BRITISH STANDARD

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

ICS 13.040.20

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British Standards

National foreword

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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of an identical text or by endorsement, at the latest by September 2008, and conflicting national standards shall be withdrawn at the latest by September 2008.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;

$s(m_E)$ 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 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).

$$R = \frac{X_a}{X_{ca}} \times 100 \qquad (1)$$

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 B*a*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 B*a*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 B*a*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 B*a*P. Calculate the detection limit as three times the average of the height of the noise at the retention time of B*a*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).

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

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.

9.4 Sample collection 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 and at least every three months, following the manufacturer's instructions. If the flow rate deviates from its nominal value by more than the deviation given by the manufacturer, calibrate the sampler by adjusting the flow rate as necessary.

Take field filter blanks periodically at each site (at least once for every twenty 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 at the end of the sampling period, replace it in its uniquely marked transport container and seal the container for transportation to the laboratory (for single filter devices). For sequential samplers, collect the used filters and prepare them for transportation to the laboratory.

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 closed vessel at a temperature below 20 °C.

NOTE Individual samples taken over a period of up to one month can be combined and analysed as a composite sample [2]. Filter cuts of identical size of single days are extracted together. If the B*a*P 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 has to 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.

Clean and grease the inlet impaction plate, if applicable, according to the manufacturer's instructions. Perform intensive cleaning of the PM10 sampling head according to the manufacturer's instructions at least once every 6 months.

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.

NOTE 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 results in a solution of B*a*P 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 HPLC/FLD analysis

11.1.1 Principle of the method [6]

The organic extract containing B*a*P 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. B*a*P is identified by its retention time. The peak area and/or peak height is used as a measure of its concentration in the sample.

NOTE In practice, extracts from PM10 particles may be carefully evaporated to dryness without reducing the recovery of B*a*P.

The response and sensitivity of the FLD is constant over a long period, so that 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.

11.1.2 Reagents

11.1.2.1 Calibration solutions

Prepare calibration solutions of B*a*P from the stock solution at a minimum of five concentration levels by adding appropriate volumes of the B*a*P 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. The concentration of these solutions shall be at a level corresponding to the target value ± 20 %.

NOTE 1 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.

NOTE 2 For example, with a sampling volume of 100 m^3 and a final volume of the extract of 1 ml and the target value of 1 ng/m^3 the concentration should be 100 ng/ml.

11.1.2.2 External standard solution

Use a calibration solution (11.1.2.1) with the concentration nearest to the one which is equivalent to the B*a*P concentration at the target value ± 20 %.

NOTE For example, with a sampling volume of 100 m^3 and a final volume of the extract of 1 ml and the target value of 1 ng/m³ the concentration should be 100 ng/ml.

11.1.2.3 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 B*aP* concentration at the target value ± 20 %.

NOTE For example, with a sampling volume of 100 m^3 and a final volume of the extract of 1 ml and the target value of 1 ng/m³ the concentration should be 100 ng/ml.

11.1.2.4 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 B*a*P concentration at the target value ± 20 %.

NOTE For example, with a sampling volume of 100 m^3 and a final volume of the extract of 1 ml and the target value of 1 ng/m³ the concentration should be 100 ng/ml.

11.1.3 Proposed parameters for HPLC/FLD operation

See example in D.1.

11.1.4 Calibration

When using the external standard method for quantification, inject the calibration solutions (see 11.1.2.1; 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 1 (see E.4.4.2.3 for calculation).

11.1.5 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 B*a*P by its retention time. Dilute an aliquot of the extract and reanalyse it, if the concentration of B*a*P 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.

11.2 GC/MS analysis

11.2.1 Principle of the method [7]

The organic extract containing B*a*P 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 B*a*P is 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.

11.2.2 Reagents

11.2.2.1 Solutions for checking the lack of fit

Prepare calibration solutions of B*a*P from the stock solution at a minimum of five concentration levels by adding appropriate volumes of the B*a*P stock solution to a volumetric flask and making up with the appropriate solvent (see B.6). 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. The concentration of one solution shall be at a level corresponding to the target value ± 20 %.

NOTE For example, with a sampling volume of 100 m^3 and a final volume of the extract of 1 ml and the target value of 1 ng/m³ the concentration should be 100 ng/ml.

11.2.2.2 Internal standard solution

Dilute the internal standard (7.4) in the appropriate solvent (see B.6). 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 B*a*P concentration at the target value ± 20 %.

11.2.2.3 Surrogate standard solution

Dilute the surrogate standard (7.5) in the appropriate solvent (see B.6). Add, for example, 10 µl of this solution to the filter before extraction. The concentration of the solution shall be equivalent to the B*a*P concentration at the target value ± 20 %.

NOTE For example, with a sampling volume of 100 m^3 and a final volume of the extract of 1 ml and the target value of 1 ng/m³ the concentration should be 100 ng/ml.

11.2.3 Proposed parameters for GC/MS operation

See example in D.2.

11.2.4 Lack of fit

In order to determine the linear working range of the detector for B*a*P inject the solutions for checking the lack of fit (see 11.2.2.1; 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 1; determination see E.4.4.2.3).

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, 2 µl) into the GC/MS system. Identify B*a*P by its retention time and its molecular ion (m/z = 252) and an appropriate qualifier, see e.g. Annex D.2. Use the integrated abundance (peak area) of the target ion (m/z =252) 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 B*a*P 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 B*a*P in the extract according to equation (5), using the calibration function:

$$m_E = \frac{A_E - b}{a} \times V_E \quad (5)$$

where

m_E is the mass of B*a*P in the extract in ng;

A_E is the peak area or peak height of B*a*P 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 (11.1.2.2) to verify the proper operation of the HPLC/FLD system (at least 10 % of the samples).

Verify the recovery efficiency (see 6.3.1), if necessary including the clean-up step, with laboratory blank filters (at least 5 % of the samples), spiked with the external standard solution (see 11.1.2.2).

12.1.2 Internal standard method

Prepare at least five solutions with B*a*P concentrations, which cover of the whole working range, and a constant concentration of the internal standard (7.4), which shall be equivalent to the B*a*P concentration at the target value ± 20 %.

NOTE The calibration solutions (see 11.1.2.1) may be used for this purpose by adding constant volumes of the internal standard solution (see 11.1.2.3).

Inject these solutions and calculate the response factor *f* of B*a*P from the peak areas of both B*a*P and the internal standard and the corresponding masses of these substances according to equation (6).

$$f = \frac{A_{IS} \times m_c}{A_c \times m_{IS}} \quad (6)$$

where

f is the response factor of B*a*P;

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

A_c is the peak area or peak height of B*a*P in the chromatogram of the calibration solution;

m_c is the mass of B*a*P in the calibration solution in ng;

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 11.1.2.3) to the sample before injection.

The mass of B*a*P in the sample extracts is calculated according to equation (7):

$$m_E = \frac{f \times A_E \times m_{ISE}}{A_{ISE}} \quad (7)$$

where

f is the response factor of B*a*P;

A_E is the peak area or peak height of B*a*P in the chromatogram of the sample extract;

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

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

m_E is the mass of B*a*P in the sample extract in ng.

Verify the recovery efficiency (see 6.3.1), if it is used, including the clean-up step, with laboratory blank filters (at least 5 % of the samples), spiked with the external standard solution (see 11.1.2.2).

12.1.3 Surrogate standard method

Correct the mass of B*a*P 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 equation (5) for the external calibration method, or using response factors in analogy to 12.1.2 and equations (6) and (7) for the internal standard method.

Add for example 10 µl of the surrogate standard solution (11.2.2.3) to the filter before the extraction step. Evaporate the solvent and calculate the mass of B*a*P in the filter according to equation (8):

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

where

m_F is the mass of B*a*P 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 B*a*P in the extract in ng, calculated according to equation (5) or equation (7);

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

12.2 GC/MS Analysis

Prepare at least five solutions with B*a*P concentrations, which cover the whole working range, and a constant concentration of the internal standard (7.4), which shall be the target value ± 20 %.

NOTE The solutions (see 11.2.2.1) may be used for this purpose by adding constant volumes of the internal standard solution (see 11.2.2.2).

Inject these solutions and calculate the response factor *f* of B*a*P from the peak areas/peak heights of both B*a*P and the internal standard and the corresponding masses of these substances according to equation (9).

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

where

f is the response factor of B*a*P;

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

A_c is the peak area or peak height of the characteristic ion of B*a*P (m/z = 252) in the chromatogram of the calibration solution;

m_c is the mass of B*a*P in the calibration solution in ng;

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 11.2.2.2 to the sample before injection.

The mass of B*a*P in the sample extracts is calculated according to equation (10):

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

where

f is the response factor of B*a*P;

A_E is the peak area or peak height of the characteristic ion of B*a*P in the chromatogram of the sample extract;

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

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

m_E is the mass of B*a*P in the sample extract in ng.

Correct the mass of B*a*P by the recovery efficiency using the surrogate standard method.

Calculate the concentration of the surrogate standard in analogy to equation (5). Add the surrogate standard solution (11.2.2.3) to the filter before the extraction step. Calculate the mass of B*a*P in the filter according to equation (11):

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

where

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

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

m_E is the mass of B*a*P in the extract in ng, calculated according to equation (5);

m_F is the mass of B*a*P on the filter sample in ng.

12.3 Concentration of B*a*P in ambient air

Calculate the concentration of B*a*P in ambient air according to equation (12):

$$C = \frac{m_F}{V} \tag{12}$$

where

C is the concentration of B*a*P in ambient air in ng/m^3;

m_F is the mass of B*a*P on the filter sample in ng;

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

NOTE The mass m_F of B*a*P should be adjusted for the fraction of the exposed filter area which was submitted for extraction.

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 B*a*P or a peak interfering with B*a*P is detected at a concentration > 4 % of the target value, suspend the analysis. Identify the source of the contamination and replace contaminated reagents.

NOTE For example, with a sampling volume of 100 m³ and a final volume of the extract of 1 ml the blank value has to be below 4 ng/ml in order to meet this requirement.

13.2 Calibration drift check

Analyse the calibration solution with a concentration corresponding to the target value ± 20 % (see 11.1.2.1 and 11.2.2.1) at least after every tenth sample. If the measured concentration of B*a*P 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 Quality control solutions

At regular intervals analyse suitable quality control solutions, other than calibration solutions, e.g. various already analysed extracts combined to form a mixture, after calibration to monitor the performance of the method. Plot control charts according to ISO 8258 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 analysis

To establish that chromatographic interferences are avoided for B*a*P and internal and surrogate standards, demonstrate that the HPLC column is able to separate these PAHs from their nearest eluting peaks with a peak resolution factor superior or equal to 1,2.

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

$$R_s = 2 \times \frac{t_{R2} - t_{R1}}{w_1 + w_2} \quad (13)$$

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 analysis

To establish that chromatographic interferences are avoided as well as possible, demonstrate that the GC column is able to separate B*a*P and B*a*P-d12. The peak resolution shall be superior or equal to 1,0.

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

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 B*a*P and a peak area or peak height indicating a concentration of more than 4 % of the target value , the filter batch shall not be used for B*a*P analysis.

NOTE 1 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.

NOTE 2 For example, with a sampling volume of 100 m³ and a final volume of the extract of 1 ml the blank value has to be below 4 ng in order to meet this requirement.

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 B*a*P and a peak area or peak height indicating a concentration of more than 4 % of the target value find out the reasons and take corrective actions.

NOTE For example, with a sampling volume of 100 m³ and a final volume of the extract of 1 ml the blank value has to be below 4 ng in order to meet this requirement.

13.8 External quality assessment

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

NOTE It is strongly recommended that the laboratory works in accordance with the requirements of EN ISO/IEC 17025 [8]. This can be demonstrated by formal accreditation.

14 Determination of measurement uncertainty

14.1 Introduction

The measurement of the concentration of B*a*P in ambient air has to fulfil the requirement of a maximum uncertainty in the measured values in the region of the target value prescribed by Directive 2004/107/EC. In order to fulfil this requirement, the measurement uncertainty has to be assessed by methods described in ENV 13005, ISO 5725-2 [9], EN ISO 20988 [10] 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).

In this European Standard the uncertainty assessment is based on results from laboratory tests that are used to determine the performance characteristics of the method used. These tests shall be applied by each individual laboratory performing measurements of B*a*P within the frame of implementation of the above Directive.

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

This information is supplemented by results from experiments that were performed in support of the validation of the standard method.

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 [9].

14.2 Parameters contributing to measurement uncertainty

14.2.1 Parameters to be assessed and minimum requirements

The parameters given in Table 1 have been identified to contribute to the uncertainty of B*a*P 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 fulfill the uncertainty requirements given in Directive 2004/107/EC.

Table 1 — Uncertainty parameters and minimum requirements

Uncertainty parameter	Symbol	Section	Minimum requirement
Sampled volume	V		
• Sample flow – calibration and measurement	ϕ	E.2.2	Difference between measured and nominal flow rate ≤ ± 5 % Uncertainty of flow calibration device ≤ ± 1 %
• Sampling time	t	E.2.3	Relative uncertainty ≤ ± 0,1 %
Mass of B*a*P sampled	m_F	E.4	
• Sampling efficiency, including effects of reactions with ozone	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 B*a*P in extract	m_E	E.4.4	
External standard method		E.4.4.2	
• Recovery efficiency	R	E.3	80 % ≤ R ≤ 120 % at the target value with a relative uncertainty of ≤ ± 3 %
• Mass of B*a*P in calibration standards	m_c	E.4.4.2.2	Relative uncertainty ≤ ± 2 %
• Lack-of-fit of calibration function	δ	E.4.4.2.3	Relative residuals over the calibration range ≤ ± 3 %; at the target value ≤ ± 2 %
• Response drift between calibrations	d	E.4.4.2.4	≤ ± 5 %
• Analytical repeatability	u_{anal}	E.3	≤ ± 3 %
• Selectivity	s	E.4.4.2.5	HPLC : Resolution factor ≥ 1,2 GC/MS : Resolution factor ≥ 1,0 for B*a*P and B*a*P-d12
Internal standard method			
• Recovery efficiency	R	E.3	80 % ≤ R ≤ 120 % at the target value with a relative uncertainty of ≤ ± 3 %
• Average response factor of B*a*P	f	E.4.4.3.2	Relative standard deviation ≤ ± 5 %
• Concentration of internal standard in extract	m_{ISE}	E.4.4.3.3	≤ ± 2 %
• Selectivity	s	E.4.4.2.5	HPLC : Resolution factor ≥ 1,2 GC/MS : Resolution factor ≥ 1,0 for B*a*P and B*a*P-d12
• Precision of response measurement	s_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 B*a*P in filter blank	m_{bl}	E.5	≤ 1 % of the target value

14.2.2 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 uncertainties are found (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 Standard. This can be achieved by allowing for individual laboratories only a fraction of the uncertainty requirement of Directive 2004/107/EC (see Clause E.9).

14.2.3 Sampling systems

Sampling systems used shall fulfil the requirements of EN 12341 (see 6.2.1). The fulfilment of this requirement does not eliminate the existence in practice of differences between comparable individual sampling systems.

Annexes F.2.2.2 and F.2.3.1 give values for between-sampler uncertainties derived from field tests.

14.3 Recommendations for use

An appropriate level of quality control according to EN ISO/IEC 17025 [8] shall be applied. In addition to the internal quality control measures described in this European Standard (see Clause 13) the laboratory should employ external quality control measures (use of reference materials, participation in interlaboratory comparisons).

A certified reference material NIST 1649a containing 2,5 µg/g of B*a*P per unit is available from NIST. Although this reference material has a matrix differing from practical B*a*P air samples, it is currently the only reference material considered suitable for quality control purposes for the measurement of B*a*P in ambient air. This certified reference material may be applied on a regular basis for checking recovery efficiencies.

In order to fulfil the requirements of the EU Air Quality Framework Directive 96/62/EC [1] the laboratories using this Standard will have to demonstrate to be working in accordance with the requirements of EN ISO/IEC 17025 [8]. One of the ways of demonstrating compliance with these requirements is through formal accreditation of the test described by an accreditation body falling under the Multi-Lateral Agreement (MLA) of the European Cooperation for Accreditation (EA).

15 Interferences

15.1 Chemical and physical interferences

Exposure to heat, ozone and ultraviolet light may cause degradation of B*a*P during sampling, sample storage and processing. Therefore this exposure to heat and ultraviolet light shall be avoided, if possible.

NOTE 1 The impact of ozone can be minimized by using a sampling system according to Annex A. However, the application of ozone denuders lacks sufficient validation to be a normative part of this European Standard.

NOTE 2 Available data do not confirm a significant on-filter effect of NO_2 on B*a*P degradation [11; 12; 13; 14].

15.2 Chromatographic interferences

Unusual results, peak forms or retention times of B*a*P may suggest that chromatographic interferences are present.

Identify co-elution of unknown substances with B*a*P as follows:

- For GC/MS: Check the relation of the characteristic peak of B*a*P (m/z: 252) to other ions of B*a*P with a high abundance (e.g. m/z: 126), check if peaks at m/z values not belonging to the mass spectrum of B*a*P are present at the retention time of B*a*P.

- For HPLC: Add a standard of known concentration of B*a*P to the sample solution. If the retention time of the peak changes by more than ca. 0,5 % of the retention time of the peak of B*a*P, or if the peak form is modified (e.g., a shoulder or a split peak appears), chromatographic interference is proved.

NOTE If the B*a*P concentration of the extract is high enough it can be reanalysed with HPLC/DAD. Check the UV spectrum of the peak. If it differs from that of pure B*a*P by more than about 10 %, chromatographic interference is proved.

If a chromatographic interference is recognised, reanalyse the sample under different chromatographic conditions, purify the sample e.g. according to Annex C or note, that analysis is not possible because of a chromatographic interference.

16 Reporting of results

The analytical report shall contain at least the following information:

a) reference to this European Standard (EN 15549:2008),

b) complete identification of the sample,

c) type of sampler used,

d) description of each sampling location,

e) sampling time,

f) volume of air pumped,

g) barometric pressure and temperature (mean values),

h) type of filter,

i) result of determination expressed in ng/m³,

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 European Standard.

Annex A
(informative)

Sampling systems

A.1 Sampling systems according to EN 12341

A sampling system according to EN 12341 can be used.

NOTE In the field test (see Annex F) samplers according to Annex B.2 of EN 12341:1998 with a daily sampling volume of about 1 600 m^3 were used.

A.2 Sampling systems with ozone denuder

A.2.1 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 % [11; 15 to 21].

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 [22, 23]. 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 equation (equation A.1, [24]).

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

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

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.

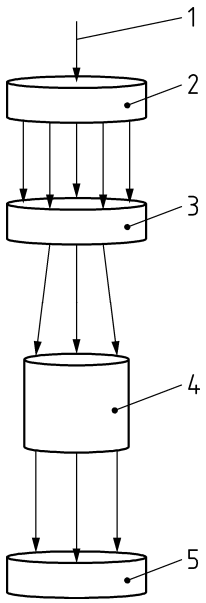
With this equation the layout of the denuder or the scale up e.g. to other flow rates can be calculated with the details given here: dimensions, gas concentrations and diffusion coefficient. The Davies equation is in principle only valid for ideal gases. The denuder has to be tested under relevant conditions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

A.2.2 Sampling system used in the field test

The field experiments were carried out using "Partisol Speciation Samplers"[1] 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

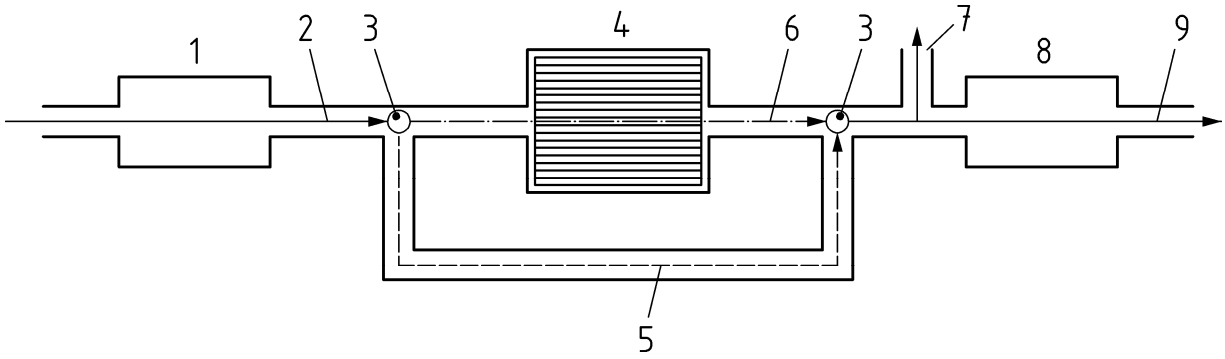
Figure A.1 – Schematic flow path way

[1] "Partisol Speciation Sampler" is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

A.3 Test of the efficiency of the denuder

— Subject the denuder to ozonised (ozone generator) synthetic air at flow rates corresponding to conditions during air sampling (e.g. 0,5 m³/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.



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 for this European Standard.

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 has to 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. 7 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 ºC, 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

NOTE 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 B*a*P or using field samples with a known content of B*a*P 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 for this European Standard.

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
- Excitation wavelength: 290 nm
- Emission wavelength: 422 nm

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 25 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.2.2.2
- Transfer line temperature: 300 °C
- Ion source temperature: approximately 180 °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
- Selected Ions: see D.2.2.3.

D.2.2.3 List of ions for selection

- Perylene-d12 (internal standard) 264
- B*a*P-d12 (surrogate standard) 264
- B*a*P 252, 126 (for confirmation)

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 14.2.1, Table 1, are evaluated on the basis of general equations 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

$$V = \varphi_{sam} \times t \quad \text{(E.1)}$$

where

φ_{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

$$\varphi_{sam} = \frac{(\varphi_1 + \varphi_2)}{2} \quad \text{(E.2)}$$

where

φ_1 is the sample flow rate at the beginning of the 24 h interval in m^3/min;

φ_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:

- measurements 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

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

where

$u(\varphi)$ is the standard uncertainty in the measurement of flow;

u_{cal} is the uncertainty due to calibration of the flow meter used for the determination of φ;

u_{meas} is the uncertainty of an individual flow measurement (see equation (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 B*a*P and its uncertainty are typically obtained from replicate measurements (six or more; usually ten) of B*a*P in a CRM. The uncertainty due to incomplete extraction for the B*a*P level corresponding to the limit value is calculated from contributions of:

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

as

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

where

m_{CRM} is the certified mass of B*a*P in the CRM;

$s(\text{m}_\text{R})$ is the standard deviation of the replicate measurement results of the mass determined;

n is the number of replicate measurements of the CRM.

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

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

E.4 Mass of B*a*P sampled

E.4.1 General

The mass of B*a*P on the filter sample may be expressed as

$$m_F = \frac{m_E}{SA} \tag{E.6}$$

where

S is the sampling efficiency;

A is the analyte stability in the sample;

m_E is the mass of B*a*P in the extract.

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 a B*a*P level corresponding to a concentration of 1 ng/m^3.

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 B*a*P in sample extract

E.4.4.1 General

For the measurement of the mass of B*a*P 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 B*a*P in a suitable solvent are used to establish response factors for B*a*P or response factors relative to the internal or surrogate standards used. The uncertainty of the B*a*P concentration is built up of contributions from

- purity of the B*a*P used ; when this is > 99 %, its contribution may be considered insignificant;
- mass fraction of B*a*P in the solvent used for the preparation of the standards;
- when gravimetry is used to prepare the calibration solutions: the uncertainties in the weighings 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.

NOTE 1 Examples of calculations of uncertainties can be found in [25] and [26].

NOTE 2 Calibration standards can be obtained commercially. These standards should be accompanied by certificates ensuring the traceability of the B*a*P concentration to internationally accepted standards.

NOTE 3 If other compounds besides B*a*P are used in calibration standards, the mass fraction of B*a*P 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 B*a*P 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

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

where

δ relative residual

m_{reg} mass of B*a*P calculated from the regression equation at the level of the calibration standard;

m_c mass of B*a*P present in the corresponding calibration standard.

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

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

where

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

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 needs not 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

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

where

r_n is the detector response for a calibration standard corresponding closest to the mass representing a sample at the limit value for response check *n;*

$r_{n\text{-}1}$ is the detector response for a calibration standard corresponding closest to the mass representing a sample at the limit value 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 B*a*P

The contributions given in Clauses E.4.4.2.1 to E.4.4.2.4 are combined to give the uncertainty of the measured mass of B*a*P as:

$$\frac{u^2(m_{\text{meas}})}{m_{\text{meas}}^2} = \frac{u^2(m_{\text{c}})}{n \cdot m_{\text{c}}^2} + u_{\text{anal}}^2 + u_{\text{F}}^2 + u_{\text{d}}^2 \qquad \text{(E.10)}$$

where

n is the number of calibration standards used to construct the calibration function.

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_E:

- uncertainty in the average response factor of B*a*P determined using equation (6) in 12.1.2;
- uncertainty in the concentration of the internal standard in the sample extract;
- precision of the measurement of responses for B*a*P and internal standard in the sample extract;
- selectivity of the chromatographic system.

E.4.4.3.2 Average response factor of B*a*P

The average response factor for B*a*P shall be determined in accordance with 12.1.2 or 12.2 (Equations (6) and (9)).

The uncertainty of the average response factor is given by

$$u_f^2 = \frac{s_f^2}{n} \qquad \text{(E.11)}$$

where

s_{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_{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 B*a*P and internal standard in the sample extract:

$$u\left(\frac{A_E}{A_{ISE}}\right) = s_f \tag{E.12}$$

E.4.4.3.5 Selectivity

See E.4.4.2.5.

E.4.4.3.6 Combined uncertainty in the measured mass of B*a*P

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 B*a*P in the extract as

$$\frac{u^2(m_{\text{meas}})}{m^2_{\text{meas}}} = \frac{u^2(m_{\text{ISE}})}{n \cdot m^2_{\text{ISE}}} + u^2_{\text{f}} + s^2_{\text{f}} \tag{E.13}$$

E.4.4.4 Surrogate standard method

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

$$r = \frac{m_{SSF}}{m_{SSE}} \tag{E.14}$$

where

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

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

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

- mass fraction of B*a*P in the solvent used for the preparation of the standards;
- when gravimetry is used to prepare the calibration solutions: the uncertainties in the weighings 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.

NOTE Since the surrogate standard is used in a relative way for correction purposes, its purity needs not to be taken into account. However, the surrogate standard should not contain B*a*P at levels contributing significantly to the measurement result.

The uncertainty in m_{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

$$u^2_r = u^2_{SSF} + u^2_{SSE} \tag{E.15}$$

E.4.5 Combined uncertainty in the mass of B*a*P in the extract

The contributions given in E.3 and E.4.5 are combined to give the uncertainty of the mass B*a*P in the air sample as

$$\frac{u^2(m_{\mathrm{E}})}{m_{\mathrm{E}}^2} = \frac{u^2(m_{\mathrm{meas}})}{m_{\mathrm{meas}}^2} + \frac{u^2(r)}{r^2} \tag{E.16}$$

E.5 Mass of B*a*P in sample blank

The typical mass of B*a*P 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 B*a*P, 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

$$m_{\mathrm{bl}} = \frac{3\, r_0}{2\, b_0} \tag{E.17}$$

where

r_0 is the noise level;

b_0 is the slope of calibration function at zero response.

E.6 Combined uncertainty in B*a*P concentration

The combined relative uncertainty of the B*a*P concentration in the air sampled is obtained by combination of contributions given in E.2, E.3 and E.4, as

$$\frac{u_C^2(c)}{c^2} = \frac{u^2(V)}{V^2} + \frac{u^2(m_{\mathrm{E}})}{m_E} + \frac{u^2(E)}{E} \tag{E.18}$$

E.7 Expanded uncertainty

The expanded relative uncertainty at the 95 % confidence level is obtained by multiplying $u_c(c)$ 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-Satterswaithe equation (see ENV 13005). For a large number of degrees of freedom, a coverage factor of two is used.

NOTE 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.

In principle this would imply a correction of the uncertainty requirement given in Directive 2004/107/EC. For example, if the relative between-laboratory uncertainty contribution found in the laboratory and field experiments for concentrations near the limit value of 1 ng/m^3 (± 15 % to ± 18 %) is used for this purpose, a maximum expanded relative uncertainty of ± 35 % (k = 2) would remain.

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.

NOTE 1 It is recommended to organise inter-laboratory comparisons on a regular basis as a part of ongoing QA/QC. Inter-laboratory comparisons may be organised in accordance with ISO 5725-2 [9] using samples of sufficient homogeneity to assure 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.

NOTE 2 It may be problematic to obtain ambient air of sufficient homogeneity for the organization of inter-comparisons involving measurements in real air without application of sampling manifolds through which ambient air is passed.

Annex F
(informative)

Results of laboratory and field tests

F.1 Laboratory tests

F.1.1 Organization

Within the frame of the validation of a reference method for the determination of B*a*P in ambient air, a validation programme based on a series of laboratory and field tests was designed. As the reference method is based on the measurement of B*a*P in the particulate phase of the air sample only, the field tests have been restricted to the analysis of filter samples that have been collected in accordance with the requirements for the sampling of PM10 dictated by EN 12341.

In the laboratory tests, attention has been focused on studying the feasibility of applying different methodologies for the extraction and analysis of B*a*P on the filter samples. In order to evaluate the applicability of these different methodologies a series of tests has been designed and performed aimed at the 'deconvolution' of the uncertainty sources associated with the measurements. This allows the between laboratory variability to be assessed. These tests comprise the analysis of:

- QC standard, containing only B*a*P in solution;
- pooled sample extract obtained by combining several stored residual sample extracts;
- samples of the NIST Standard Reference Material 1649a;
- filter cuts from air samples obtained by high-volume sampling of particulate matter.

These samples require – in the order listed – an increasing number of experimental steps to provide the analytical (end) result; the resulting uncertainties are therefore expected to increase accordingly and have provided insight in the contributions of the respective 'actions': analysis, inclusive of calibration, separation/selectivity and extraction/clean-up.

F.1.2 Conclusions

The results of the laboratory tests have led to the following conclusions.

1. No significant differences can be found between the mean results obtained by the two analytical methods used (HPLC-FLD and GC-MS).

2. Lowest between-laboratory and reproducibility standard deviations are found for the results of analysis of the QC standard (± 3,8 % and ± 4,6 %, respectively). These figures increase to about ± 6 % and ± 8 %, respectively, for the results of analysis of the sample extract and NIST SRM samples.

3. Standard deviations do not increase for the analysis of NIST SRM 1649a in comparison to the sample extract, as might have been expected because of the introduction of an additional operation (extraction). This may be due to

    - differences in matrices between extracts;
    - prior knowledge of target values for NIST SRM 1649a.

4. Within-laboratory standard deviation increases accordingly from standard to SRM, but the ratio of the reproducibility and within-laboratory standard deviations is always < 2, indicating robustness of the laboratory methods used.

5. Results of an ISO 5725-2 evaluation of the results of the analyses of the filter cuts indicate that if all results available are considered, the between-laboratory uncertainty and reproducibility uncertainty are ± 18 % and ± 20 %, respectively. When duplicate extraction methods are excluded, these figures are ± 13 % and ± 15 %. This uncertainty includes the contribution of filter inhomogeneity, for which a pooled relative standard deviation of ± 4 % was calculated from the results of the QC samples.

6. The following methods have been shown to give satisfactory extraction recoveries for filter cuts:

   - Soxhlet extraction using dichloromethane;
   - Accelerated solvent extraction using toluene;
   - Accelerated solvent extraction using dichloromethane;
   - Ultrasonic extraction using dichloromethane;
   - Ultrasonic extraction using toluene;
   - Microwave-assisted extraction using hexane-acetone.

F.2 Field tests

F.2.1 Organization

One of the objectives of the field trials has been to evaluate the performance characteristics of a high-volume sampler for the measurement of B*a*P in ambient air. For this purpose six pilot laboratories participating in the field trials each used two Andersen samplers[2] in parallel to sample the ambient PM10 fraction during a minimum of twenty consecutive days.

The Andersen samplers were equipped with quartz-fibre filters. The nominal sampling period was 24 h, during which about 1 600 m^3 of air was sampled. From the filters two sets of four circular filter cuts of 47 mm diameter are taken and distributed amongst the pilot laboratory and the five other analytical laboratories.

The pilot laboratory analysed two filter cuts alternately from each sampler in order to evaluate the between sub-sample uncertainty. The other samples were analysed by all the other participating laboratories, each using its own methodology; approved in the laboratory tests.

NOTE The method described in this European Standard was validated using PM10 reference samplers with a flow rate of 68 m^3/h (as described in Annex B.2 of EN 12341:1998). Therefore all specifications (e.g. performance characteristics, overall uncertainty) are given for this type of sampler.

F.2.2 Results

F.2.2.1 Andersen between-sub-sample uncertainty

From the full results of the field trial the absolute between-sub-sample uncertainty u_{bs} were calculated from the differences of results of the sub-samples analysed by the pilot laboratory as:

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[2] "Andersen sampler" (exactly: Andersen Model 1 200 PM10 High Volume Air Sampler with a volumetric flow controller) is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

$$u_{bs}^2 = \frac{\sum_{j=1}^{m}\left(x_{j,1} - x_{j,2}\right)^2}{2m} \quad \text{(F.1)}$$

where

$x_{j,1}, x_{j,2}$ are the results of the duplicate analysis from one filter for sampling day *l*;

m is the number of sampling days of the field trial.

The Andersen sampler between sub-sample uncertainty was found to be 3,3 ng per sub-sample, resulting in an uncertainty for a 1 600 m^3 sample volume of 0,06 ng/m^3.

F.2.2.2 Comparability of parallel samplers

From the full results of the field trial the absolute between-sampler uncertainty u_{bA} were calculated from the differences of results of the subsamples analysed by the pilot laboratory as:

$$u_{bA}^2 = \frac{\sum_{j=1}^{m}\left(y_{j,1} - y_{j,2}\right)^2}{2m} \quad \text{(F.2)}$$

where

$y_{j,1}, y_{j,2}$ are the results of the parallel samplers for sampling day *l*;

m is the number of sampling days of the field trial.

Without correction for the contribution of the analysis of different filter cuts, the between-Andersen uncertainty would be 0,080 ng/m^3. When applying a correction for the random effect of the analysis of different filter cuts by subtracting the between-subsample uncertainty (see F.2.2.1), the resulting between-Andersen uncertainty is 0,056 ng/m^3.

F.2.2.1 Uncertainty assessment

F.2.2.1.1 Principles

The uncertainties were assessed for each field trial separately. For this purpose all individual results obtained were converted to concentrations, using the sample volume of the appropriate sampler. For the pilot laboratory, only one result was included.

$$c_{i,jn} = \frac{x_{i,j}}{\pi\left(\frac{4,7}{2}\right)^2 V_j} \times 500 \quad \text{(F.3)}$$

where

$x_{i,j}$ is the result of laboratory *i* for sampling day *j* in ng B*a*P per filter cut;

V_j is the sample volume for sampling day *j* for the sampler from which the laboratory sample was taken;

$c_{i,jn}$ is the concentration for laboratory *i* for day *j.*

The subsequent uncertainty assessment is based on the procedure used in EN 14902 [27]

. In summary the following steps are taken. From the concentration values for day *j* the mean concentration is calculated:

$$\bar{c}_j = \frac{\sum_i c_{I,j}}{n} \quad \text{(F.4)}$$

in which *n* is the number of laboratories.

For each laboratory the deviation $d_{i,j}$ of its result from the daily mean is calculated:

$$d_{i,j} = c_{I,j} - \bar{c}_j \quad \text{(F.5)}$$

The values of $d_{i,j}$ are used to calculate the mean deviation from the daily mean values for each laboratory over the trial period and its variance s_i^2.

$$\bar{d}_i = \frac{\sum_j d_{i,j}}{m} \quad \text{(F.6)}$$

$$s_i^2 = \frac{\sum_j \left(d_{i,j} - \bar{d}_i\right)^2}{m-1} \quad \text{(F.7)}$$

where

m is the number of sampling days for which the concentration of B*a*P is > 0,05 ng/m^3.

The value of $\bar{d}_i$ represents the mean bias of a laboratory's results from the mean results for all laboratories.

Subsequently, the random uncertainty over the field trial period is calculated for each laboratory as:

$$u_{i,r} = \sqrt{\frac{s_i^2}{m}} \quad \text{(F.8)}$$

When assuming the mean results of all laboratories to represent the 'true' B*a*P contents of the filters, the combined uncertainty for each laboratory over the trial period can be calculated as

$$u_{i,c} = \sqrt{u_{i,r}^2 + \bar{d}_i^2} \quad \text{(F.9)}$$

In order for this assumption to be true, the results of all laboratories should be traceable to accepted measurement standards.

The mean uncertainty over the field trial is then calculated as

$$\bar{u} = \frac{\sum_i u_l}{n} \quad \text{(F.10)}$$

F.2.2.1.2 Results and discussion

The results of the uncertainty assessments for each field trial are given in Table F.1.

Table F.1 — Results of the uncertainty assessments for the field trials

Field trial	Number of days with B*a*P > 0,05 ng/m^3	Mean B*a*P concentration over trial period ng/m^3	Mean random uncertainty over trial period ng/m^3	Mean combined uncertainty over trial period ng/m^3
1	18	0,12	0,013	0,025
2	20	0,27	0,017	0,045
3	20	0,41	0,041	0,17
4	20	0,92	0,047	0,15
5	21	0,14	0,010	0,085
6	14	0,08	0,005	0,015

From these results it is observed that for all trials the combined relative uncertainty for the analytical procedure varies from approximately ± 0,02 to ± 0,17 ng/m^3.

When extrapolating to the target value concentration of 1 ng/m^3 B*a*P, the relative random uncertainty for the analytical procedure is about ± 5,5 %; the relative combined uncertainty is about ± 18 %. This uncertainty includes all random effects, such as between–sub-sample, between procedure, between laboratory and between sampler contributions. In order to calculate the 'overall' uncertainty, non-random contributions of flow calibration and measurement, sampling efficiency (B*a*P degradation), sample (in)stability, and recovery efficiency need to be added.

When these are based on the performance requirements given in Clause 14, the overall combined uncertainty will be ± 18 %. Using a coverage factor of 2, the resulting expanded uncertainty at the B*a*P target value is ± 37 %.

F.2.3 Effect of ozone on sampling efficiency

F.2.3.1 Experimental setup

An additional objective of the field trials was to evaluate the effect of applying an ozone denuder when sampling the PM10 fraction of suspended particles for the purpose of the measurement of B*a*P in ambient air.

For this purpose each pilot laboratory participating in the field trials used a Partisol sampler to sample the ambient PM10 fraction during a minimum of twenty consecutive days. The Partisol sampler was equipped with 4 inlets containing quartz-fibre filters; two of these are 'plain' PM10 inlets, two others are equipped with ozone denuders. The nominal sampling period is 24 h, during which about 24 m^3 of air per inlet is sampled. The samples have been analysed by the pilot laboratory. The results of the analyses are used to assess the effect of the ozone denuder on the measured concentrations of B*a*P.

F.2.3.2 Results

The mean ratios found for each field trial of concentrations of B*a*P measured using samplers with (P+) and without (P-) an ozone denuder are given in Table F.2.

Table F.2 — Mean ratios for the B*a*P concentrations measured with and without ozone denuder

		B*a*P ng/m^3)	Ozone ppb	Mean ratio P+/P-	Uncertainty P+/P- (95 % confidence)
Trial	Period				
1	Aug-Oct04	2,72	15	1,48	0,20
2	Sep04	0,21	17	1,27	0,18
3	Dec04-Jan05	0,34	13	1,24	0,13
4	Mar-Apr05	0,35	19	1,12	0,05
5	Jan-Apr05	1,18	32	1,05	0,18

The effect of adding ozone denuders on the B*a*P concentration has been further investigated by performing regression analysis in accordance with [3]. The resulting equation

$$P+ = -0,04(\pm 0,07) + 1,28(\pm 0,03) \quad \times \quad P- \qquad \text{(F.11)}$$

suggests a significant effect of > + 20 %, although the dataset is relatively small (n = 95).

The additional random standard uncertainty contribution from the inclusion of the denuder may be estimated from the between-inlet uncertainties of the ‘plain’ Partisol samplers and Partisol samplers equipped with a denuder operated in parallel to be ± 0,046 ng/m^3.

Recent investigations have shown that the use of an ozone denuder may lead to losses of maximum 10 % of the particle mass [16].

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