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**Zunanji zrak - Metoda za določevanje benzo[a]antracena, benzo[b]fluorantena, benzo[j]fluorantena, benzo[k]fluorantena, dibenzo[a,h]antracena, indeno[1,2,3-cd]pirena in benzo[ghi]perilena**

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

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

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

**Ta slovenski standard je istoveten z: CEN/TS 16645:2014**

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 SPÉCIFICATION TECHNIQUE  
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**CEN/TS 16645**

April 2014

ICS 13.040.20

English Version

**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 ambient - 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

This Technical Specification (CEN/TS) was approved by CEN on 16 December 2013 for provisional application.

The period of validity of this CEN/TS is limited initially to three years. After two years the members of CEN will be requested to submit their comments, particularly on the question whether the CEN/TS can be converted into a European Standard.

CEN members are required to announce the existence of this CEN/TS in the same way as for an EN and to make the CEN/TS available promptly at national level in an appropriate form. It is permissible to keep conflicting national standards in force (in parallel to the CEN/TS) until the final decision about the possible conversion of the CEN/TS into an EN is reached.

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**CEN/TS 16645:2014 (E)****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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

According to the CEN-CENELEC Internal Regulations, the national standards organizations of the following countries are bound to announce this Technical Specification: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

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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.

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## CEN/TS 16645:2014 (E)

## 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 PM<sub>10</sub> 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<sup>3</sup> to approximately 20 ng/m<sup>3</sup> for BaA, BbF, BjF, BkF, BaP, INP and BghiP and 0,02 ng/m<sup>3</sup> to approximately 2 ng/m<sup>3</sup> 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 PM<sub>10</sub> at sampling sites with different characteristics (in ng/m<sup>3</sup>)**

Compound	Industrial <sup>a</sup>	Urban background <sup>b</sup>	Traffic <sup>c</sup>	Rural background <sup>d</sup>
BaA	0,85	0,24	0,24	0,06
BbF	2,44	0,62	0,48 <sup>e</sup>	0,16 <sup>e</sup>
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 <sup>f</sup>	0,20 <sup>g</sup>	0,34	0,09
DBahA	0,20	0,10	0,05 <sup>f</sup>	0,07 <sup>h</sup>
INP	1,60	0,43	0,23	0,08

<sup>a</sup> Bottrop (Germany, 2010), HPLC/FLD.  
<sup>b</sup> Mülheim-Styrum (Germany, 2010), HPLC/FLD.  
<sup>c</sup> London Crystal Palace Parade (UK, 2010), GC-MS.  
<sup>d</sup> Harwell (UK, 2010), GC-MS.  
<sup>e</sup> (Bbf+BjF).  
<sup>f</sup> Wijk aan Zee (The Netherlands, 2011), GC-MS.  
<sup>g</sup> Rotterdam (The Netherlands, 2011), GC-MS.  
<sup>h</sup> (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 PM<sub>10</sub> or PM<sub>2,5</sub> 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*

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## 3 Terms and definitions (standards.iteh.ai)

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

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### 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]]

**CEN/TS 16645:2014 (E)****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]]

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**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 $\text{ng}/\text{m}^3$
$D_C$	is the detection limit, in $\text{ng}/\text{m}^3$
$D_M$	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
$S_{lib}$	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

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

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**5 Principle of the method**

The method is divided into two main parts: the sampling of PM<sub>10</sub> 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):

$$R = \frac{X_a}{X_{ca}} \cdot 100 \quad (1)$$

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where

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

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.

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### 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<sup>3</sup>. If the 3 benzofluoranthene species are analysed as a sum, their cumulated detection limit shall be less than 0,1 ng/m<sup>3</sup>. If B<sub>j</sub>F is analysed by HPLC-FLD, its detection limit is about 0,4 ng/m<sup>3</sup>.

#### 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):

$$S_{\text{lfb}} = \sqrt{\frac{\sum_{i=1}^n (\bar{m}_b - m_i)^2}{n-1}} \quad (2)$$

where

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

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

$m_i$  is the individual filter blank, in ng;

$n$  is the number of analysed filters. [SIST-TS CEN/TS 16645:2014](https://standards.iteh.ai/catalog/standards/sist/5b9ab105-3dc4-4325-ad38-1b5b0086131f/sist-ts-cen-ts-16645-2014)

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

$$D_M = t_{n-1;0,95} \cdot S_{\text{lfb}} \quad (3)$$

where

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

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

$S_{\text{lfb}}$  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  $\pm$  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<sup>3</sup>, is calculated introducing the nominal daily sampling volume according to Formula (4).

$$D_c = \frac{D_M}{V_n} \quad (4)$$

where

- $D_C$  is the detection limit, expressed in  $\text{ng}/\text{m}^3$ ;
- $D_M$  is the minimal detectable mass of the PAH compound, in ng;
- $V_n$  is the nominal daily sampling volume, in  $\text{m}^3$ .

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

NOTE The volume is, for example, ca.  $720 \text{ m}^3/\text{d}$  for high volume samplers and  $55 \text{ m}^3/\text{d}$  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).

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### 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).