic aromatic hydrocarbon |
| PTFE | Polytetrafluoroethylene |
| QA/QC | Quality Assurance/Quality Control |
| TSP | Total suspended particulates |

## 5 Principle of the method

The method is divided into two main parts: the sampling of PM10 in the field and the analysis of the specified PAHs in the laboratory.

The sampling time is 24 h. The filter is transported to the laboratory. The PAH compounds are extracted using an organic solvent. If necessary, the extract is cleaned up. The resulting solution is analysed by HPLC/FLD or GC-MS.

## 6 Requirements

### 6.1 Siting requirements

Specific siting requirements depend on the objectives of the measurements. For measuring in compliance with Directive 2004/107/EC [11] then the instructions for siting samplers given in [11] will need to be followed.

## 6.2 Sampling requirements

The sampling system shall fulfil the requirements of EN 12341.

In the presence of oxidants (e.g. ozone, OH radicals) PAH compounds may degrade. Whenever these effects are expected to be significant, the PM10 sampler may be equipped with an oxidant (e.g. ozone) denuder (see Annex A). However, the application of these denuders lacks sufficient validation to be a normative part of this Technical Specification.

NOTE The analytical methods are also suitable for PAH determination in other PM particle size fractions (e.g. PM2.5 and TSP).

## 6.3 Analysis

### 6.3.1 Recovery efficiency

Using the external or internal standard method for quantification check the recovery efficiency within every analytical batch by spiking laboratory blank filters with a known amount of the PAH compounds and process them as usual. The recovery efficiency shall be between 80 % and 120 %.

If the surrogate standard method (see 12.1.3) is used this recovery check is not necessary. The surrogate recovery for field samples shall not be less than 50 %, otherwise the sample shall be discarded.

If the surrogate recovery is constantly less than 70 %, this indicates problems with the sample preparation procedure. These problems should be eliminated.

Check the recovery efficiency of the method for the PAH compounds in certified reference material (e.g. NIST 1649b, ERM-CZ 100) using Formula (1):

$$R = \frac{X_{\mathrm{a}}}{X_{\mathrm{ca}}} \cdot 100 \qquad (1)$$

where

$R$ is the recovery efficiency of the PAH compound, in %;

$X_{\mathrm{a}}$ is the measured mass fraction of the PAH compound, in mg/kg;

$X_{\mathrm{ca}}$ is the certified mass fraction of the PAH compound, in mg/kg.

The recovery efficiency shall be between 80 % and 120 %.

NOTE A certified reference material containing the same matrix as ambient PM10 particles collected on filters is not available at the moment. Interferences occurring to field samples, e.g. chemical reactions of the PAH compounds during extraction, can be identified, for example, by:

- repeating the extraction step with a different method and comparing the results;
- comparing the ratio of the PAH compounds to at least one more stable and high-boiling PAH like benzo[*e*]pyrene or benzo[*k*]fluoranthene: an indication for problems occurring during the sample preparation procedure is that deviations (lower ratios) with respect to previous measurements at the same location and in the same season are observed; changing the sample preparation procedure (different extraction solvent, different purification procedure) can verify the problem.

### 6.3.2 Detection limit

#### 6.3.2.1 General

The detection limit can be calculated either based on laboratory filter blanks or, if no peaks corresponding to the PAH compounds can be identified in filter blanks, based on the signal-to-noise ratio.

In general the detection limit shall be less than 0,04 ng/m$^3$. If the 3 benzofluoranthene species are analysed as a sum, their cumulated detection limit shall be less than 0,1 ng/m$^3$. If BjF is analysed by HPLC-FLD, its detection limit is about 0,4 ng/m$^3$.

#### 6.3.2.2 Determination based on laboratory filter blanks

Determine the detection limit from the standard deviation of at least 10 laboratory filter blanks, analysed like the real samples, using Formula (2):

$$S_{\mathrm{lfb}} = \sqrt{\frac{\sum_{i=1}^{n} (\overline{m}_{\mathrm{b}} - m_{\mathrm{i}})^2}{n-1}} \qquad (2)$$

where

$S_{\mathrm{lfb}}$ is the standard deviation of laboratory filter blanks, in ng;

$\overline{m}_{\mathrm{b}}$ is the mean of laboratory filter blanks, in ng;

$m_{\mathrm{i}}$ is the individual filter blank, in ng;

$n$ is the number of analysed filters.

The minimal detectable mass of the PAH compounds is calculated using Formula (3):

$$D_{\mathrm{M}} = t_{n-1;0,95} \cdot S_{\mathrm{lfb}} \qquad (3)$$

where

$D_{\mathrm{M}}$ is the minimal detectable mass of the PAH compound, in ng;

$t_{\mathrm{n\text{-}1;0,95}}$ is the Student factor for $n$ measurements and a 95 % confidence interval;

$S_{\mathrm{lfb}}$ is the standard deviation of laboratory filter blanks, in ng.

#### 6.3.2.3 Determination based on the signal-to-noise ratio

Perform a chromatographic analysis with a reagent blank. Keep the chromatographic parameters as used for the calibration and the detection of the PAH compounds. Calculate the detection limit as three times the average of the height of the noise at the retention time of the PAH compounds ± 10 times the peak width at half peak height at the lowest calibration level.

#### 6.3.2.4 Calculation of the detection limit

The detection limit, expressed in ng/m$^3$, is calculated introducing the nominal daily sampling volume according to Formula (4).

$$D_{\mathrm{C}} = \frac{D_{\mathrm{M}}}{V_{\mathrm{n}}} \qquad (4)$$

where

$D_C$ is the detection limit, expressed in ng/m$^3$;

$D_M$ is the minimal detectable mass of the PAH compound, in ng;

$V_n$ is the nominal daily sampling volume, in m$^3$.

For the nominal daily sampling volume data shall be used which are usually obtained during sampling.

NOTE The volume is, for example, ca. 720 m$^3$/d for high volume samplers and 55 m$^3$/d for low volume samplers.

# 7 Reagents and gases

## 7.1 Solvents

High purity solvents, suitable for trace analysis (see 13.1), e.g. toluene, cyclohexane, dichloromethane, acetonitrile and water.

## 7.2 Gases

Helium or hydrogen (purity 99,999 %) used as carrier gas for GC-MS and Helium (purity 99,9 %) for degasification of solvents of the HPLC method.

## 7.3 External standard

A solution of the PAH compounds in an appropriate organic solvent, e.g. a dilution of the stock standard solution (7.6).

## 7.4 Internal standard

— Methylated or halogenated PAH, e.g. 6-methylchrysene (for HPLC/FLD);

— deuterated or carbon-13-labelled PAH, e.g. perylene-d12 (for GC-MS).

Make sure that the standards contain less than 1 % (relative) of the native (carbon-12) PAH compounds.

## 7.5 Surrogate standard

— Methylated or halogenated PAH, e.g. 7-methylbenzo[*a*]pyrene (for HPLC/FLD);

— deuterated or carbon-13-labelled substances of the PAH compounds to be analysed (for GC-MS).

Make sure that the standards contain less than 1 % (relative) of the native (carbon-12) PAH compounds.

In case of HPLC/FLD analysis check carefully that the signal of the surrogate standard does not overlap with signals of known or unknown PAH compounds.

## 7.6 Stock standard solution

Dilution of a solution of the PAH compounds with a concentration traceable to internationally accepted standards, e.g. NIST 1647e.

## 7.7 Certified reference material

Containing a certified concentration of the PAH compounds, in a matrix similar to PM 10 particles (e.g. NIST 1649b, ERM-CZ 100).

# 8 Apparatus

## 8.1 Sampling equipment

### 8.1.1 PM10 sampler.

The sampling system shall fulfil the requirements of EN 12341.

**8.1.2 Greasing agent**, if required, suitable for greasing the sampler impaction plate (see manufacturer's instructions).

**8.1.3 Quartz fibre, glass fibre or PTFE coated glass fibre filters**, of a diameter suitable for use with the samplers (8.1.1), with a separation efficiency of at least 99,5 % at an aerodynamic diameter of 0,3 µm. This criterion has also to be met after pre-treatment of filters according to the 2nd paragraph of Subclause 13.6.

The purity of the filters shall be checked according to 13.6.

It is recommended that filter manufacturers determine the filter separation efficiency according to standard methods such as EN 13274-7 [2] or EN 1822-1 [1].

**8.1.4 Flow meter**, which meets the requirements of EN 12341.

## 8.2 Sample preparation/extraction

The following apparatus is required:

- round-bottomed flask with reflux condenser; or
- Soxhlet assembly; or
- microwave digestion system; or
- accelerated solvent extraction apparatus; or
- sonication bath.

For examples or details of the procedure see Annex B.

In some cases it is necessary to carry out a clean-up according to Annex C.

## 8.3 Laboratory apparatus

### 8.3.1 HPLC/FLD apparatus

Liquid chromatograph fitted with injection system, a reverse phase column suitable for PAH analysis, a temperature controlled oven, a pump system and a FLD (see also D.1). Furthermore a system for solvent degassing (internal or external) is required.

NOTE If the PAH compounds concentration in the extract is high enough a DAD can be used (see 15.2).

### 8.3.2 GC-MS apparatus

Gas chromatograph, e.g. with split/splitless injector or on column injector, capillary column suitable for PAH analysis, and a mass selective detector (see also D.2).

# 9 Sampling

## 9.1 Preparation of the equipment before sampling

Consult the manufacturer's instruction manual to determine the minimum voltage and power requirements of the sampler and ensure that an adequate power supply is available at the sampling site.

Clean the sampler inlet, suction pipe, and all other parts of the sampler, such as filter a change mechanism and filter cassettes, which may come in contact with the filter before use according to the manufacturer's specifications. Similarly, inspect greased parts like impaction plates before use, clean them if necessary and grease them again.

A leak test and flow rate calibration shall be carried according to EN 12341.

## 9.2 Handling of filters

Handle small filters with blunt tweezers, so as to avoid contamination and damage. For large filters this procedure might not be practicable. In this case handle them carefully using gloves made of an appropriate material (e.g. polyacrylnitrile), touching only the outside edges of the filters.

## 9.3 Preparation of filters

Filters that have visibly been contaminated, e.g. during packing and/or transport shall be rejected.

Inspect each filter before use for pin holes and other imperfections, such as chaffing, loose material, dislocation and non-uniformity. For example, use a magnifying lens with a light or check in front of an area light. Reject any filter if its integrity is suspect.

Assign each filter a unique identifier and place it in a labelled, sealed container for storage and transportation to the field.

The container should be made of appropriate material (e.g. glass, PTFE).

If the filter shall be marked for identification purposes, do not mark it in an area that will be analysed.

Establish a filter log (i.e. a chain of custody book/record) to document the use of each filter. Record the number of filters in the filter log. If the sampler to be used is a sequential sampler that operates continuously for a programmed period, load the required number of filters into a labelled filter cartridge and seal it ready for transportation to the field. It shall be recorded which filter was located into which position in the cartridge.

Handle laboratory blank filters in the same way as real samples, but do not transport them and do not draw air through them. Each batch of filters shall be checked before use by analysing at least 5 filters (see 13.6).

Prepare field blank filters and process them as far as possible as real samples. Transport them to the sampling site, mount them into the sampler (without switching on the pump), dismount them, return them to the laboratory and process them in the same way as real samples. At least one of every 20 filters ore one filter per month shall be analysed as field filter blank. If the field filter blank significantly exceeds the average laboratory filter blank (e.g. > 3 times the standard deviation of the laboratory filter blank determination), the sources of contamination shall be investigated and eliminated. If the results of real samples are significantly affected by the field filter blank, the samples shall be reanalysed, if possible.

### 9.4 Sample collection, transport and storage

Set up the sampler in the field according to the manufacturer's instructions, ensuring that the siting requirements (see 6.1) are met. Then carry out a leak test and check the flow rate of the sampler using the calibrated flow meter before use according to EN 12341, following the manufacturer's instructions.

Take field filter blanks periodically at each site (at least once for every 20 filters used for sampling, see 9.3).

Load either an unexposed filter (for single filter devices) or a cartridge of unexposed filters (for sequential samplers) into the sampler at the start of the sampling period. Program the sampler following the manufacturer's instructions, start the timer and record the start time.

The sampling time is 24 h.

Collect the filter from the sampler, replace it in its uniquely marked transport container and seal the container for transportation to the laboratory (for single filter devices). If filters are stored in the samplers, the temperature shall be below 23 °C [13], storage time shall not exceed 21 days. If the temperature during storage is higher than 23 °C the user shall demonstrate that no PAH losses occur.

The conditions during transport shall be the same as during storage.

If filters are folded for storage (for easier transportation), then it will be necessary to analyse the whole filter as folding can affect the distribution of particles on the filter surface. In this case the marked part of the filter (see 9.3) shall be cut out before extraction.

The filters shall be extracted not later than two months after sampling. They shall be stored in the dark in a tightly closed vessel at a temperature below 23 °C. The storage time can be extended to 12 months if the samples are stored at temperatures below –10 °C.

Individual samples taken over a period of up to one month can be combined and analysed as a composite sample [11]. Filter cuts of identical size of single days can be extracted together. If the PAH compounds content of these composite extracts is divided by the sum of the air volumes sampled with the filter cuts the result is the mean value for that period. The minimum time coverage of the sampling period shall be 33 %.

Record all details of each sample in the filter log, including stop time, flow rate, air sample volume in cubic metre, any mechanical or electrical failures during the sampling period and any other data that could be important for the evaluation of the sampling.

## 10 Sample preparation

### 10.1 Cleaning of the laboratory apparatus

Cleaning of extraction devices and labware shall be carried out in a way that blank values are avoided or lower than a mass corresponding to a final concentration of 0,04 ng/$m^3$ after usual work-up.

For example, with a sampling volume of 100 $m^3$ and a final volume of the extract of 1 ml the blank value should be lower than 4 ng.

### 10.2 Extraction

The following techniques have been shown to meet the requirements of 6.3.1:

- extraction by reflux;
- Soxhlet extraction;

- accelerated solvent extraction;
- ultrasonic extraction;
- microwave extraction.

The methods are described in Annex B.

Any extraction method leads to a solution of the PAH compounds and other substances in an organic solvent. For GC-MS the extract can directly be analysed, if it is reduced to a known volume and if no further purification is necessary. For HPLC/FLD the extract shall be carefully evaporated to dryness and shall be dissolved in a known volume of acetonitrile. If necessary, the extract shall be cleaned before reducing it in volume to at least 10 % of the final volume (see, for example, Annex C). If the solutions are not analysed immediately, they shall be stored in the dark to avoid compound degradation and at a temperature less than 6 °C to avoid the evaporation of the solvent. The maximum permissible storage period is one month.

# 11 Analysis

## 11.1 General

For BaP, the analysis procedure is consistent with EN 15549 [5], for the other PAH compounds it is consistent with EN 15980 [6].

## 11.2 HPLC/FLD analysis

### 11.2.1 Principle of the method [8]

The organic extract containing the PAH compounds is filtered, if necessary purified by column chromatography (e.g. Annex C), reduced in volume and dissolved in acetonitrile. An aliquot of the solution is injected into the HPLC/FLD apparatus. The PAH compounds are identified by their retention time. The peak area and/or peak height is used as a measure of its concentration in the sample.

In practice, extracts from PM10 particles may be carefully evaporated to dryness without reducing the recovery of the PAH compounds.

As the response and sensitivity of the FLD is sufficiently constant (<5 % drift per day, see 14.2.1), either the internal or the external standard method can be used for quantification. If the clean-up procedure or a complex sample matrix affects the recovery efficiency, the surrogate standard method can be used to correct losses during sample preparation.

### 11.2.2 Reagents

#### 11.2.2.1 Calibration solutions

Prepare calibration solutions of the PAH compounds from the stock solution at a minimum of five concentration levels by adding appropriate volumes of the PAH stock solution to a volumetric flask and making up with acetonitrile. The concentrations shall cover a working range corresponding to the expected range of concentrations found in real samples. The lowest concentration shall be near but above the detection limit.

NOTE For the external standard method (see 12.1.1) these solutions are used for calibration purposes, for the internal and surrogate standard method (see 12.1.2, 12.1.3) these solutions are used for the check of the lack of fit.

The expected range of concentrations may vary depending on the season. It is advisable to change the calibration range accordingly.

#### 11.2.2.2 External standard solution

Use a calibration solution (11.2.2.1) with concentrations of the PAH compounds close to the expected concentrations in extracts of real samples.

The highest calibration solution (11.2.2.1) can usually be used as external standard solution.

#### 11.2.2.3 Internal standard solution

Dilute the internal standard (7.4) in acetonitrile. Add, for example, 10 µl of this solution to the sample extracts (after clean-up, if any) before analysis. The concentration of the solution shall be equivalent to the expected PAH concentrations in real sample extracts.

#### 11.2.2.4 Surrogate standard solution

Dilute the surrogate standard (7.5) in acetonitrile. Add, for example, 10 µl of this solution to the filter before extraction. The concentration of the solution shall be equivalent to the expected PAH concentrations in real sample extracts.

### 11.2.3 Proposed parameters for HPLC/FLD operation

See example in D.1.

### 11.2.4 Calibration and lack-of-fit test

When using the external standard method for quantification, inject the calibration solutions (see 11.2.2.1; aliquots of 20 µl, for example) directly into the HPLC system and plot the peak area or the peak height versus the concentration. Calculate the calibration function using linear regression. The lack of fit of the calibration function shall fulfil the requirements in 14.2.1, Table 2 (see E.4.4.2.3 for calculation).

### 11.2.5 Detection and measurement

Remove the sample extracts from cold storage and allow them to warm up to room temperature. Inject an aliquot of the sample (for example 20 µl) into the HPLC system, identify the PAH compounds by their retention time. Dilute an aliquot of the extract and reanalyse it, if the concentration of the PAH compounds in the extract is above the upper limit of the working range. For quantification use either the external, or the internal or the surrogate standard technique.

## 11.3 GC-MS analysis

### 11.3.1 Principle of the method [7]

The organic extract containing the PAH compounds may be purified by column chromatography (see, for example, Annex C), if necessary. Then the extract is concentrated. An aliquot of the solution is injected into the GC-MS system. After separation in a capillary column the PAH compounds are detected by a mass spectrometric detector. The substance is identified by its retention time and by the m/z values of specific ions; the peak area or the peak height is a measure of its concentration in the sample.

For GC-MS analysis a combination of the internal standard method and the surrogate standard method is required for quantification.

#### 11.3.2 Reagents

##### 11.3.2.1 Calibration solutions

Prepare calibration solutions of the PAH compounds from the stock solution at a minimum of five concentration levels by adding appropriate volumes of the PAH stock solution to a volumetric flask and making up with the appropriate solvent (see B.7). The lowest concentration shall be near, but above the detection limit. The other concentrations shall cover a working range corresponding to the expected range of concentrations found in real samples.

##### 11.3.2.2 Internal standard solution

Dilute the internal standard (7.4) in the appropriate solvent (see B.7). Add, for example, 10 µl of this solution to the sample extracts (after clean-up, if any) before analysis. The concentration of the solution shall be equivalent to the expected PAH concentrations.

##### 11.3.2.3 Surrogate standard solution

Dilute the surrogate standard (7.5) in the appropriate solvent (see B.7). Add, for example, 10 µl of this solution to the filter before extraction. The concentration of the solution shall be equivalent to the expected PAH concentrations.

#### 11.3.3 Proposed parameters for GC-MS operation

See example in D.2.

#### 11.3.4 Lack of fit

In order to determine the linear working range of the detector for the PAH compounds inject the solutions for checking the lack of fit (see 11.3.2.1; aliquots of 2 µl, for example) directly into the GC-MS system and plot the peak area or peak height versus the concentration. Check the lack of fit of the function (requirement see 14.2.1, Table 2; determination see E.4.4.2.3).

#### 11.3.5 Detection and measurement

Remove the sample extracts from cold storage and allow them to warm up to room temperature. Inject an aliquot of the sample (for example, 2 µl) into the GC-MS system. Identify the PAH compounds by their retention time and their molecular ions and appropriate qualifiers, see e.g. D.2. Use the integrated abundance (peak area) of the target ion for quantification. Quantification shall be carried out by a combination of the internal standard and the surrogate standard technique (see 12.1.2 and 12.1.3). Dilute an aliquot of the extract and reanalyse it if the concentration of the PAH compounds in the extract is above the upper limit of the working range.

## 12 Quantification

### 12.1 HPLC/FLD analysis

#### 12.1.1 External standard method

Calculate the mass of the PAH compounds in the extract according to Formula (5), using the calibration function:

$$m_{\mathrm{E}} = \frac{A_{\mathrm{E}} - b}{a} \cdot V_{\mathrm{E}} \qquad (5)$$

where

$m_E$ is the mass of the PAH compounds in the extract, in ng;

$A_E$ is the peak area or peak height of the PAH compounds in the extract;

$b$ is the intercept of the linear calibration function;

$a$ is the slope of linear calibration function, in ml/ng;

$V_E$ is the volume of the extract, in ml.

Use the external standard solution (11.2.2.2) to verify the proper operation of the HPLC/FLD system (at least every tenth sample).

Verify the recovery efficiency (see 6.3.1), if necessary including the clean-up step, with laboratory blank filters (at least every twentieth sample), spiked with the external standard solution (see 11.2.2.2).

#### 12.1.2 Internal standard method

Prepare at least five solutions with PAH concentrations, which cover of the whole working range, and a constant concentration of the internal standard (7.4), which shall be equivalent to the expected PAH concentrations.

The calibration solutions (see 11.2.2.1) may be used for this purpose by adding constant volumes of the internal standard solution (see 11.2.2.3).

Inject these solutions and calculate the response factor *f* of the PAH compounds from the peak areas of both the PAH compounds and the internal standard and the corresponding masses of these substances according to Formula (6):

$$f = \frac{A_{IS} \cdot m_c}{A_c \cdot m_{IS}} \tag{6}$$

where

$f$ is the response factor of the PAH compounds;

$A_{IS}$ is the peak area or peak height of the internal standard in the chromatogram of the calibration solution;

$m_c$ is the mass of the PAH compounds in the calibration solution, in ng;

$A_c$ is the peak area or peak height of the PAH compounds in the chromatogram of the calibration solution;

$m_{IS}$ is the mass of the internal standard in the calibration solution, in ng.

The average values of the response factors can be used for further analysis.

Add the internal standard solution (see 11.2.2.3) to the sample before injection.

The mass of the PAH compounds in the sample extracts is calculated according to Formula (7):

$$m_E = \frac{f \cdot A_E \cdot m_{ISE}}{A_{ISE}} \tag{7}$$

where

$m_E$ is the mass of the PAH compounds in the sample extract, in ng;

$f$ is the response factor of the PAH compounds;

$A_E$ is the peak area or peak height of the PAH compounds in the chromatogram of the sample extract;

$m_{ISE}$ is the mass of the internal standard in the sample extract, in ng;

$A_{ISE}$ is the peak area or peak height of the internal standard in the chromatogram of the sample extract.

Verify the recovery efficiency (see 6.3.1), if it is used, including the clean-up step, with laboratory blank filters (at least every twentieth sample), spiked with the external standard solution (see 11.2.2.2).

#### 12.1.3 Surrogate standard method

Correct the mass of the PAH compounds for the recovery efficiency as follows: Calculate the concentration of the surrogate standard either using a calibration function in analogy to 12.1.1 and Formula (5) for the external calibration method, or using response factors in analogy to 12.1.2 and Formulae (6) and (7) for the internal standard method.

Add for example 10 µl of the surrogate standard solution (11.2.2.4) to the filter before the extraction step. Evaporate the solvent and calculate the mass of the PAH compounds in the filter according to Formula (8):

$$m_F = \frac{m_{SSF} \cdot m_E}{m_{SSE}} \quad (8)$$

where

$m_F$ is the mass of the PAH compounds on the filter sample, in ng;

$m_{SSF}$ is the mass of the surrogate standard added to the filter, in ng;

$m_E$ is the mass of the PAH compounds in the extract, in ng, calculated according to Formula (5) or Formula (7);

$m_{SSE}$ is the mass of the surrogate standard in the sample extract, in ng, calculated according to Formula (5) or Formula (7).

### 12.2 GC-MS Analysis

Prepare at least five solutions with PAH concentrations, which cover the whole working range, and a constant concentration of the internal standard (7.4).

The calibration solutions (see 11.2.2.1) may be used for this purpose by adding constant volumes of the internal standard solution (see 11.2.2.3).

Inject these solutions and calculate the response factor *f* of the PAH compounds from the peak areas/peak heights of both the PAH compounds and the internal standard and the corresponding masses of these substances according to Formula (9):

$$f = \frac{A_{IS} \cdot m_c}{A_c \cdot m_{IS}} \quad (9)$$

where

$f$ is the response factor of the PAH compounds;

$A_{IS}$ is the peak area or peak height of the characteristic ion of the internal standard (e.g. m/z = 264 for benzo[*a*]pyrene-d12) in the chromatogram of the calibration solution;

$m_c$ is the mass of the PAH compounds in the calibration solution, in ng;

$A_c$ is the peak area or peak height of the characteristic ion of the PAH compounds in the chromatogram of the calibration solution;

$m_{IS}$ is the mass of the internal standard in the calibration solution, in ng.

The average values of the response factors for the injections can be used for further analysis.

Add the internal standard solution 11.2.2.3 to the sample before injection.

The mass of the PAH compounds in the sample extracts is calculated according to Formula (10):

$$m_E = \frac{f \cdot A_E \cdot m_{ISE}}{A_{ISE}} \quad (10)$$

where

$m_E$ is the mass of the PAH compounds in the sample extract, in ng;

$f$ is the response factor of the PAH compounds;

$A_E$ is the peak area or peak height of the characteristic ion of the PAH compounds in the chromatogram of the sample extract;

$m_{ISE}$ is the mass of the internal standard in the sample extract, in ng;

$A_{ISE}$ is the peak area or peak height of the characteristic ion of the internal standard in the chromatogram of the sample extract.

Correct the mass of the PAH compounds by the recovery efficiency using the surrogate standard method.

Calculate the concentration of the surrogate standard in analogy to Formulae (9) and (10). Add the surrogate standard solution (11.2.2.4) to the filter before the extraction step. Calculate the mass of the PAH compounds in the filter according to Formula (11):

$$m_F = \frac{m_{SSF} \cdot m_E}{m_{SSE}} \quad (11)$$

where

$m_F$ is the mass of the PAH compounds on the filter sample, in ng;

$m_{SSF}$ is the mass of the surrogate standard added to the filter, in ng;

$m_E$ is the mass of the PAH compounds in the extract in ng, calculated according to Formula (5);

$m_{SSE}$ is the mass of the surrogate standard (e.g. m/z = 264 for perylene-d12) in the extract, in ng.

## 12.3 Concentration of the PAH compounds in ambient air

Calculate the concentration of the PAH compounds in ambient air according to Formula (12):

$$C = \frac{m_F}{V} \quad (12)$$

where

$C$ is the concentration of the PAH compound in ambient air, in ng/m$^3$;

$m_F$ is the mass of the PAH compound on the filter sample, in ng;

$V$ is the sampled volume in ambient conditions, in m$^3$.

# 13 Quality control

## 13.1 Reagent blank check

Analyse one reagent blank solution at least every fiftieth sample and if new reagents or new batches of reagents are used. If a PAH compound or a peak interfering with the PAH compounds is detected at a concentration higher than the required detection limit (see 6.3.2.1), suspend the analysis. Identify the source of the contamination and replace contaminated reagents.

## 13.2 Calibration drift check

Analyse the calibration solution with a concentration corresponding to the expected PAH concentrations (see 11.2.2.1 and 11.3.2.1) at least after every tenth sample. If the measured concentration of a PAH compound has changed by more than 10 % (5 % in case of the HPLC/external standard method (see 12.1.1)) suspend analysis and recalibrate the chromatography system. Reanalyse the sample solutions that were analysed during the period in which the sensitivity change occurred, or if this is not possible reprocess the data to take account of the sensitivity change. In this case it is necessary to take account of any significant additional sources of uncertainty.

NOTE When using the HPLC/external standard method variations of the detector sensitivity affect directly the measurement result. Therefore the requirements for the detector stability are more stringent.

## 13.3 Control solutions

At regular intervals (daily or at least every twentieth sample) analyse suitable certified control solutions, other than calibration solutions, after calibration to monitor the performance of the method. Plot control charts according to ISO 7870-2 and if the results indicate that the method is out of control, investigate the reasons for this, take corrective action and repeat the analysis, if necessary.

## 13.4 Recovery efficiency check

Separately extract and analyse at least five suitable portions of a certified reference material (7.7) in order to demonstrate the efficiency of the method. The average of the recovery efficiencies of all portions for each analyte with respect to the certified values shall be between 80 % and 120 %. Check the method recovery efficiency at least every six months by extracting and analysing the CRM. If this requirement is not met, take corrective action and repeat the recovery efficiency check.

## 13.5 Chromatographic interference check

### 13.5.1 HPLC/FLD

To establish that chromatographic interferences are avoided for the PAH compounds and internal and surrogate standards, demonstrate that the system is able to separate these PAHs from their nearest eluting peaks with a high abundance with a peak resolution factor superior or equal to 1,2.

NOTE The peak resolution can, for example, be calculated according to Formula (13):

$$R_s = 2 \cdot \frac{t_{R2} - t_{R1}}{w_1 + w_2} \tag{13}$$

where

$R_s$ is the peak resolution;

$t_{R1}$ is the retention time for peak 1, in min;

$t_{R2}$ is the retention time for peak 2, in min;

$w_1$ is the peak width of peak 1, in min;

$w_2$ is the peak width of peak 2, in min.

Repeat the check after each change of the chromatographic column and at least every month.

#### 13.5.2 GC-MS

Depending on the column, different substances may interfere (see 15.3). Demonstrate that the column is able to separate the substances of interest from their nearest eluting peak with a similar mass spectrum with a peak separation factor equal or superior to 1,2.

### 13.6 Laboratory filter blank check

Only use the laboratory filter blank check for quality assurance purposes to verify the purity of the filters. If the chromatogram shows a peak at the retention time of a PAH compound and a peak area or peak height indicating a concentration of more than 1 % of the expected value, the filter batch shall not be used for PAH analysis.

Contamination may be reduced by heating filters up to 300 °C for at least 12 h (cf. 8.1.3). Filters treated in this way may become brittle.

### 13.7 Field filter blank check

Use the field filter blank only for quality assurance purposes. If the chromatogram shows a peak at the retention time of a PAH compound and a peak area or peak height indicating a concentration of more than 5 % of the expected value find out the reasons and take corrective actions.

### 13.8 External quality assessment

If laboratories carry out analysis of samples of PAH in ambient air on a regular basis it is necessary that they participate in a relevant external quality assessment scheme or proficiency testing scheme.

It is strongly recommended that the laboratory works in accordance with the requirements of EN ISO/IEC 17025. This can be demonstrated by formal accreditation.

## 14 Determination of measurement uncertainty

### 14.1 Introduction

The measurement uncertainty shall be assessed by methods described in ISO/IEC Guide 98-3, ISO 5725-2, EN ISO 20988 or equivalent documents. In practice, input data for uncertainty assessment may be obtained from different experimental sources, e.g. validation studies (comprising laboratory tests, field tests and/or interlaboratory comparisons) or QA/QC procedures (including replicate measurements of blank and control samples and certified reference materials, and calibration procedures).

The tests presented in this clause shall be carried out by each individual laboratory performing measurements of PAH.

The uncertainty evaluation is based on Formula (12) that – in general terms – describes the measurement problem under consideration.

This approach is not meant to exclude evaluations based on data from ongoing QA/QC procedures, field studies or inter-laboratory comparisons as long as these evaluations are consistent with ENV 13005 and/or ISO 5725-2.

## 14.2 Parameters contributing to measurement uncertainty

### 14.2.1 Parameters to be assessed and minimum requirements

The parameters given in Table 2 have been identified to contribute to the uncertainty of PAH concentrations measured in filter samples. For each of these parameters minimum requirements are given; these serve as the basis for the establishment of ongoing QA/QC programmes. Annex E gives an example of uncertainty calculations which allow the user to fulfil the uncertainty requirements given in Directive 2004/107/EC [11] for BaP measurements. If the minimum requirements given in Table 2 are fulfilled for a PAH compound its measurement uncertainty probably is below 50 % if the concentration of a PAH compound is about 1 ng/m$^3$.

**Table 2 — Uncertainty parameters and minimum requirements**

| Uncertainty parameter | Symbol | Section | Minimum requirement |
|---|---|---|---|
| Sampled volume | $V$ | | |
| • Sample flow – calibration and measurement | $\phi$ | E.2.2 | Difference between measured and nominal flow rate ≤ 5 %<br>Uncertainty of flow calibration device ≤ 2 % |
| • Sampling time | $t$ | E.2.3 | Relative uncertainty ≤ 0,1 % |
| Mass of the PAH compound sampled | $m_{\mathrm{F}}$ | E.4 | |
| • Sampling efficiency, including effects of reactions with oxidants | $S$ | E.4.2 | ≥ 99 % in the concentration range above the upper assessment threshold |
| • Analyte stability | $A$ | E.4.3 | No significant difference between results of analysis of samples before and after storage |
| Mass of the PAH compound in extract | $m_{\mathrm{E}}$ | E.4.4 | |
| **External standard method** | | E.4.4.2 | |
| • Recovery efficiency with CRM | $R$ | E.3 | 80 % ≤ $R$ ≤ 120 % with a relative uncertainty of ≤ 6 % |
| • Mass of the PAH compounds in calibration standards | $m_{\mathrm{c}}$ | E.4.4.2.2 | Relative uncertainty ≤ 2 % |
| • Lack-of-fit of calibration function | $\delta$ | E.4.4.2.3 | Relative residuals over the calibration range ≤ 3 %; at concentrations of 1 ng/m$^3$ ≤ 2 % |
| • Response drift between calibrations | $d$ | E.4.4.2.4 | ≤ 5 % |
| • Analytical repeatability | $u_{\mathrm{anal}}$ | E.3 | ≤ 3 % |
| • Selectivity | $s$ | E.4.4.2.5 | Resolution factor ≥ 1,2 |
| **Internal standard method** | | | |
| • Recovery efficiency with CRM | $R$ | E.3 | 80 % ≤ $R$ ≤ 120 % with a relative uncertainty of ≤ 6 % |
| • Average response factor of the PAH compound | $f$ | E.4.4.3.2 | Relative standard deviation ≤ 5 % |
| • Concentration of internal standard in extract | $m_{\mathrm{ISE}}$ | E.4.4.3.3 | ≤ 2 % |
| • Selectivity | $s$ | E.4.4.2.5 | Resolution factor ≥ 1,2 |
| • Precision of response measurement | $s_{\mathrm{f}}$ | E.4.4.3.4 | ≤ 3 % |
| **Surrogate standard method** | | | |
| • Recovery of surrogate standard | $r$ | E.4.4.4 | > 50 % with a relative uncertainty of ≤ 5 % |
| Mass of the PAH compound in filter blank | $m_{\mathrm{bl}}$ | E.5 | ≤ 1 % of the amount of a PAH compound on the filter, if its concentration is about 1 ng/m$^3$ |

#### 14.2.2 Between-laboratory uncertainty

The procedures described in Clauses 11 and 12 are not restrictive but allow variations in approaches between laboratories. The validation tests [14] for EN 15549 [5] and EN 15980 [6] showed that even for experienced laboratories significant between-laboratory uncertainties exist (see Annex E). However, this uncertainty cannot be attributed to a single source, but is the combination of contributions from several sources.

In principle, this between-laboratory uncertainty needs to be taken into account to ensure that comparable measurement data will be obtained by laboratories using this Technical Specification. This can be achieved by allowing for individual laboratories only a fraction of the uncertainty requirement of Directive 2004/107/EC [11] (see E.9).

NOTE At concentrations of 1 ng/m$^3$ the between-laboratory uncertainty is about 30 %.

#### 14.2.3 Sampling systems

Sampling systems used shall fulfil the requirements of EN 12341 (see 6.2). The fulfilment of this requirement does not eliminate the existence in practice of differences between comparable individual sampling systems.

Values for between-sampler uncertainties derived from field tests are given in Annex F.

### 14.3 Recommendations for use

An appropriate level of quality control according to EN ISO/IEC 17025 shall be applied. In addition to the internal quality control measures described in this Technical Specification (see Clause 13) the laboratory should employ external quality control measures (use of reference materials, participation in interlaboratory comparisons).

A certified reference material containing PAH compounds in the concentration of 1,7 µg/g per unit to 6 µg/g per unit (0,09 µg/g per unit for DBahA) is available (NIST1649b). ERM-CZ 100 can also be used as CRM.

Although these reference materials have a matrix differing from real air samples, they are currently the only reference materials considered suitable for quality control purposes according to this Technical Specification. These certified reference materials may be applied on a regular basis for checking recovery efficiencies.

## 15 Interferences

### 15.1 General

Heat, oxidants and ultraviolet radiation cause the degradation of PAH compounds during sampling, sample storage and sample work up. The exposition of samples and sample extracts against heat, irradiation and oxidants shall therefore be avoided.

Unusual results, peak forms or retention times of PAH may suggest that chromatographic interferences are present. Attention shall be given to interferences concerning BaA, BbF+BjF+BkF and DBahA in GC-MS and BjF in HPLC/FLD.

### 15.2 HPLC/FLD method

The separation efficiency of the column and the retention times of the PAH compounds strongly depend on the temperature of the column. Therefore its temperature shall be kept constant, e.g. at 20° C.

BjF is not or at least not completely separated from benzo[*e*]pyrene using reversed phase columns and acetonitrile/water eluents. For its determination, suitable excitation and emission wavelengths are 382 nm and 517 nm respectively: using these conditions co-elution of BjF and benzo[*e*]pyrene does not have an effect on

the analytical results. At the wavelength pairs used for the determination of the benzopyrene species and the other benzofluoranthene species (see Table D.1) the fluorescence of BjF is very low.

### 15.3 GC-MS method

Using the 5 % diphenyldimethylpolysiloxane (5 % Ph, Me-siloxane) phase, as is usual for PAH analysis, attention shall be paid to the interferences concerning BaA, BbF+BjF+BkF and DBahA [15].

**a) BaA:**

1) Using the 5 % Ph, Me-siloxane phase, BaA may not be fully resolved from CPP (primary ion may be the same as a secondary ion of BaA) and from CHR + TRI (same characteristic ions as BaA); so the column shall be previously checked for the efficiency in separating BaA from interferences.

2) If necessary, BaA may be resolved from CPP using a column with a phase equivalent to 50 % phenylpolysiloxane, such as DB-17ms [1)] or BPX50 [1)].

**b) BbF+BjF+BkF:**

1) Using the 5 % Ph, Me-siloxane phase, they are not resolved and shall be quantified cumulatively.

2) They may be separated using the above mentioned DB-17ms [1)] or BPX50 [1)] phases. When the former is used, a 60-m length gives a baseline separation.

**c) DBahA and INP:**

1) Using the 5 % Ph, Me-siloxane phase, they are resolved but DBahA co-elutes with the ‘a,c’ isomer (DBacA), which implies an overestimation of the DBahA concentration. The ‘a,j’ isomer (DBajA) does not interfere.

2) If necessary, e.g. if the overestimation of DBahA is critical for the sake of compliance, DBahA may be quantified individually using a BPX50 phase. In this case DBahA is separated from DBacA but attention shall be paid to the quantification of INP, as DBacA co-elutes with INP (primary ion of INP may be the same as a secondary ion of the dibenzanthracene isomers).

3) Using a DB-17ms phase, INP and DBahA co-elute and the DBacA peak is separated from the INP+DBahA peak.

## 16 Reporting of results

The analytical report shall contain at least the following information:

a) reference to this Technical Specification,

b) complete identification of the sample,

c) type of sampler used,

d) description of each sampling location,

e) sampling time,

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1) DB-17ms and BPX50 are examples of suitable products available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of these products.

f) volume of air pumped (expressed in ambient conditions),

g) barometric pressure and temperature (mean values during sampling sequence),

h) type of filter,

i) result of determination expressed in ng/$m^3$,

j) unusual features noted during sampling and determination in the laboratory,

k) limits of detection,

l) laboratory filter blank values,

m) field filter blank values,

n) analysis procedure,

o) deviations from this Technical Specification.

# Annex A
(informative)

# Sampling systems with oxidant denuder

## A.1 Principle

Essential progress has been made in the last years and a modification of the common sampling method has been developed, namely PM10 sampling systems which allow for integrating an ozone catalyst (denuder) in the cartridge main housing. The function of the catalyst is to remove selectively the ozone from the sampled air flow, before it gets in contact with the surface of the sample collection filter. By using such ozone removing devices the B*a*P degradation can be reduced, which has shown to be in the range up to approximately 50 % [16 to 23].

The ozone denuder consists of a ceramic support which is shaped like a honeycomb structure. It contains numerous identical parallel small channels of square shapes. The number of channels per unit surface area determines the cell density, expressed as *cpsi* (cells per square inch). In order to make the catalyst active, the walls are covered with a manganese oxide layer, which colours the denuder dark brown. The preparation of the catalyst is described for example in [24, 25]. As the surface area of the ceramic honeycomb is not porous enough to ensure an efficient gas adsorption, the body is coated with a layer of inorganic oxide with a high internal surface area, before the manganese oxide is applied to the ceramic structure. This step usually occurs by wet impregnation using aqueous solutions of manganese salts, followed by drying at different temperatures.

A scheme how the sampling device is constructed to integrate the ozone denuder is shown in Figure A.1. In any case, the modification is not undertaken at the PM inlet. In that way the sampling characteristic of the inlet is not affected. The ozone denuder is added behind the impactor plate. The ozone removal efficiency can be calculated theoretically by using the Davies Formula (Formula (A.1), [26]).

$$\frac{C}{C_0} = 0,819 \cdot \exp(-14,6272 \cdot \delta) + 0,0976 \cdot \exp(-89,22 \cdot \delta) + 0,01896 \cdot \exp(-212 \cdot \delta) \quad \text{(A.1)}$$

$$\delta = \pi \cdot \frac{D \cdot L}{4 \cdot Q}$$

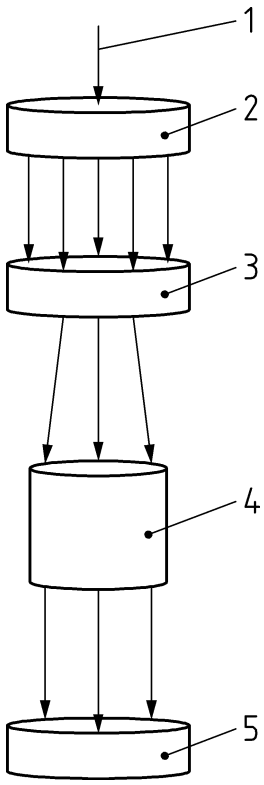
where

- $C$ is the gas concentration downstream of the denuder in µg/cm$^3$;
- $C_0$ is the gas concentration upstream of the denuder in µg/cm$^3$;
- $D$ is the diffusion coefficient in cm$^2$/s;
- $L$ is the denuder length, in cm;
- $Q$ is the flow rate per channel, in cm$^3$/s.

With this formula the layout of the denuder or the scale up e.g. to other flow rates can be calculated with the details given here: dimensions, gas concentrations and diffusion coefficient. The Davies Formula is in principle only valid for ideal gases. The denuder shall be tested under relevant conditions e.g. in a laboratory experiment to check the ozone removal behaviour.

## A.2 Sampling system used in the field test

The field experiments [5] were carried out using “Partisol Speciation Samplers”[2)] equipped with denuder cartridges. The cartridge was equipped with a PM10 inlet. The cartridge main housing was a stainless steel cylinder, in which the ozone denuder was located, fixed in its position by means of two glass spacers, a PTFE ring and a metal spring in order to guarantee the tightness of the system. The denuder was positioned in the central part of the cartridge to allow a homogeneous distribution of the sampled gas in the denuder channels. The ozone denuder was based on a manganese oxide catalyst and had the shape of a honeycomb body. The denuder was 35 mm in length and had an active diameter of 43 mm. The denuder body consisted of approximately 400 channels which offered a large surface for efficient ozone decomposition. The sample collection filter was placed behind the ozone denuder. The daily sampling volume was about 24 $m^3$. The principle of the cartridge design is shown in Figure A.1.




**Key**

1 air flow
2 PM10 inlet
3 impactor
4 ozone denuder
5 filter holder

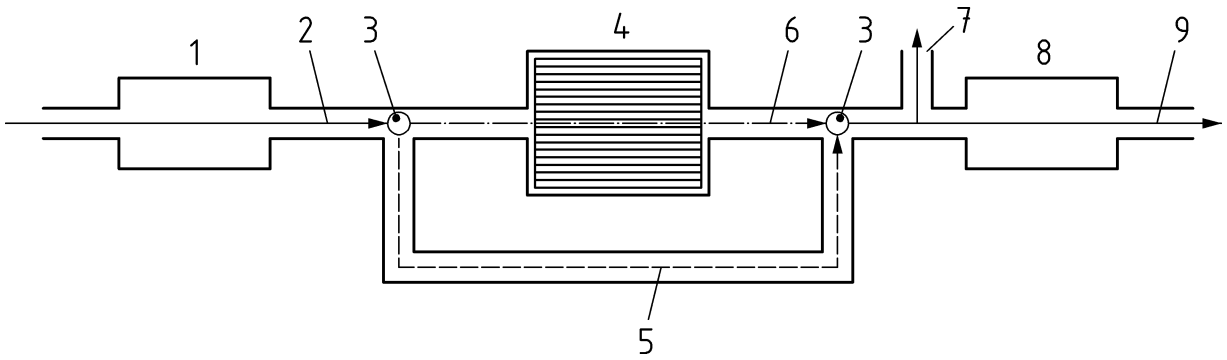
**Figure A.1 — Schematic flow path way**

2) "Partisol Speciation Sampler" is an example of a suitable product available commercially. This information is given for the convenience of users of this Technical Specification and does not constitute an endorsement by CEN of this product.

## A.3 Test of the efficiency of the denuder

— Subject the denuder to ozonized (ozone generator) synthetic air at flow rates corresponding to conditions during air sampling (e.g. 520 l/min for high volume sampling or 40 l/min for low volume sampling), see Figure A.2.

— Control the ozone concentration of the air at the inlet and the outlet of the denuder, e.g. using an ozone measuring device according to EN 14625 [3].




**Key**

1 ozone generator
2 air flow (in)
3 bidirectional valve
4 ozone denuder
5 air flow to measure the ozone concentration
6 air flow to control the ozone denuder function
7 outlet
8 ozone analyser
9 outlet from ozone analyser (bypass)

**Figure A.2 — Schematic view of a device to test the efficiency of the ozone denuder**

# Annex B
(informative)

# Extraction methods (examples of experimental conditions)

## B.1 General

The extraction conditions described in this annex have been used in the laboratory and field validation tests [14] for EN 15549 [5] and EN 15980 [6].

If particles or filter material are observed after the extraction process, the extract is filtered (e.g. on an appropriate filter, or pre-washed glass wool or pre-washed cotton wool). In order to avoid losses during filtration, the material used for filtration shall be rinsed sufficiently.

## B.2 Extraction under reflux

The filter is cut into pieces. The filter cuts are placed on the bottom of the vessel of the extraction apparatus. Seven ml of toluene are added and the filter cuts are extracted for 1 h. After cooling, the solution is transferred into a testing tube via a Pasteur pipette. The extraction vessel is rinsed three times with ca. 3 ml of toluene, the rinsing solutions are added to the extract. The solution is concentrated under nitrogen to e.g. 1 ml for GC-MS analysis. For HPLC/FLD analysis it is carefully evaporated to dryness, the residue is dissolved in e.g. 1 ml of acetonitrile.

## B.3 Soxhlet extraction

Each filter is placed in a Soxhlet extractor using solvent cleaned tweezers. The filters are extracted using approximately 200 ml of toluene for a minimum of 20 h. Each extractor is wrapped with aluminium foil to reduce the amount of light reaching the samples and to keep the extractor warm, thus improving the cycle time of the extraction. When the solvent has cooled, the extractor is removed and any solvent is poured back into the round bottom flask. The solution is concentrated under nitrogen to e.g. 1 ml for GC-MS analysis. For HPLC/FLD analysis it is carefully evaporated to dryness, the residue is dissolved in e.g. 1 ml of acetonitrile.

## B.4 Microwave extraction

The extraction is carried out using a microwave digestion system. To ensure proper operation follow the instructions of the manufacturer. Filters are transferred into the PTFE vessels where e.g. 15 ml of the solvent is added. After extraction, all PTFE vessels are cooled down to room temperature before opening. The extracts are filtered and concentrated under nitrogen to e.g. 1 ml for GC-MS analysis. For HPLC/FLD analysis it is carefully evaporated to dryness, the residue is dissolved in e.g. 1 ml of acetonitrile.

EXAMPLE Extractions are carried out at 400 W for 20 min (eight vessels).

## B.5 Accelerated solvent extraction

For proper operation follow the instructions of the manufacturer. Sand may be used to reduce the volume of required solvent.

The filter is placed in the extraction cell and is extracted with dichloromethane at 120 °C, 140 bar, for 5 min; extraction is carried out three times. The resulting extracts are automatically combined. The solution is concentrated under nitrogen to e.g. 1 ml for GC-MS analysis. For HPLC/FLD analysis it is carefully evaporated to dryness, the residue is dissolved in e.g. 1 ml of acetonitrile.

## B.6 Ultrasonic extraction

The filter is cut, if necessary, into pieces, placed in a beaker, covered with the solvent and extracted in an ultrasonic bath for 15 min. The extract is filtered (B.1). The whole filtration residue is placed into the beaker and the extraction is repeated. The whole procedure is repeated twice. The three filtered extracts are combined. The solution is concentrated under nitrogen to e.g. 1 ml for GC-MS analysis. For HPLC/FLD analysis it is carefully evaporated to dryness, the residue is dissolved in e.g. 1 ml of acetonitrile.

## B.7 Recommended solvents

Table B.1 lists the solvents which are recommended for the extraction step.

**Table B.1 — Recommended solvents**

| **Extraction method** | **Solvent** |
|---|---|
| Extraction under reflux | Toluene |
| Soxhlet extraction | Toluene, hexane/acetone mixture (1:1), dichloromethane |
| Microwave extraction | Hexane/acetone mixture (1:1) |
| Accelerated solvent extraction | Toluene, dichloromethane, dichloromethane/hexane mixture 1:1 |
| Ultrasonic extraction | Dichloromethane, toluene |

Non-stabilized solvents may contain reactive impurities, such as peroxides, acids or radicals. During the field test, as an example, the extraction of field filter samples with the accelerated solvent technique and dichloromethane as solvent lead to degradation of benzo[*a*]pyrene and benz[*a*]anthracene, if no sand was used to reduce the solvent volume. The Soxhlet extraction of filter samples with toluene lead to losses of surrogate standard (benzo[*a*]pyrene-d12) in a range up to more than 50 %. In both cases the degradation rate was not constant; furthermore it was not observed using certified reference material (NIST 1649a). To avoid these problems, the sample preparation procedure should carefully be checked using blank filters, spiked with a known amount of the PAH compound or using field samples with a known content of the PAH compound if new solvents are used. Alternatively the method should be checked by comparison with another sample preparation procedure (see also 6.3.1).

# Annex C
(informative)

# Example for clean-up procedure

## C.1 General

The clean-up procedure described in this annex has been used in the field validation test [24] for EN 15549 [5] and EN 15980 [6].

## C.2 Reagents and materials

### C.2.1 Organic solvents

See 7.1.

### C.2.2 Solid-phase extraction cartridges (SPE)

Cartridges with high purity grade silica gel or cyanopropylsilane coated silica gel as sorbent, e.g. 1 g.

## C.3 Procedure

The cartridge is conditioned with 6 ml of hexane. Then the sample, diluted with hexane, is added to the cartridge and interferents are eluted with 6 ml of hexane. Then 6 ml of hexane: dichloromethane (40:60 v/v) are added to the cartridge and collected to recover the benzo[a]pyrene fraction. This fraction is carefully evaporated to dryness in a nitrogen stream and e.g. 1 ml of hexane is added.

# Annex D
(informative)

# Parameters for analysis (examples)

## D.1 HPLC/FLD

- HPLC-column: RP-C18 250 mm; 4,6 mm
- Injector: 20 µl
- Oven temperature: 30 °C ± 1 °C
- Mobile phase: mixture of acetonitrile and water
- Flow rate: 1,5 ml/min

**Table D.1 — Suitable pairs of wavelengths of excitation and emission for the detection of PAH compounds**

| Compounds | Excitation wavelength in nm | Emission wavelength in nm |
|---|---|---|
| BaA, 6-methylchrysene, CHR | 275 | 390 |
| BaP, BeP (suitable also for BbF and BkF) | 260 | 415 |
| DBahA | 297 | 405 |
| INP | 250 | 500 |
| BjF | 382 | 517 |
| BghiP | 297 | 445 |
| NOTE DAD wavelength: 290 nm or 385 nm. | | |

## D.2 GC-MS

### D.2.1 Proposed parameters for GC operation

- GC column: fused silica capillary column (30 m, 0,25 mm ID, 0,25 µm film thickness cross linked 5 % PhMe Siloxane)
- Carrier gas: Helium (99,999 %)
- Oven temperatures: initial: 120 °C for 2 min
  rate: 5 °C/min to 300 °C, then hold for 5 min
  rate: 20 °C/min to 320 °C then hold for 5 min
- Flow: constant flow: 1,2 ml/min
- Injection mode: splitless or on-column.

### D.2.2 Proposed parameters for MS operation

#### D.2.2.1 Quadrupole MS

- Mode: Selected Ion Monitoring (SIM), see list in D.2.2.3
- Transfer line temperature: 300 °C
- Ion source temperature: approximately 250 °C
- Ion source energy 70 eV

#### D.2.2.2 Ion trap

- Ion source temperature: 250 °C
- Transfer line temperature: 250 °C
- Mode: SIM, see list in D.2.2.3.
- Ion source energy: 70 eV
- Trap offset: 10
- Emission current: 250 µA
- Selected Ions: see D.2.2.3.

#### D.2.2.3 List of ions for selection

The masses of the molecular ions and of some characteristic fragment ions of the substances are listed in Table D.2. The list of the most abundant ions may depend on the instrumental conditions.

**Table D.2 — Molecular ions and examples of masses of characteristic fragment ions of PAH compounds**

| Compound | Primary ion | Secondary ion 1 | Secondary ion 2 |
|---|---|---|---|
| Perylene d12 | 264 | 265 | 132 |
| BaA, CHR | 228 | 229 | 114 |
| BaP, BeP, BbF, BjF, BkF | 252 | 253 | 126 |
| DBahA | 278 | 279 | 139 |
| INP, BghiP | 276 | 277 | 138 |

# Annex E
(informative)

# Assessment of performance indicators and uncertainty contributions

## E.1 General

In the example below, the uncertainty contributions of the parameters given in Table 2 are evaluated on the basis of general formulae describing typical expressions used for their measurement.

## E.2 Sample volume

### E.2.1 General

Unless the manufacturer's specifications on the uncertainty of the sampling volume are used, the uncertainty can be determined in the following way.

The sampled volume of air is calculated on the basis of a sample flow rate measured before sampling as

$$V = \varphi_{\text{sam}} \cdot t \tag{E.1}$$

where

$\varphi_{\text{sam}}$ is the sample flow rate;

$t$ is the sampling time.

The sample flow rate shall be appropriate to the sampling device for the sampling of the PM10 fraction of total suspended particles in ambient air. After adjustment to the appropriate value the sample flow rate is determined by adjusting the flow rate performing two consecutive measurements over an interval of 24 h as

$$\phi_{\text{sam}} = \frac{(\phi_1 + \phi_2)}{2} \tag{E.2}$$

where

$\varphi_1$ is the sample flow rate at the beginning of the 24 h interval, in $m^3$/min;

$\varphi_2$ is the sample flow rates at the end of the 24 h interval, in $m^3$/min.

The uncertainty in the volume of air sampled is built up of contributions from:

- measurement of the flow rates;
- measurement of the sampling time.

### E.2.2 Sample flow calibration and measurement

The uncertainty in the measurement of the flow rate is calculated from the uncertainty in the readings of the flow meter used which can be derived from calibration certificates, assuming the calibration is fully traceable to primary standards of flow, and the uncertainty of the actual flow rate measurement results, as:

$$\frac{u^2(\varphi_{\text{sam}})}{\varphi_{\text{sam}}^2} = \frac{u_{\text{cal}}^2 + 2u_{\text{meas}}^2}{\varphi_{\text{sam}}^2} \quad \text{(E.3)}$$

where

$u(\varphi_{\text{sam}})$ is the standard uncertainty in the measurement of flow;

$u_{\text{cal}}$ is the uncertainty due to calibration of the flow meter used for the determination of $\varphi$;

$u_{\text{meas}}$ is the uncertainty of an individual flow measurement (see Formula (E.2); this is usually determined by the resolution of the flow reading or pressure reading device used.

### E.2.3 Sampling time

The sampling time *t* can be measured to within ± 0,5 min. For a sampling time of 24 h the relative uncertainty due to the measurement of *t* is negligible.

## E.3 Recovery efficiency

The recovery efficiency of a PAH compound and its uncertainty are typically obtained from replicate measurements (six or more; usually 10) of a PAH compound in a CRM. The uncertainty due to incomplete extraction for the PAH compound level is calculated from contributions of:

- uncertainty in the concentration of the CRM;
- standard deviation of the mean recovery;
- mean mass determined

as:

$$\frac{u^2(R)}{R^2} = \frac{u^2(m_{\text{CRM}})}{m_{\text{CRM}}^2} + \frac{s^2(m_{\text{E}})}{n \cdot m_{\text{E}}^2} \quad \text{(E.4)}$$

where

$m_{\text{CRM}}$ is the certified mass of the PAH compound in the CRM;

$s(m_{\text{E}})$ is the standard deviation of the replicate measurement results of the mass determined;

$n$ is the number of replicate measurements of the CRM;

$R$ is the recovery of the PAH compound;

$m_{\text{E}}$ is the mass of the PAH compound in the extract.

The value of $s(m_{\text{R}})$ may be used as an indicator of the relative uncertainty due to analytical repeatability $u_{\text{anal}}$:

$$u_{\text{anal}}^2 = \frac{s^2(m_{\text{R}})}{m_{\text{R}}^2} \quad \text{(E.5)}$$

## E.4 Mass of PAH compound sampled

### E.4.1 General

The mass of PAH compound on the filter sample may be expressed as:

$$m_F = \frac{m_E}{S \cdot A} \quad \text{(E.6)}$$

where

$S$ is the sampling efficiency;

$A$ is the analyte stability in the sample.

Hence, the uncertainty is built up of contributions from the above three parameters.

### E.4.2 Sampling efficiency

When the sample flow rate is set in accordance with the specifications of the sampler for the sampling of the PM10 fraction of total suspended particles in ambient air, the sampling efficiency for PM10 is assumed to be 100 %.

### E.4.3 Sample stability

The sample stability shall be experimentally established for storage under conditions (time, temperature, environment) typical to the individual laboratory. Tests shall be performed at PAH compound levels typically found in the environment (see Table 1).

At the start and the end of the storage time *n* samples each shall be analysed under repeatability conditions ($n \geq 6$). For both times the samples shall be randomly picked from a batch of representative samples in order to minimize possible systematic concentration differences. As a test of (in)stability a *t*-test will be performed (95 % confidence, two-sided).

The uncertainty of the stability determination consists of contributions from:

- extraction (random part of recovery efficiency);
- calibration (random part of calibration);
- analytical precision;
- inhomogeneity of the sample batch.

As such – providing the *t*-test shows no significant difference between the results of analysis before and after storage – the contribution of the determination of $A$ will already be incorporated in other contributions and needs not to be taken into account.

### E.4.4 Mass of PAH compound in sample extract

#### E.4.4.1 General

For the measurement of the mass of a PAH compound in the sample extract ($m_E$) three methods are given in Clause 11:

- external standard method (ES), see 12.1.1;
- internal standard method (IS), see 12.1.2 for HPLC/FLD and 12.2 for GC-MS;
- surrogate standard method (SS), see 12.1.3.

#### E.4.4.2 External standard method

##### E.4.4.2.1 General

When applying the external standard method, the following parameters will contribute to the uncertainty in $m_E$:

- uncertainty in the concentrations of the calibration standard(s) used;
- lack-of-fit of the calibration function;
- drift of detector response between calibrations;
- analytical repeatability;
- selectivity of the chromatographic system.

##### E.4.4.2.2 Calibration standards

Calibration standards consisting of PAH compounds in a suitable solvent are used to establish response factors for PAH compounds or response factors relative to the internal or surrogate standards used. The uncertainty of the concentration of a PAH compound is built up of contributions from:

a) purity of the PAH compound used; when this is > 99 %, its contribution may be considered insignificant;

b) mass fraction of the PAH compound in the solvent used for the preparation of the standards;

   1) when gravimetry is used to prepare the calibration solutions: the uncertainties in the weighing of compounds and solutions;

   2) when volumetric techniques are used to prepare the calibration solutions: the uncertainties in the calibrated volumes of glassware and syringes used.

Examples of calculations of uncertainties can be found in [9] and [27].

Calibration standards can be obtained commercially. These standards should be accompanied by certificates ensuring the traceability of the PAH compound concentration to internationally accepted standards.

If other compounds besides PAH compound are used in calibration standards, the mass fraction of PAH compound in the parent compounds used should be established and accounted for, or be insignificant.

##### E.4.4.2.3 Lack-of-fit of calibration function

The calibration function used will generally be obtained by regression. When calibration standards are used in which the concentrations or masses of a PAH compound differ by equal intervals, then ordinary least-squares regression can be used. Else, weighted regression can be performed. An appropriate weighting factor may be the standard deviation of the measured response. In case of single measurements per concentration level, the concentration itself may be used as a weighting factor. In order to test the 'goodness-of-fit' of the regression, the relative residuals are calculated at each of the levels of the calibration standards as:

$$\delta = \frac{\left| m_{\mathrm{reg}} - m_{\mathrm{c}} \right|}{m_{\mathrm{c}}} \qquad \text{(E.7)}$$

where

$\delta$ is the relative residual;

$m_{\mathrm{reg}}$ is the mass of the PAH compound calculated from the regression formula at the level of the

calibration standard;

$m_c$ is the mass of the PAH compound present in the corresponding calibration standard.

The uncertainty due to lack-of-fit of the calibration function is calculated from the maximum relative residual found as:

$$u_F = \frac{\delta_{max}}{\sqrt{3}} \quad \text{(E.8)}$$

where

$\delta_{max}$ is the maximum relative residual found;

$u_F$ is the uncertainty due to lack of fit.

NOTE The lack of fit of the calibration function will contribute to the uncertainty due to incomplete extraction if the recovery efficiency is significantly different from 1. In that case the uncertainty due to lack of fit of the calibration function does not need to be taken into account in the uncertainty assessment.

#### E.4.4.2.4 Response drift between calibrations

Normally, the current response factor will be used until a new one is established. In the interval between the re-establishment of its uncertainty, response checks – and, when necessary, adjustments of response factors – shall be performed as an element of ongoing quality control.

In the interval before the next checks response drift may occur. The relative uncertainty due to response drift for the period between subsequent adjustments of response factors (adjustments $n$ – *1* and $n$) shall then be estimated from data on the relative differences in responses between subsequent checks, as:

$$u_d = \frac{|r_n - r_{n-1}|}{\sqrt{3} \cdot \left( \frac{r_n + r_{n-1}}{2} \right)} \quad \text{(E.9)}$$

where

$r_n$ is the detector response for a calibration standard for response check $n$*;*

$r_{n-1}$ is the detector response for a calibration standard for response check $n$ – 1.

This approach assumes that no correction is applied for response drift, e.g. by averaging of subsequently determined response factors.

#### E.4.4.2.5 Selectivity

The separation system used shall be optimized in order to minimize uncertainty due to (unnoticed) co-elution of potential interferents. The peak resolution (see 13.5.1) shall be ≥ 1,2. In this case the uncertainty contribution due to lack of selectivity will be insignificant.

#### E.4.4.2.6 Combined uncertainty in the measured mass of PAH compound

The contributions given in E.4.4.2.1 to E.4.4.2.4 are combined to give the uncertainty of the measured mass of a PAH compound as:

$$u^2(m_{meas}) = \frac{u^2(m_c)}{n} + u_{anal}^2 + u_F^2 + u_d^2 \quad \text{(E.10)}$$

where

$n$ is the number of calibration standards used to construct the calibration function;

$m_c$ is the mass of a PAH compound in the calibration standard;

$u_{\text{anal}}$ is the uncertainty due to analytical interferences.

#### E.4.4.3 Internal standard method

##### E.4.4.3.1 General

When applying the internal standard method, the following parameters will contribute to the uncertainty in $m_{\text{E}}$:

- uncertainty in the average response factor of PAH compound determined using Formula (6) in 12.1.2;
- uncertainty in the concentration of the internal standard in the sample extract;
- precision of the measurement of responses for PAH compound and internal standard in the sample extract;
- selectivity of the chromatographic system.

##### E.4.4.3.2 Average response factor of PAH compound

The average response factor for PAH compound shall be determined in accordance with 12.1.2 or 12.2 (Formulae (6) and (9)).

The uncertainty of the average response factor is given by:

$$u_{\text{f}}^2 = \frac{s_{\text{f}}^2}{n} \tag{E.11}$$

where

$s_{\text{f}}$ standard deviation of the response factor;

$n$ number of calibration solutions used.

Here it is assumed that the random contributions of the uncertainties in the preparation of the calibration solutions are negligible.

##### E.4.4.3.3 Concentration of internal standard in sample extract

The uncertainty can be estimated using the approach given in E.4.4.2.2.

##### E.4.4.3.4 Precision of response measurement

It may be assumed that $s_{\text{f}}$ (standard deviation of the response factor, see E.4.4.3.2) is a good measure of the uncertainty of the determination of the response ratio of a PAH compound and the internal standard in the sample extract:

$$u\left(\frac{A_{\text{E}}}{A_{\text{ISE}}}\right) = s_{\text{f}} \tag{E.12}$$

where

$A_{\text{E}}$ is the peak area of a PAH compound in the extract;

$A_{\text{ISE}}$ is the peak area of the internal standard in the extract.

#### E.4.4.3.5 Selectivity

See E.4.4.2.5.

#### E.4.4.3.6 Combined uncertainty in the measured mass of PAH compound

The contributions given in E.4.4.3.1 to E.4.4.3.4 are combined to give the uncertainty of the measured mass of PAH compound in the extract as:

$$u^2(m_{\text{meas}}) = u^2(m_{\text{ISE}}) + u_{\text{f}}^2 + s_{\text{f}}^2 \quad \text{(E.13)}$$

and

$$u^2(m_{\text{ISE}}) = \frac{s^2(m_{\text{ISE}})}{n} \quad \text{(E.14)}$$

where

$s^2(m_{\text{ISE}})$ standard deviation of measurements of the mass of ISE;

$n$ number of replicate measurements.

In analogy to Formula (E.4):

$$\frac{u^2(m_{\text{meas}})}{m_{\text{meas}}^2} = \frac{u^2(m_{\text{ISE}})}{n \cdot m_{\text{ISE}}^2} + u_{\text{f}}^2 + s_{\text{f}}^2 \quad \text{(E.15)}$$

### E.4.4.4 Surrogate standard method

The surrogate standard is used to apply corrections for recovery efficiency. The recovery factor used is:

$$r = \frac{m_{\text{SSF}}}{m_{\text{SSE}}} \quad \text{(E.16)}$$

where

$m_{\text{SSF}}$ is the mass of surrogate standard added to the filter before extraction;

$m_{\text{SSE}}$ is the mass of surrogate standard measured in the sample extract.

The uncertainty in $m_{\text{SSF}}$ can be assessed in accordance with E.4.4.2.2, taking into account contributions of:

— mass fraction of PAH compound in the solvent used for the preparation of the standards;

— when gravimetry is used to prepare the calibration solutions: the uncertainties in the weighing of compounds and solutions;

— when volumetric techniques are used to prepare the calibration solutions: the uncertainties in the calibrated volumes of glassware and syringes used.

Since the surrogate standard is used in a relative way for correction purposes, its purity does not need to be taken into account. However, the surrogate standard should not contain PAH compound at levels contributing significantly to the measurement result.

The uncertainty in $m_{\text{SSE}}$ can be assessed in analogy with one of the approaches given in E.4.4.2 or E.4.4.3. When applying the external standard method, the uncertainty due to response drift needs not to be included.

The resulting uncertainty in $r$ is:

$$u_{\mathrm{r}}^2 = \frac{u_{\mathrm{SSF}}^2}{m_{\mathrm{SSE}}^2} + \frac{m_{\mathrm{SSF}}^2}{m_{\mathrm{SSE}}^4} \cdot u_{\mathrm{SSE}}^2 \tag{E.17}$$

or

$$\frac{u_{\mathrm{r}}^2}{r^2} = \frac{u_{\mathrm{SSF}}^2 + u_{\mathrm{SSE}}^2}{m_{\mathrm{SSF}}^2} \tag{E.18}$$

### E.4.5 Combined uncertainty in the mass of PAH compound in the extract

The contributions given in E.3 and E.4.5 are combined to give the uncertainty of the mass PAH compound in the air sample as:

$$\frac{u^2\left(m_{\mathrm{E}}\right)}{m_{\mathrm{E}}^2} = \frac{u^2\left(m_{\mathrm{meas}}\right)}{m_{\mathrm{meas}}^2} + \frac{u^2(r)}{r^2} \tag{E.19}$$

## E.5 Mass of PAH compound in sample blank

The typical mass of PAH compound in a sample blank is determined by analysis under repeatability conditions of a series of sample blanks; a minimum of six replicate analyses shall be performed.

In case the blank response is below three times the noise level of the detector at the retention time of PAH compound, then the blank level and its uncertainty shall be calculated from the detector noise level using the slope of the calibration function extrapolated to zero response assuming a uniform distribution as:

$$m_{\mathrm{bl}} = \frac{3 \cdot r_0}{2 \cdot b_0} \tag{E.20}$$

where

$r_0$ is the noise level;

$b_0$ is the slope of calibration function at zero response.

## E.6 Combined uncertainty in PAH compound concentration

The combined relative uncertainty of the PAH compound concentration in the air sampled is obtained by combination of contributions given in E.2, E.3 and E.4, as:

$$\frac{u_{\mathrm{C}}^2(c)}{c^2} = \frac{u^2(V)}{V^2} + \frac{u^2\left(m_{\mathrm{E}}\right)}{m_{\mathrm{E}}} + \frac{u^2(E)}{E^2} \tag{E.21}$$

## E.7 Expanded uncertainty

The expanded relative uncertainty at the 95 % confidence level is obtained by multiplying $u_{\mathrm{c}}(c)$ with a coverage factor appropriate to the number of degrees of freedom of the dominant components of the uncertainty resulting from the performance of the test programme. This can be calculated by applying the Welch-Satterthwaite Formula (see ENV 13005). For a large number of degrees of freedom, a coverage factor of two is used.

As a first approximation, the number of degrees of freedom may be based on that of an uncertainty contribution covering more than 50 % of the total uncertainty budget.

## E.8 Uncertainty from performance requirements

When combining the uncertainties specified for the performance characteristics a worst-case situation will result. The resulting combined relative uncertainty, calculated as described in E.5, will be about 6,5 %. The expanded relative uncertainty, assuming $k$ = 2, will be 13 %.

## E.9 Between-laboratory uncertainty

The procedures described in Clauses 11 and 12 are not restrictive but allow variations in approaches between laboratories. In a limited series of inter-laboratory comparisons that have been performed within the frame of the evaluation of the above standard method it has been found that – even for laboratories that on an individual basis are proficient in the performance of the analysis – significant between-laboratory deviations occur when samples from homogeneous batches are analysed (see Annex F). In order to ensure that comparable measurement data will be obtained by using this European Standard these deviations need to be taken into account when performing an uncertainty assessment.

However, the value used for the between-laboratory uncertainty is based on a limited amount of data. In order to permit a valid correction more information should become available about the between-laboratory uncertainty.

It is recommended to organize inter-laboratory comparisons on a regular basis as a part of ongoing QA/QC. Inter-laboratory comparisons may be organized in accordance with ISO 5725-2 using samples of sufficient homogeneity to ensure that the contribution to the between-laboratory uncertainty due to inhomogeneity is negligible. In practice an uncertainty due to inhomogeneity of < 5 % will usually be sufficient.

# Annex F
(informative)

# Calculation of uncertainty using interlaboratory comparison and field validation data

The total uncertainty of the measurement of a PAH compound can be calculated from the between laboratory uncertainty as a result of a laboratory intercomparison with filter pieces of real PAH sampling according to Formula (F.1):

$$s_{\mathrm{L}} = \sqrt{\frac{\sum_{i=1}^{p} (\bar{c}_i - \bar{c})^2}{p-1}} \qquad \text{(F.1)}$$

where

$s_{\mathrm{L}}$ is the between laboratory standard deviation;

$\bar{c}_i$ is the mean concentration of a compound obtained by laboratory *I*;

$\bar{c}$ is the mean concentration of a compound obtained by the participating laboratories;

$p$ is the number of participating laboratories;

combined with the between sampler uncertainties (see Formula (F.2)) for the compounds as a result of field tests. The between sampler uncertainty $w_{\mathrm{bs}}$ includes the uncertainty due to using different samplers and the within laboratory uncertainty, which in fact is a combination of the contributions of all uncertainty sources during sample work up, calibration and instrumental measurement of the compounds.

$$w_{\mathrm{bs},j} = \sqrt{\frac{\sum_{i} (x_{i,j,1} - x_{i,j,2})^2}{2 \cdot n}} \qquad \text{(F.2)}$$

where

$x_{i,j,1}$, $x_{i,j,2}$ are results for Samplers 1 and 2 for each day $i$ and compound $j$;

$i$ is the index for the sampling day;

$n$ is the total number of sampling days.

Table F.1 shows the results of the PAH intercomparison exercise of European national reference laboratories carried out in 2010. Pieces of filters from PM10 sampling campaigns in Prague and Madrid were distributed to the laboratories where they were analysed according to the methods described in this Technical Specification and in EN 15549 [5] and EN 15980 [6]. Only the results of expert laboratories are used after Grubbs outlier exclusion.

**Table F.1 — Results of the PAH intercomparison exercise of European national reference laboratories [28]**

| | Madrid Jul 2009 | | | Prague Jul 2009 | | | Madrid Nov 2009 | | | Prague Nov 2009 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Compound** | **Mean ng/filter** | **ng/m³** | **$s_L$ %** | **Mean ng/filter** | **ng/m³** | **$s_L$ %** | **Mean ng/filter** | **ng/m³** | **$s_L$ %** | **Mean ng/filter** | **ng/m³** | **$s_L$ %** |
| BaA | 2,0 | 0,04 | 34,7 | 2,8 | 0,06 | 13,1 | 23,0 | 0,46 | 31,3 | 337,0 | 6,74 | 8,2 |
| BbF | 5,2 | 0,10 | 25,2 | 4,0 | 0,08 | 29,6 | 31,9 | 0,64 | 19,6 | 335,5 | 6,71 | 11,8 |
| BjF | 2,2 | 0,04 | 3,3 | 1,9 | 0,04 | 3,8 | 16,4 | 0,33 | 10,5 | 223,7 | 4,47 | 17,1 |
| BkF | 2,2 | 0,04 | 34,4 | 1,7 | 0,03 | 26,3 | 15,1 | 0,30 | 26,0 | 194,7 | 3,89 | 13,7 |
| BaP | 2,8 | 0,06 | 20,5 | 3,4 | 0,07 | 19,6 | 21,8 | 0,44 | 32,8 | 372,0 | 7,44 | 10,0 |
| INP | 4,3 | 0,09 | 28,8 | 3,9 | 0,08 | 18,6 | 23,8 | 0,48 | 17,0 | 288,2 | 5,76 | 13,6 |
| DBahA | 0,5 | 0,01 | 22,0 | 0,3 | 0,01 | 42,0 | 3,0 | 0,06 | 43,2 | 45,4 | 0,91 | 18,0 |
| BghiP | 5,5 | 0,11 | 26,6 | 7,3 | 0,15 | 22,8 | 34,2 | 0,68 | 17,7 | 258,9 | 5,18 | 18,8 |
| ΣBF | 8,7 | 0,17 | 30,9 | 8,8 | 0,18 | 39,2 | 56,2 | 1,12 | 14,7 | 757,0 | 15,14 | 17,9 |

Table F.2 shows results of a similar intercomparison exercise of some German, French and Dutch laboratories in 2010.

**Table F.2 — Results of a laboratory intercomparison of filter pieces of PM10 sampling in Baden-Wuerttemberg 2010 (3 filters)**

| **Compound** | **Mean ng/filter** | **ng/m³** | **$s_L$ %** | **Mean ng/filter** | **ng/m³** | **$s_L$ %** | **Mean ng/filter** | **ng/m³** | **$s_L$ %** |
|---|---|---|---|---|---|---|---|---|---|
| BaA | 22,4 | 0,41 | 21 | 38,0 | 0,69 | 12 | 71,3 | 1,30 | 14 |
| BbF | 41,8 | 0,76 | 16 | 135,3 | 2,45 | 17 | 200,7 | 3,65 | 15 |
| BjF | 23,6 | 0,43 | 34 | 76,4 | 1,39 | 32 | 101,5 | 1,85 | 27 |
| BkF | 17,5 | 0,32 | 11 | 48,5 | 0,88 | 13 | 70,9 | 1,29 | 20 |
| BaP | 38,4 | 0,70 | 19 | 96,4 | 1,75 | 16 | 136,6 | 2,48 | 17 |
| INP | 44,1 | 0,80 | 19 | 141,2 | 2,56 | 16 | 181,7 | 3,30 | 24 |
| DBahA | 7,0 | 0,13 | 53 | 19,7 | 0,36 | 49 | 26,8 | 0,49 | 54 |

The results of both intercomparisons are well comparable. For lower PAH amounts (below 5 ng/filter) the relative between laboratory standard deviations are about 20 % to 30 %, for amounts between 20 ng and 100 ng they are about 15 % to 20 % and at very high PAH amounts the are about 10 % to 15 %. For DBahA and BjF the uncertainties are higher due to chromatographic difficulties as they are described in Clause 15.

Only few field experiments have been carried out to calculate the between sampler standard deviation for PAH compounds other than BaP.

The Czech Institute of Hydrometeorology performed parallel measurements of 12 PAH compounds in 2011 and 2012 at Radvanice. The results are summarized in Table F.3.

**Table F.3 — Between-sampler deviations for several PAH compounds measured at Ústí nad Labem**

| Compound | Mean concentration ng/m³ | | $w_{bs}$ % | |
|---|---|---|---|---|
| | 2011 | 2012 | 2011 | 2012 |
| BaA | 2,16 | 2,08 | 7,67 | 11,56 |
| BbF+BjF | 2,52 | 3,17 | 8,54 | 5,68 |
| BkF | 1,33 | 1,10 | 9,24 | 7,44 |
| BaP | 1,06 | 1,54 | 7,41 | 7,51 |
| INP | 1,42 | 1,45 | 7,32 | 7,53 |
| DBahA | 0,34 | 0,29 | 7,61 | 7,18 |
| BghiP | 1,16 | 0,98 | 6,82 | 6,75 |
| COR | | 0,29 | | 4,22 |

Two laboratories tested the between sampler standard deviation for BaP and BghiP at a sampling site close to a coking plant (Bottrop) in 2003. The results are shown in Table F.4. The compounds were analysed after PM10 sampling with Digitel DH 80 devices.

**Table F.4 — Between-sampler deviations for BaP and BghiP**

| Compound | Mean concentration ng/m³ | $w_{bs}$ % |
|---|---|---|
| BaP | 3,83 | 11,7 |
| BghiP | 4,15 | 7,7 |

A relative between sampler deviation of about 10 % to 15 % can be assumed for every PAH compound.

The combination of the standard deviations according to the rules of error propagation (see Formula (F.3)) leads to the combined uncertainty $u_c$.

$$u_c = \sqrt{s_L^2 + w_{bs}^2} \quad \text{(F.3)}$$

This value is multiplied by a factor of 2 to obtain the expanded uncertainty at the 95 % confidence interval.

Table F.5 shows a calculation of the uncertainty of PAH measurements.

**Table F.5 — Uncertainty of PAH measurements**

| Compound | Amount ng/filter | Concentration (low volume sampling) ng/m$^3$ | $s_L$ % | $w_{bs}$ % | $u_c$ % | $U$ % |
|---|---|---|---|---|---|---|
| BaA | 2 to 340 | 0,04 to 7 | 35 to 8 | | 40 to 13 | 80 to 26 |
| BbF | 4 to 340 | 0,08 to 7 | 25 to 12 | | 30 to 16 | 60 to 32 |
| BjF | | 0,04 to 5 | | | | |
| BkF | 2 to 200 | 0,03 to 4 | 34 to 14 | | 40 to 17 | 80 to 34 |
| BaP | 3 to 370 | 0,06 to 8 | 20 to 10 | 15 to 10 | 25 to 15 | 50 to 30 |
| INP | 2 to 288 | 0,08 to 6 | 30 to 13 | | 33 to 17 | 66 to 34 |
| DBahA | 0,3 to 45 | 0,01 to 1 | 50 to 20 | | 53 to 23 | 106 to 46 |
| BghiP | 5 to 260 | 0,1 to 6 | 30 to 15 | | 34 to 18 | 68 to 36 |
| ΣBF | 9 to 760 | 0,2 to 15 | 40 to 80 | | 42 to 20 | 84 to 40 |

For BaP the estimation of the expanded uncertainty corresponds well with the results of the field test for EN 15549 [5]. For the other compounds the relative expanded uncertainty generally is lower than 70 % at concentrations above 0,2 ng/m$^3$.

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