SLOVENSKI STANDARD
SIST EN 15549:2008

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Kakovost zraka - Standardna metoda za določevanje koncentracije benzo[a]pirena (B[a]P) v zunanjem zraku

Air quality - Standard method for the measurement of the concentration of benzo[a] pyrene in ambient air

Luftbeschaffenheit - Messverfahren zur Bestimmung der Konzentration von Benzo[a] pyren in Luft

Méthode de mesurage de la concentration du benzo [a] pyrene dans l'air ambiant

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English Version

Air quality - Standard method for the measurement of the concentration of benzo[a]pyrene in ambient air

Qualité de l'air - Méthode normalisée pour le mesurage de la concentration de benzo[a]pyrène dans l'air ambiant

Luftbeschaffenheit - Messverfahren zur Bestimmung der Konzentration von Benzo[a]pyren in Luft

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EUROPEAN COMMITTEE FOR STANDARDIZATION
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EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36 B-1050 Brussels

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Contents

Foreword

This document (EN 15549:2008) has been prepared by Technical Committee CEN/TC 264 “Air quality”, the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by September 2008, and conflicting national standards shall be withdrawn at the latest by September 2008.

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Introduction

The European Directive 2004/107/EC prescribes the reference methodology for the measurement of benzo[*a*]pyrene (B*a*P) in ambient air and states that the method shall be a method based on manual PM10 sampling systems described in EN 12341 or equivalent.

Hence, this European Standard describes a method in which the sampling systems fulfil this requirement.

However, in the course of drafting this European Standard it became clear that in certain circumstances, in the presence of oxidants such as ozone, B*a*P may be degraded. In specific situations this may result in losses of B*a*P of > 50 %. It has been shown that the degradation due to ozone can be substantially reduced by including an ozone denuder in the sampling system.

To date only a limited number of experiments has been performed in order to evaluate the particular conditions under which the denuder systems can be efficiently used. Consequently, the application of ozone denuders lacks sufficient validation to be a normative part of this European Standard.

In order to have a complete picture of the performance of ozone denuder systems further information is required on:

- efficiency under variable atmospheric conditions,
- regeneration time after exposure to high humidity,
- maximum capacity for ozone,
- maximum sample volume and maximum sampling period,
- stability of catalyst,
- maximum period of use,
- particle losses.

Examples of sampling using an ozone denuder are given in Annex A.

The experimental evidence collected so far is presented in Annex F.

It is recommended that further work is undertaken to provide data of B*a*P comparisons with and without ozone denuders.

1 Scope

This document specifies a measurement method for the determination of particulate benzo[*a*]pyrene (B*a*P) in ambient air, which can be used in the framework of the Council Directive 96/62/EC [1] and the Directive 2004/107/EC [2]. This document specifies performance characteristics and performance criteria for the measurement method when it is used as a reference method. The performance characteristics of the measurement method are based on a sampling period of 24 h.

This document describes a measurement method which comprises sampling of B*a*P 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 B*a*P in the concentration range from approx. 0,04 ng/m^3 to approximately 20 ng/m^3.

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

NOTE If the B*a*P concentration exceeds the calibration range the extract can be diluted.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 12341:1998, *Air quality – Determination of the PM 10 fraction of suspended particulate matter – Reference method and field test procedure to demonstrate reference equivalence of measurement methods*

ENV 13005:1999, *Guide to the expression of uncertainty in measurement*

ISO 8258, *Shewhart control charts (including ISO 8258:1993 Technical Corrigendum 1)*

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

3.2
certified reference material (CRM)
reference material one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation that is issued by a certifying body

3.3
external standard solution
solution of the analyte of known concentration

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

3.5
internal standard solution
solution of a known substance of known concentration, 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

3.7
PM10
target specification for sampling the thoracic particles

[EN 12341:1998]

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

[EN 14902:2005] [27]

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

3.10
surrogate standard solution
solution of a known substance and of known concentration, used to spike filters before extraction in order to check the recovery efficiency

3.11
target value
concentration in the ambient air fixed with the aim of avoiding, preventing or reducing harmful effects on human health and the environment, as a whole, to be attained where possible over a given period

NOTE This definition originates from [2]. The current value for B*a*P is 1 ng/m^3 for the total content in the PM10 fraction averaged over a calendar year.

3.12
uncertainty (of measurement)
parameter associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand

[ENV 13005:1999]

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 B*a*P or of its characteristic ion in the chromatogram of the calibration solution;
A_E	is the peak area or peak height of B*a*P 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 B*a*P in ambient air in ng/m³;
D_C	is the detection limit, expressed in ng/m³;
D_M	is the absolute detection limit in the sample in ng;
f	is the response factor of B*a*P;
$\overline{m}$	is the mean of laboratory filter blanks in ng;
m_C	is the mass of B*a*P in the calibration solution in ng;
m_CRM	is the certified mass in the CRM in ng;
m_E	is the mass of B*a*P in the sample extract in ng;
m_F	is the mass of B*a*P 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 B*a*P calculated from the regression equation 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 B*a*P in %;
R_s	is the peak resolution;
S_{lfb}	is the standard deviation of laboratory filter blanks in ng;
$s(m_{\mathrm{E}})$	is the standard deviation of the replicate measurement results of the mass determined in ng;
t	is the sampling time in h;
$t_{\mathrm{n-1;0,95}}$	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 B*a*P in mg/kg;
X_{ca}	is the certified mass fraction of B*a*P in mg/kg.

4.2 Abbreviations

B*a*P	Benzo[*a*]pyrene
CRM	Certified reference material
DAD	Diode array detector
FLD	Fluorescence detector
GC	Gas chromatography
HPLC	High performance liquid chromatography
MS	Mass spectrometry

5 Principle of the method

The method is divided into two main parts: first the sampling in the field and second the analysis in the laboratory. During sampling, particles are collected on a filter by sampling a measured volume of air by means of a sampler equivalent to one of those described in EN 12341.

The sampling time is 24 h. The filter is transported to the laboratory. B*a*P is 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 then the instructions for siting samplers given in [2] shall be followed.

6.2 Sampling requirements

The sampling system shall be equivalent to EN 12341 (see [2]).

NOTE 1 Equivalence can be demonstrated by performing a side-by-side comparison of the system with a PM10 reference sampler. Guidance for the performance of such comparisons is given in [3].

NOTE 2 In the presence of ozone B*a*P may degrade. In specific situations this may lead to losses of B*a*P of > 50 %. Whenever these effects are expected to be significant, the PM10 sampler may be equipped with an ozone denuder (see Annex A). The experimental evidence collected so far is presented in Annex F. However, the application of ozone denuders lacks sufficient validation to be a normative part of this European Standard.

NOTE 3 Examples of sampling systems with and without denuder are presented in Annex A.

6.3 Analysis

6.3.1 Recovery efficiency

Using the external or internal standard method for quantification check the recovery efficiency periodically by spiking laboratory blank filters with a known amount of B*a*P and process them as usual. The recovery efficiency shall be between 80 % and 120 %, otherwise the surrogate standard method shall be used. The recovery efficiency shall be checked with a frequency to ensure that 95 % probability for a correct measurement is maintained (see 12.1.1).

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

NOTE 1 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 B*a*P in certified reference material (e. g. NIST 1649a) using equation (1).

$$R = \frac{X_a}{X_{ca}} \times 100 \tag{1}$$

where

R is the recovery efficiency of B*a*P in %;

X_a is the measured mass fraction of B*a*P in mg/kg;

X_ca is the certified mass fraction of B*a*P in mg/kg.

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

NOTE 2 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 B*a*P during extraction, can be identified, for example, by

- Repeating the extraction step with a different method and comparing the results;

- Comparing the ratio of Ba*P* 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 shall be less than 0,04 ng/m³.

6.3.2.2 Determination based on laboratory filter blanks

Determine the detection limit from the standard deviation of at least ten laboratory filter blanks using equation (2).

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

where

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

$\overline{m}$ 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.

The minimal detectable mass of Ba*P* is calculated using equation (3).

$$D_M = t_{n-1;0,95} \times S_{lfb} \qquad (3)$$

where

D_M is the minimal detectable mass of Ba*P* in ng;

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

S_{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 without injecting any solution. Keep the chromatographic parameters as used for the calibration and the detection of Ba*P*. Calculate the detection limit as three times the average of the height of the noise at the retention time of Ba*P* ± 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/m³, is calculated introducing the nominal daily sampling volume according to equation (4).

$$D_C = \frac{D_M}{V_n} \tag{4}$$

where

D_{C} is the detection limit, expressed in ng/m³;

D_{M} is the minimal detectable mass of B*a*P in ng;

V_{n} is the nominal daily sampling volume in m³.

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

NOTE The volume is, for example, approximately 1 630 m³ for the sampler type, which has been used in the field test (see Annex F.2), or approximately 64 m³ for cuts of 50 mm diameter of the filter samples, collected with this sampler type.

6.4 Oven temperature for HPLC

The temperature of the HPLC column oven shall kept constant to at least ± 1 °C.

7 Reagents and gases

7.1 Solvents

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

7.2 Gases

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

7.3 External standard

B*a*P, 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 B*a*P.

7.5 Surrogate standard

- Methylated or halogenated PAH, e.g. 7-methylbenzo[*a*]pyrene (for HPLC/FLD);
- deuterated or carbon-13-labelled 5-ring PAH, e. g. B*a*P -d12 (for GC/MS).

Make sure that the standards contain less than 1 % (relative) of the native B*a*P.

7.6 Stock standard solution

Dilution of a solution of B*a*P with a concentration traceable to internationally accepted standards, e.g. NIST 1647e.

7.7 Certified reference material

Containing a certified concentration of B*a*P, in a matrix similar to PM 10 particles, e.g. NIST 1649a.

8 Apparatus

8.1 Sampling equipment

8.1.1 PM10 sampler

The sampling system shall be equivalent to EN 12341 (see [2]).

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

8.1.3 Quartz fibre or 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 NOTE 1 in 13.6.

The purity of the filters shall be checked according to 13.7.

NOTE It is recommended that filter manufacturers determine the filter separation efficiency according to standard methods such as EN 13274-7 [4] or EN 1822-1 [5].

8.1.4 Flow meter, with a measurement uncertainty that is sufficient to enable the volumetric flow rate of the samplers (8.1.1) to be measured within ± 5 %. The calibration of the flow meter shall be traceable to internationally accepted standards.

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.

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 B*a*P concentration in the extract is high enough a DAD can be used (see 15.2).

8.3.2 GC/MS apparatus

Gas chromatograph 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 out before deploying the sampler in the field in order to identify problems with the sampler in an early stage.

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, 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.

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

If the filter has to 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 one filter (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 twenty filters shall be analysed as field filter blank. If the field filter blank significantly exceeds the average laboratory filter blank, 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.