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Air quality — Determination of the deposition of benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene and indeno[1,2,3-cd]pyrene

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Qualité de l'air - Détermination du benzo[a]anthracène, benzo[b]fluoranthène, benzo[j]fluoranthène, benzo[k]fluoranthène, benzo[a]pyrène, dibenz[a,h]anthracène et indeno[1,2,3-cd]pyrène dans les dépôts atmosphériques

Luftqualität - Bestimmung der Deposition von Benz[a]anthracen, Benzo[b]fluoranthen, Benzo[j]fluoranthen, Benzo[k]fluoranthen, Benzo[a]pyren, Dibenz[a,h]anthracen und Indeno[1,2,3-cd]pyren

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Foreword

This document (EN 15980:2011) 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of an identical text or by endorsement, at the latest by November 2011, and conflicting national standards shall be withdrawn at the latest by November 2011.

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Introduction

Directive 2004/107/EC [2] requires the measurement of the "total or bulk deposition" of benz[*a*]anthracene (BaA), benzo[*b*]fluoranthene (BbF), benzo[*j*]fluoranthene (BjF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenz[*a,h*]anthracene (DBahA) and indeno[1,2,3-*cd*]pyrene (INP) at background sites, one every 100 000 km². Wet-only sampling may be used instead of bulk sampling if it can be shown that the difference between their results is within 10 %. Where appropriate, monitoring shall be coordinated with the European Monitoring and Evaluation Programme (EMEP).

The Directive uses "total deposition" and "bulk deposition" as synonyms and defines it as the total mass of pollutants which is transferred from the atmosphere to surfaces (e.g. soil, vegetation, water, buildings) in a given area within a given time. The considered polycyclic aromatic hydrocarbons (PAH) are predominantly bound to particles. The mass of PAH bound to non sedimenting particles is thought to be low compared to the mass of the compounds bound to sedimenting wet and dry particles. Consequently the sum of the deposition of sedimenting wet and dry particles (defined as "bulk deposition" in this European Standard) and total deposition has been considered as substantially equivalent for the purposes of this document. At sites far enough from obstacles like buildings and trees the influence of specific surface characteristics on the deposition of PAH can be neglected.

This document describes the measurement of the deposition of PAH using collectors designed for bulk and wet-only deposition. The validation field test demonstrated that the funnel-bottle bulk collector provided the most reliable and robust results. Therefore this collector type has been chosen as standard collector.

1 Scope

This document specifies a method for the determination of the bulk deposition of benz[*a*]anthracene (BaA), benzo[*b*]fluoranthene (BbF), benzo[*j*]fluoranthene (BjF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenz[*a,h*]anthracene (DBahA) and indeno[1,2,3-*cd*]pyrene (INP), which can be used in the framework of Directive 2004/107/EC. This European Standard specifies performance requirements with which the method has to comply in order to meet the data quality objectives given in this Directive.

This document specifies methods for sampling, sample preparation and analysis using gas chromatography with mass spectroscopic detection (GC/MS) or high performance liquid chromatography with fluorescence detection (HPLC/FLD). The funnel-bottle bulk collector is used as the standard collector.

The method is applicable for deposition measurements in

— rural and remote areas,

— industrial areas,

— urban areas.

The standard is applicable in the range from a few ng/($m^2 \cdot d$) to a few hundred ng/($m^2 \cdot d$).

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 15549:2008, *Air quality — Standard method for the measurement of the concentration of benzo[a]pyrene in ambient air*

3 Terms and definitions

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

3.1
analysis
all operations carried out after sample preparation to determine the amount or concentration of the polycyclic aromatic hydrocarbons of interest present in the sample

3.2
bulk collector
equipment to collect bulk deposition, permanently open to the atmosphere

NOTE In this document, two types of bulk collectors are described: a funnel-bottle bulk collector and a cylindrical gauge (Bergerhoff collector).

3.3
bulk deposition
sum of the deposition of sedimenting wet and dry particles

NOTE Bulk deposition does not contain gases and non-sedimenting particles. The bulk deposition of the polycyclic aromatic hydrocarbons is considered as substantially equivalent to total deposition.

3.4
detection limit
lowest deposition rate of an analyte detectable using the specified procedure

3.5
expanded uncertainty
quantity defining an interval about the result of a measurement that can be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand

[ISO/IEC Guide 98-3:2008 [9]]

3.6
field blank
artificial sample (e.g. distilled water) transported to the sampling site, mounted in the sampling unit, but not left exposed to ambient air, returned to the laboratory and worked up in the same way as the deposition sample

3.7
laboratory blank
artificial sample (e.g. distilled water) worked up in the same way as the deposition sample in the laboratory

3.8
precipitation
rain, snow, sleet, graupel, hail and dew

3.9
sample extraction
sample dissolution process to obtain a solution containing the analyte of interest in an organic solvent

3.10
sample preparation
all operations carried out on a sample, after transportation and storage, to prepare it for analysis

NOTE Such operations are, e.g. extraction, purification, evaporation, solvent exchange.

3.11
standard uncertainty
uncertainty of the results of measurements expressed as a standard deviation

[ISO/IEC Guide 98-3:2008 [9]]

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

[ISO/IEC Guide 98-3:2008 [9]]

3.13
wet-only collector
equipment to collect wet deposition, consisting of a funnel-bottle combination, open to the atmosphere only during precipitation events

4 Symbols and abbreviations

4.1 Symbols

A area of the cross-section of the collector opening;

$\overline{c}$ mean value of the concentration of a compound in a solution;

$\overline{c}_i$ mean value of the concentration of a compound, obtained by laboratory i;

c_j concentration of a compound in the solution j;

$d_{(1,j)}$ deposition in collector 1;

$d_{(2,j)}$ deposition in collector 2;

D_{a} deposition rate of compound a;

$D_{\mathrm{L,a}}$ detection limit of compound a;

$D_{\mathrm{M,a}}$ minimal detectable mass of compound a;

k coverage factor;

m_{a} mass of compound a;

$m_{\mathrm{a,d}}$ detected mass of compound a;

$\overline{m}_{\mathrm{a}}$ mean of laboratory blank value;

$m_{\mathrm{a},i}$ individual laboratory blank value for compound a;

n number of measurements;

rss residual sum of squares from the fit;

s_i within-laboratory standard deviation;

s_{L} between-laboratory standard deviation;

s_{d} between-collector standard deviation;

s_{R} reproducibility standard deviation;

s_{ri} standard deviation of repeated measurements of laboratory i;

S_{m} mass of surrogate standard, added to the sample;

S_{d} mass of surrogate standard detected in the sample extract;

$S_{\mathrm{lb,a}}$ standard deviation of laboratory blank value for compound a;

t sampling duration;

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

$u_{bc,j}$ between-collector uncertainty for collector type j;

u_D uncertainty of measured depositions;

u_M standard uncertainty of the deposition measurement;

$U_p(y)$ expanded uncertainty of the measured value y with a coverage probability p;

$w_{bc,j}$ relative between-collector uncertainty for collector type j;

w_{fit} random relative uncertainty of the fits.

4.2 Abbreviations

BaA Benz[*a*]anthracene

BaP Benzo[*a*]pyrene

BeP Benzo[*e*]pyrene

BbF Benzo[*b*]fluoranthene

BjF Benzo[*j*]fluoranthene

BkF Benzo[*k*]fluoranthene

CHR Chrysene

CRM Certified reference material

CPP Cyclopenta[*cd*]pyrene

DAD Diode array detection

DBacA Dibenz[*a,c*]anthracene

DBahA Dibenz[*a,h*]anthracene

DBajA Dibenz[*a,j*]anthracene

DCM Dichloromethane

EMEP Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air pollutants in Europe (European Monitoring and Evaluation Programme)

FLD Fluorescence detection

GC Gas chromatography

HPLC High performance liquid chromatography

INP Indeno[1,2,3-*cd*]pyrene

MS Mass spectrometry

PAH Polycyclic aromatic hydrocarbons

PTFE	Polytetrafluoroethylene
QA/QC	Quality Assurance/Quality Control
SOP	Standard operating procedure
SPE	Solid phase extraction
TRI	Triphenylene
WMO/GAW	World Meteorological Organization / Global Atmosphere Watch

5 Principle

Deposition samples for the determination of specified PAH compounds are taken in funnel-bottle bulk collectors for a measured period of time (see Clause 7). Samples are prepared using liquid-liquid or solid phase extraction with organic solvent (see 8.2). Identification and quantification of the substances are performed by either GC/MS or HPLC/FLD (see 8.3).

6 Apparatus, reagents and materials

6.1 Reagents

High purity reagents:

— solvents: e.g. acetone, acetonitrile, cyclohexane, dichloromethane (DCM), methanol, toluene, water;

— solid substances: NaCl, anhydrous Na_2SO_4.

6.2 Materials

— Ordinary laboratory materials;

— wiping material, e.g. glass wool, quartz wool or pre-extracted cotton wool.

6.3 Sampling equipment

Funnel-bottle bulk collectors consist of a cylindrical funnel and a sample collection vessel (see A.2). The vertical section of the funnel shall be at least as high as its diameter. The collection vessels shall have a cylindrical vertical section of sufficient height to avoid sampling losses resulting from splashing. The collector is permanently open to the atmosphere. The collector shall be equipped with a device for keeping birds off.

The area of the cross-section of the funnel opening and the size of the sample collection vessel shall be adjusted to the precipitation amount which is expected in the chosen sampling period in order to avoid overflow. Typical sampling periods vary between one week and one month. The area of the cross-section of the funnel opening shall be large enough to provide sufficient sample for analysis at a minimum precipitation height of 1 mm per week.

NOTE 1 The funnel diameter should be at least 15 cm.

The funnel opening shall be at least 1,5 m above ground. For areas that receive high snowfall accumulations, the collector may be raised onto a platform above the snow.

NOTE 2 An extra large and deep cylindrical collector may be used for snow sampling (see [1]).

Funnel and sample collection vessel shall be made of glass. If connectors, which come into contact with sampled material, are not made of glass, only PTFE or other fluoroelastomers are permissible. All parts shall be able to be easily cleaned.

6.4 Laboratory equipment

6.4.1 General

Ordinary laboratory apparatus and the items given in 6.4.2 and 6.4.3 are required.

6.4.2 Apparatus for sample extraction

Liquid-liquid or solid phase extraction apparatus (see B.2.2.2 and B.2.2.3).

6.4.3 Apparatus for sample analysis

6.4.3.1 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 an FLD. Furthermore a system for solvent degassing (internal or external) is required.

NOTE If the amounts of PAH are high, also the HPLC/DAD technique can be used.

6.4.3.2 GC/MS apparatus

Gas chromatograph with split/splitless injector or on-column injector, a capillary column suitable for PAH analysis, and a mass selective detector.

7 Sampling

7.1 General

The validation field test was carried out using funnel-bottle bulk collectors, cylindrical gauges and wet-only collectors (see Annex A). The results showed that the deposition rates of PAH measured with the funnel-bottle bulk collector were in most cases higher than those measured with the cylindrical gauges or the wet-only collector. The between-collector uncertainty in general was the lowest for the funnel-bottle bulk collector (see D.4.2). Therefore the funnel-bottle bulk collector shall be used as the standard collector for the determination of the deposition of BaA, BbF, BjF, BkF, BaP, DBahA and INP.

NOTE When the deposition rates were high and the climatic conditions moderate the results of cylindrical gauges were similar to those obtained with the funnel-bottle bulk collectors. When the precipitation was high and the climatic conditions were cold the results of wet-only and funnel bottle bulk collectors were similar. Therefore in special cases, if equivalence with the funnel-bottle bulk collector can be shown different types of collectors like wet-only collectors and cylindrical gauges can be used to measure the deposition of PAH.

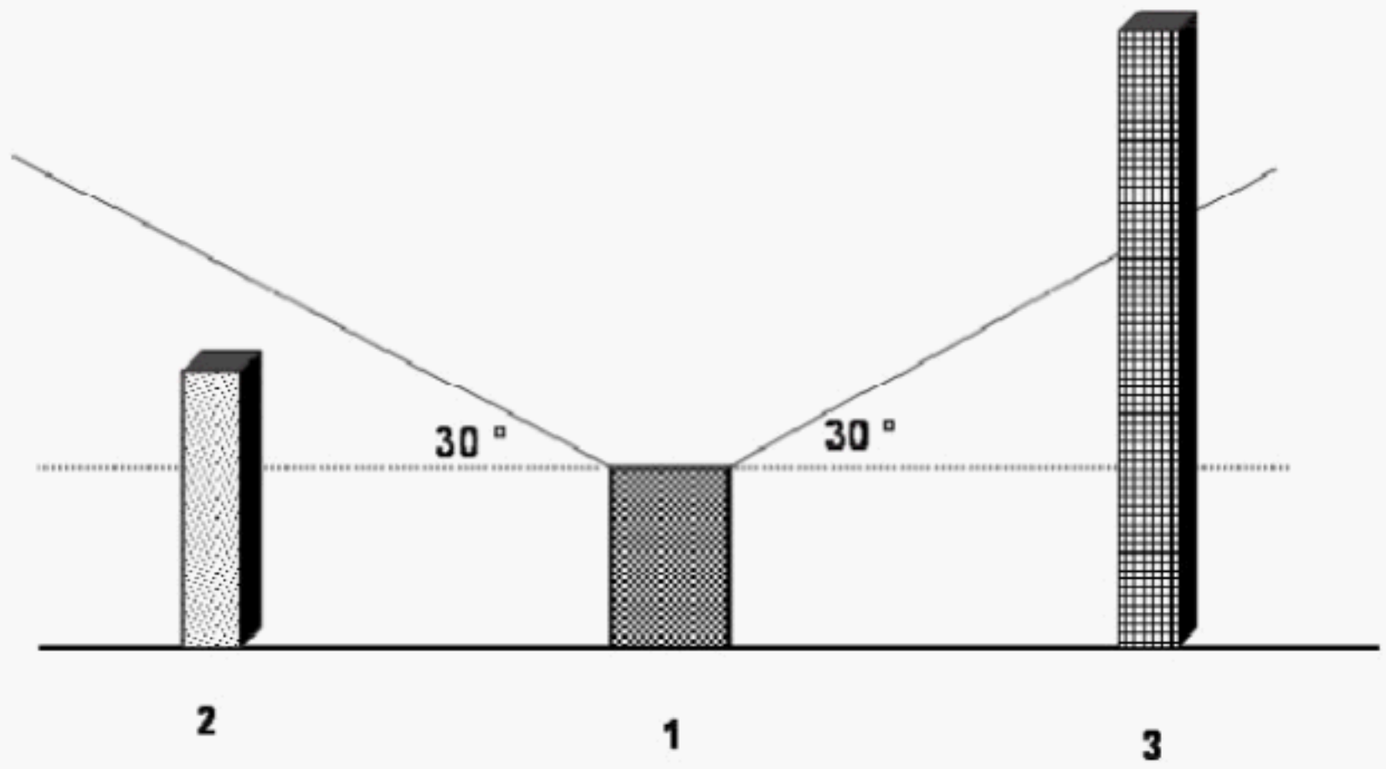
7.2 Sampling location

Macroscale and microscale siting shall follow the guidelines of Directive 2004/107/EC [2], which are harmonized with the guidelines from EMEP [1] and WMO/GAW [3] for deposition measurements in rural areas.

The collector shall as far as possible not be exposed in areas where strong winds occur like shores, cliffs and top of hills, but it shall also not be sheltered by tall trees or buildings. The flow around the collector should be unrestricted, without any obstructions affecting the airflow in the vicinity of the collector. The criteria depend on the site characteristic:

— rural site: as far as practicable no obstacles such as trees, buildings, hedges or topographical features above 30° (see Figure 1) from the rim of the collector, which may give rise to updraughts or downdraughts;

— urban and industrial site: as far as possible away from buildings, trees and other obstacles.



Key
1 collector
2 obstacle, acceptable
3 obstacle, too high

Figure 1 — Position of obstacles which affect sampling

7.3 Sampling requirements

Handle sampling equipment such that contamination is avoided. Avoid contact of skin with the glassware of the exposed side of the collector, e.g., by wearing cotton gloves during mounting and dismounting of the collector. The procedures used in the field test are described in B.3 and B.4.

NOTE 1 In order to avoid breaking of glassware due to freezing 100 ml of a saturated NaCl solution may be added before sampling, if low temperatures are expected.

If materials like leaves or insects clog the pipe of the funnel, remove them carefully with tweezers and rinse them with water. The rinsing water is added to the collected rain water. Also rinse the funnel carefully.

Cleaning of the funnel can be done either at the sampling site or in the laboratory depending on local conditions. Parts of the collector which are transported to the laboratory shall be carefully wrapped, e.g. with aluminium foil.

NOTE 2 The sampled water amount can be determined by weighing the collector before and after exposure. The precipitation rate can be calculated from the water amount, the cross-section of the funnel opening and the exposure time. These data can be compared with meteorological data to check the plausibility of the results.

Store equipment in the field so that contamination is prevented, e.g. wrapped in aluminium foil, and kept it in an as clean and dust-free place as possible.

Clean the funnel between exposures with wiping material moistened with acetone or methanol, followed by rinsing with water. Send the funnel to the laboratory for thorough cleaning, if necessary.

The sampling duration shall not exceed 1 month.

SOPs are given in Annex B.

7.4 Sample transport

The sample consisting of deposited liquid and solid material and the solution of funnel rinsing shall be transported in suitable containers to the laboratory directly after the end of sampling. The samples shall be kept as cool as practically possible while avoiding exposure to sunlight and contaminants.

NOTE 1 It is recommended to keep the temperature below 30 °C.

NOTE 2 Possible sources of contamination are e.g. vehicle exhausts and tobacco smoke.

8 Sample preparation and analysis

8.1 Sample storage

Store the samples cool and dark before processing. Sample preparation shall be carried out within 1 month after end of sampling.

NOTE A degradation test as part of the method validation procedure demonstrated that the composition of a synthetic sample, CRM (urban dust) suspended in rain water, did not change during exposure in the field within a period of 1 month.

8.2 Extraction

Both liquid-liquid extraction in combination with filtration and solid phase extraction (SPE) have been shown to be effective for the quantitative extraction of PAH in the laboratory test. These methods are specified in Annex B.

8.3 Analysis

The analysis procedure is specified in Annex C. For BaP it is consistent with EN 15549.

8.4 Interferences

Unusual results, peak forms or retention times of PAH may suggest that chromatographic interferences are present. Attention shall be given to interferences concerning BaA, BbF+BjF+BkF and DBahA in GC/MS and BjF in HPLC/FLD (see C.3).

9 Quality assurance

The low ambient concentration of PAH can cause erroneous results unless strict precautions are taken to prevent contamination and other sources of errors. The laboratories collecting PAH data shall therefore have a QC procedure according to the relevant items of EN 15549:2008, Clause 13, which is designed for their sampling and analytical procedures.

Laboratory equipment used for storage of samples shall be properly cleaned before use.

Laboratory and field blanks shall be taken regularly to check for potential contamination.

The check of the purity of reagents is part of the normal laboratory QA/QC programme. The laboratory blanks are used to identify potential contamination sources in the laboratory. The laboratory blanks shall be used to calculate the detection limit (see D.2). If the laboratory blank contributes significantly to the amount of deposition samples for the same period, necessary steps shall be taken to identify the contamination sources and correct the procedure accordingly. Laboratory blanks shall be analysed at least once in every set of extracted samples.

Field blanks shall be taken regularly, twice per year per site. In case of a laboratory being responsible for samples from more than one site the number of field blanks may be reduced. In any case, the minimum number of field blanks shall be 10 % of the number of the deposition samples. Results that are judged to be suspect based on the level of the field blanks shall be flagged. When reporting the results the reason for flagging shall be indicated.

NOTE The interpretation of the results of the field blanks is a matter of expert judgement. As a rule of thumb, a blank value of twice the detection limit of a component or greater is an indication of contamination. If this blank value is ≥ 10 % of the level of a sample, the sample result should be flagged.

If laboratories carry out routine analyses of PAH deposition samples it is recommended that they participate in a relevant external quality assessment scheme or proficiency testing scheme like laboratory and field intercomparisons.

10 Calculation of results

The amount of PAH in depositions shall be given in ng, the deposition rate in ng/(m^2·d). The deposition in the collectors shall be calculated according to Equation (1).

$$D_{\mathrm{a}} = \frac{m_{\mathrm{a}}}{A \times t} \tag{1}$$

where

D_{a} is the deposition rate of compound a in ng/(m^2·d);

m_{a} is the mass of compound a in ng;

A is the area of the cross-section of the collector opening in m²;

t is the sampling duration in d.

The masses of the compounds shall be corrected by the recovery of the surrogate standard (see B.4.1) according to Equation (2).

$$m_{\mathrm{a}} = m_{\mathrm{a,d}} \times \frac{S_{\mathrm{m}}}{S_{\mathrm{d}}} \tag{2}$$

where

$m_{\mathrm{a,d}}$ is the detected mass of compound a in ng/(m^2·d);

S_{m} is the mass of surrogate standard added to the sample, in ng;

S_{d} is the mass of surrogate standard detected in the sample extract, in ng.

11 Performance characteristics

The performance characteristics of the method were determined from the data of the laboratory and field validation tests. The results are given in Annex D.

12 Uncertainty

Sampling and between-laboratory differences provide the main contributions to the uncertainty of the measurement of PAH depositions (see Annex D). The uncertainty of sampling and analysis shall be assessed by the laboratory for all compounds to be measured. The laboratory shall perform tests to ensure that

— the requirements for the analytical uncertainty as defined in EN 15549 are met;

— the recovery of the surrogate standard added to the collected sample before extraction is ≥ 50 % with a relative uncertainty ≤ 5 %;

— the between-collector uncertainty, determined by duplicate sampling (minimum 10 duplicate measurements) is ≤ 20 % of the mean value of the deposition rate.

If these requirements are met, the combined uncertainty of these contributions is ≤ 25 % of the measured deposition rates. The expanded uncertainty, using a coverage factor of 2, is then ≤ 50 %. As Directive 2004/107/EC [2] requires an uncertainty of 70 % for fixed deposition measurements, a buffer of 20 % is left for the between-laboratory uncertainty, which cannot be determined by an individual laboratory.

13 Reporting of results

The report shall include the following information:

a) reference to this European Standard;

b) identification of the sampling location;

c) description of the collector type used;

d) sampling duration and period (start and end dates);

e) results of the determination expressed as $ng/(m^2 \cdot d)$;

f) expanded uncertainty and how this was calculated;

g) any unusual features noted during the determination;

h) detection limit;

i) short description of analysis procedure including analytical technique.

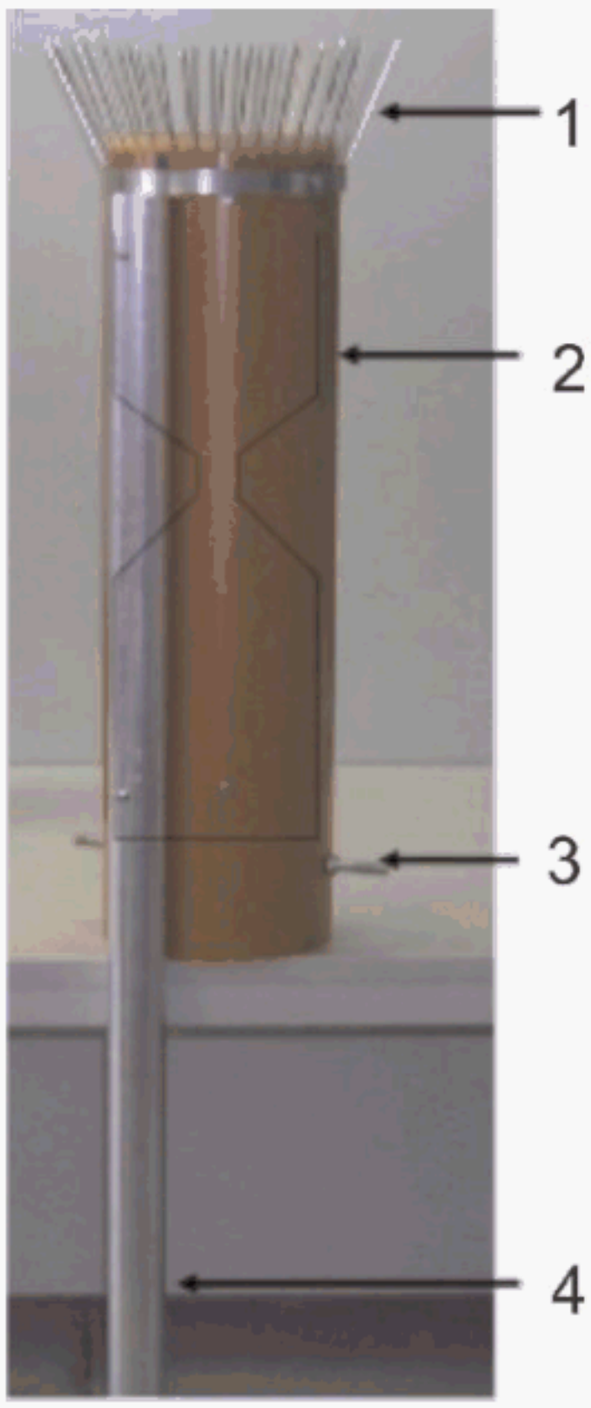
Annex A
(informative)

Collectors used in the field trial

A.1 General

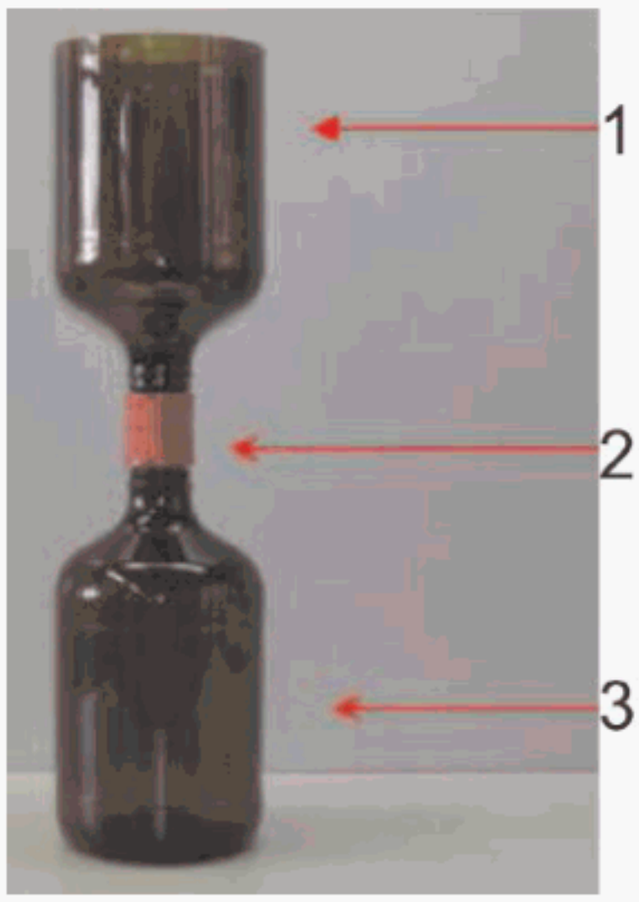
The 3 different types of collectors which were used in the field trial are illustrated in Figures A.1 to A.5. Figures A.1, A.2, A.3 and A.4 illustrate the funnel-bottle bulk collector, Figure A.5 illustrates the cylindrical gauge (Bergerhoff collector) and Figure A.6 illustrates the wet-only collector.

A.2 Funnel-bottle bulk collector



Key
1 protective basket
2 tube, 190 mm diameter
3 stopper to fix funnel and bottle
4 post

Figure A.1 — Housing and protective basket

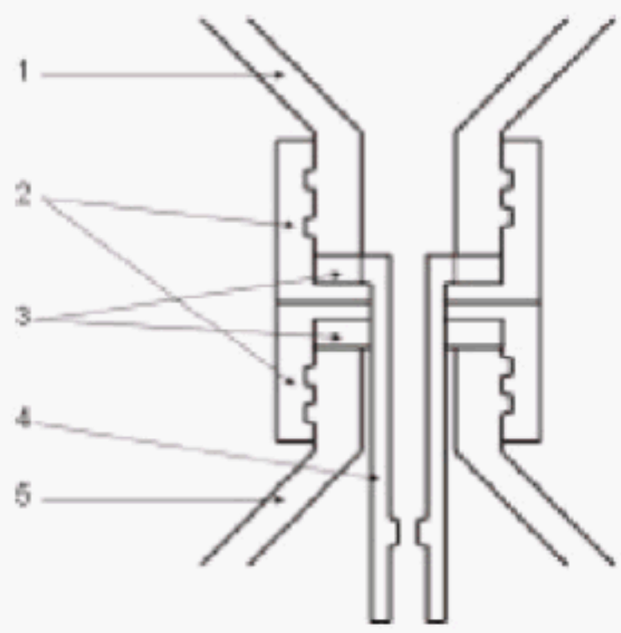


Key
1 funnel (brown glass)
2 connector
3 bottle (brown glass)

Dimensions:

Diameter of funnel and bottle:	165 mm
Height of the vertical section of the funnel:	200 mm
Height of the complete collector:	700 mm

Figure A.2 — Funnel and bottle



Key
1 funnel with thread GL 45
2 screw caps with thread GL 45
3 ferrules, coated with PTFE
4 glass liner
5 bottle with thread GL 45

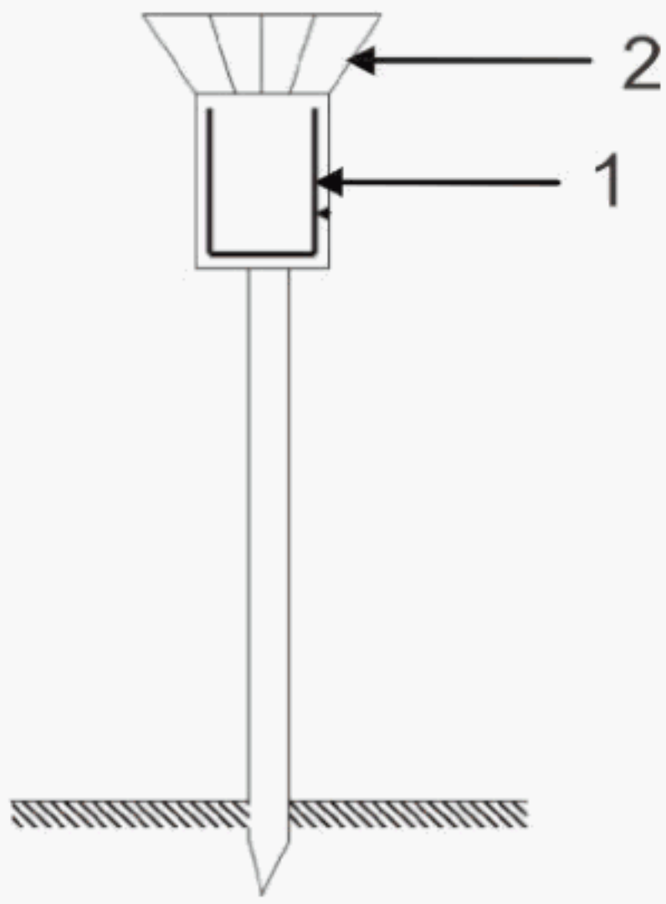
Dimensions:
Glass liner

Inner diameter:	22 mm
Diameter of capillary section:	3 mm
Length:	125 mm
Inner diameter of bottleneck:	28 mm

Figure A.3 — Detailed illustration of the connector

Figure A.4 — Glass liner (left) and glass liner within the screw caps (right)

A.3 Cylindrical gauge (Bergerhoff collector)



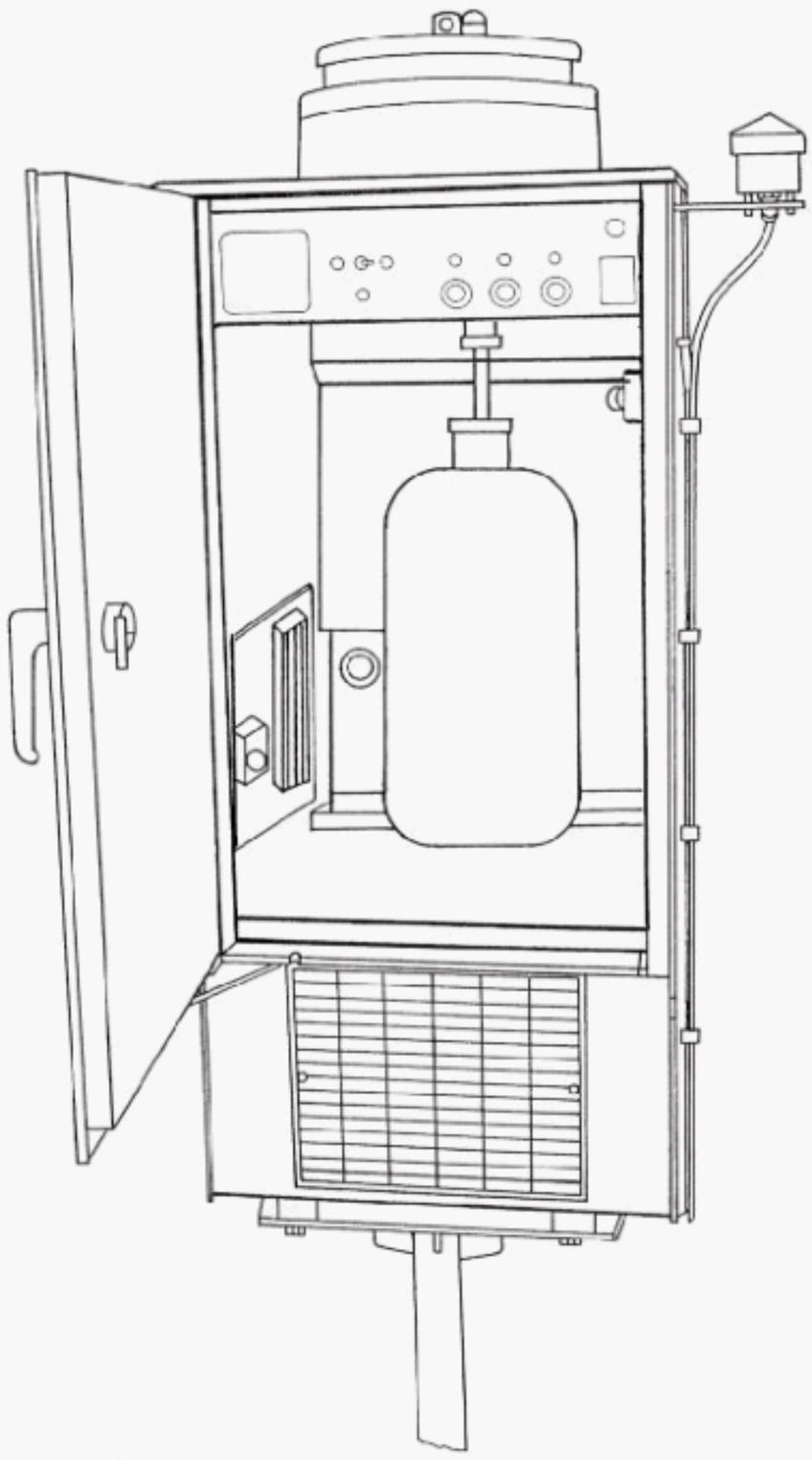
Key
1 deposition gauge
2 protective basket

Dimensions:

Total height:	ca. 150 cm
Diameter of deposition gauge:	110 mm
Height of deposition gauge:	190 mm
Diameter of protective basket:	350 mm

Figure A.5 — Cylindrical gauge (Bergerhoff collector)

A.4 Wet-only collector



Dimensions:

Total height:	ca. 150 cm
Diameter of the funnel:	252 mm
Height of the vertical section of the funnel:	250 mm

Figure A.6 — Wet-only collector

Annex B
(normative)

Work-up of deposition samples for PAH analysis

B.1 Schematic representation

Figure B.1 shows the schematic representation of the sample work-up procedure.

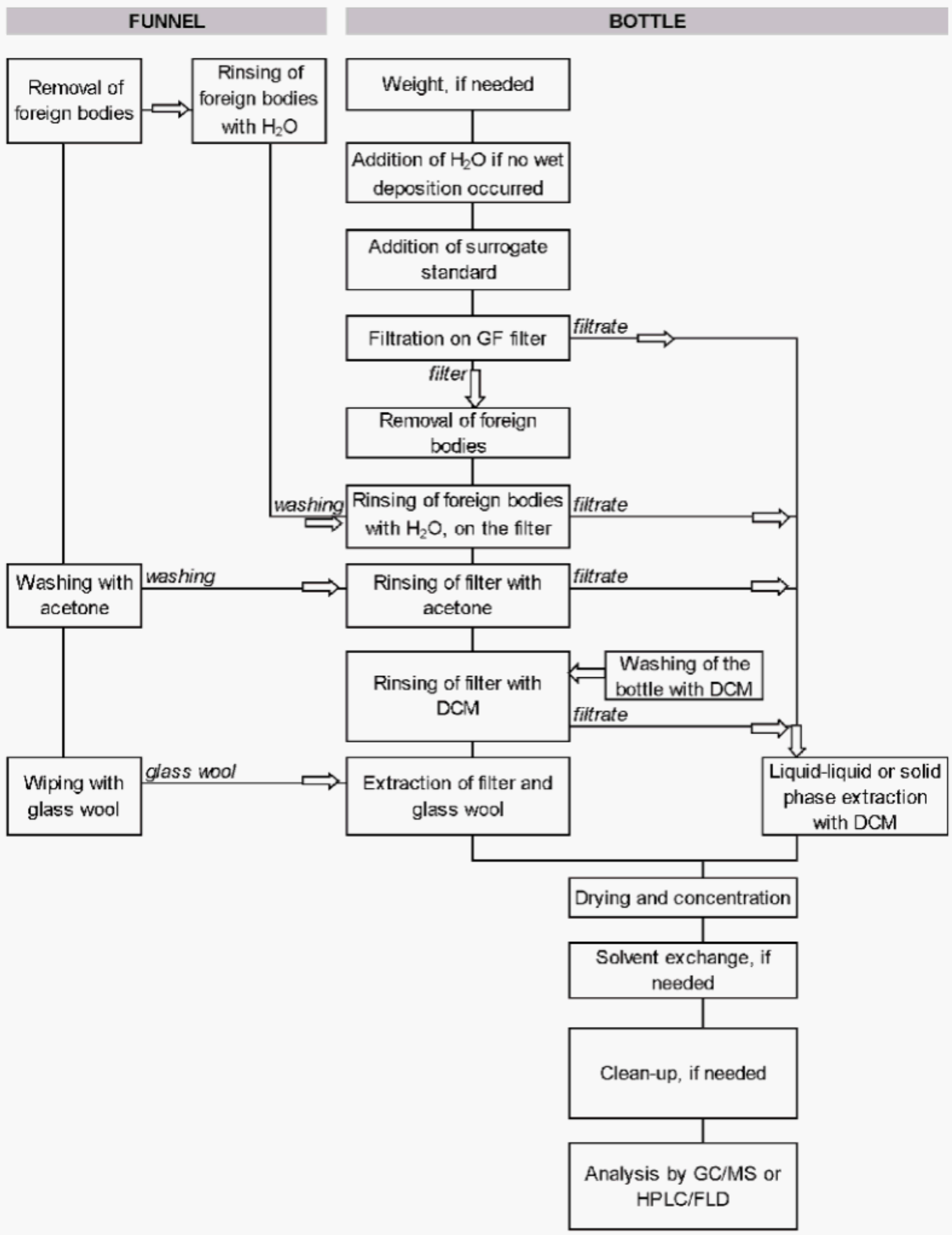


Figure B.1 — Flow-chart of sample processing (adapted from [4])

B.2 Materials and reagents

B.2.1 For use in the field

B.2.1.1 Funnel-bottle and wet-only collector

— Acetone, high purity, ca. 1 l

— Water, high purity, ca. 1 l

— Wiping material (glass wool, quartz wool or pre-extracted cotton wool)

— Paper towels

— Gloves

— Tweezers

— Aluminium foil (for wrapping the funnels and bottles)

B.2.1.2 Funnel-bottle bulk collector

— 1 bottle (volume e.g. 4 l) with screw cap

— 1 bottle (volume e.g. 500 ml) with screw cap, thread fitting to the funnel, for the funnel rinsing solutions

B.2.1.3 Wet-only collector

— 1 bottle (volume e.g. 10 l) with screw cap

— 1 bottle (volume e.g. 500 ml) with screw cap, thread fitting to the funnel, for the funnel rinsing solutions

B.2.1.4 Bergerhoff collector

— 4 Bergerhoff collectors with lids made of glass

NOTE 4 collectors are recommended for one monthly sample in order to obtain sufficient sample amount.

B.2.2 For use in the laboratory

B.2.2.1 General

— High purity solvents, e.g. toluene, cyclohexane, DCM, acetonitrile, *n*-hexane and water

— Anhydrous sodium sulphate, high purity

— Sodium chloride, high purity

— Ultrasonic bath

— Internal standard, e.g. 6-methylchrysene or perylene-d12 (approximately 100 µg/ml in the appropriate solvent)

— Vials, volume e.g. 2 ml

B.2.2.2 Materials for liquid–liquid extraction

— Funnels for filtration, diameter e.g. 200 mm

— Glass fibre filters

— Separation funnels, volume e.g. 2 l

— Beakers, volume e.g. 500 ml

— Round bottom flasks, volume e.g. 100 ml

B.2.2.3 Materials for SPE

— Extraction station containing: extraction disk holder, reservoir for extraction medium, collection chambers, flask adapter

— Reversed phase or hydrophilic extraction disk

— 1 l flasks

B.3 Work to be done in the field

B.3.1 Bulk collectors

Handle the collector according to the manufacturer's instructions, if commercially purchased. The following example is given for the funnel-bottle bulk collector described in A.2.

— Remove one screw from the stopper.

— Hold the complete glassware deposition sampling equipment and lift it a few millimetres.

— Pull out the stopper.

— Remove the glassware downwards carefully.

— Use tweezers to remove coarse impurities (e.g. insects, leaves) from the funnel and rinse them carefully with high purity water, collect the rinsing water into a bottle, close and store the bottle, discard the impurities.

— Disconnect the screw cap from the collector.

— Close the collector.

— Connect the funnel to a clean 500 ml bottle.

— Clean the funnel with approximately 150 ml of e.g. acetone and wiping material (use gloves) and collect the solvent in the 500 ml bottle.

— Store the wiping material in the bottle, disconnect the bottle and close it tightly.

— Connect the funnel with an empty 4 l collecting bottle.

— Put the bottle and the funnel into the tube.

— Transport the filled bottles to the laboratory.

NOTE 1 In order to avoid breaking of glassware due to freezing 100 ml of a saturated NaCl solution may be added before sampling, if low temperatures are expected.

NOTE 2 When using a bulk collector for snow sampling, the funnel can be filled before the end of the sampling period. The station operator should therefore take the collector (both funnel and bottle) indoor whenever it is full, and cover the opening of the funnel, e.g. with aluminium foil. The covering shall have been cleaned before use and it should be kept on during the entire melting process. While this sample is melting another collector and funnel can be installed. Samples of one period can be combined.

NOTE 3 If the collected water is weighed in order to measure the precipitation amount, a separate bottle is used to collect the water from impurities rinsing.

B.3.2 Wet-only collectors

— Use tweezers to remove coarse impurities (e.g. insects, leaves) from the funnel and rinse them carefully with high purity water, collect the rinsing water into a bottle, close and store the bottle, discard the impurities.

— Disconnect the funnel and the collecting bottle (volume: 10 l), close the bottle tightly.

— Place the 500 ml bottle under the funnel.

— Clean the funnel with approximately 150 ml of e.g. acetone and wiping material (use gloves) and collect the solvent in the 500 ml bottle.

— Put the wiping material in the bottle, disconnect the bottle and close it tightly.

— Connect the funnel with an empty 10 l bottle.

— Wipe the funnel with high purity water and paper towels.

NOTE If the collected water is weighed in order to measure the precipitation amount, a separate bottle is used to collect the water from impurities rinsing.

B.3.3 Bergerhoff collectors

— Dismount the deposited Bergerhoff collectors (4 collectors), close them with the lids.

— Mount 4 empty, open collectors.

NOTE In order to avoid breaking of glassware due to freezing 100 ml of a saturated NaCl solution may be added before sampling, if low temperatures are expected.

B.4 Work to be done in the laboratory

B.4.1 Wet-only and funnel-bottle bulk collectors: treatment of collected water using liquid-liquid extraction

— Add e.g. 1 µg of surrogate standard (see EN 15549; e.g. 6-methylchrysene (for HPLC) or perylene-d12 (for GC/MS) in 1 ml of appropriate solvent) to the sample.

— Filter the collected water through a glass fibre filter into a separation funnel (volume: e.g. 2 l; caution: If the volume of the collected water is too high, divide into separate fractions!).

— In case of coarse impurities (which may occur in the bottle of the wet-only collector) remove them by using tweezers, rinse the impurities carefully on the filter with high purity water, pour the rinsing water into the separation funnel.

— Rinse the bottle of the collector, and, in case of wet-only collector, the lid, e.g., first with 20 ml of acetone, then twice with 20 ml of toluene or DCM. Filter the solutions of bottle and funnel rinsing through the glass fibre filter into the separation funnel.

— Extract the filter together with the wiping material used to wipe the funnel as described in EN 15549, e.g. three times with 25 ml of toluene or DCM in an ultrasonic bath for 15 min. Squeeze the filter (e.g. with a glass rod) after the last extraction, use glass wool, quartz wool or pre-extracted cotton wool to filter solids, if necessary. Pour the extracts into the separation funnel and add 100 ml of toluene or DCM.

— Close the separation funnel, cover it with aluminium foil and shake it for at least 8 h.

— Separate the phases, collect the organic layer e.g. in a 500 ml Erlenmeyer flask.

— Extract the water layer two more times with 50 ml of toluene or DCM by shaking it for at least 2 h.

— Combine the three organic layers. Dry with anhydrous sodium sulphate, filter, rinse Erlenmeyer flask and solid material 3 times with 10 ml of toluene or DCM, evaporate to a low volume or to dryness (use round bottom flasks). Transfer the content quantitatively into a vial. Work up the extracts for GC/MS or HPLC/FLD analysis as described in EN 15549.

NOTE 1 If sampling is on a weekly basis, 4 weekly extracts are combined to one sample. In this case only 0,25 µg of surrogate standard is added to each weakly sample. The 4 weeks sample contains 1 µg of surrogate standard, if extraction is complete.

NOTE 2 High amounts of acetone (or other water soluble organic solvents like methanol) can inhibit the separation of water and the organic phase.

B.4.2 Wet-only and funnel-bottle bulk collectors: treatment of collected water using SPE

B.4.2.1 Sample preparation

— Add 75 g of sodium chloride to one litre of collected water.

— Add 1 µg of the surrogate standard to the sample.

— Shake the water sample until the salt is in solution.

B.4.2.2 Extraction procedure

B.4.2.2.1 Conditioning of the extraction disk

— Connect the extraction disk to the extraction station.

— Pour 20 ml of DCM on the extraction disk and elute the DCM through the disk until all DCM is passed.

— Repeat the above mentioned procedure with e.g. 10 ml of acetone and 20 ml of high purity water.

B.4.2.2.2 Extraction of the sample

— Extract the whole sample over the extraction disk (for approximately 1 l the extraction time shall be 45 min to 60 min).

NOTE The maximum sample volume is 5 l.

B.4.2.2.3 Desorption of the extraction disk

— Pour 15 ml DCM on to the extraction disk and let the DCM interact (moisten) with the extraction disk for one minute.

— Then adjust the vacuum to approximately 900 hPa resulting in dropwise elution of all DCM through the disk (about 1 min).

— Repeat the above mentioned procedure 4 times with 5 ml of *n*-hexane.

— Collect the fractions in an Erlenmeyer flask.

B.4.2.2.4 Rinsing of sample bottle and work-up of the rinsing solution

— Rinse the sample bottle two times with 15 ml of *n*-hexane. Add the hexane layers to the Erlenmeyer flask.

— Dry the rinsing solution with sodium sulphate and transfer the dried extract to a round bottom flask.

— Evaporate the rinsing solution until 2 ml to 3 ml and transfer the extract quantitatively to a test tube.

— Work up the rinsing solution for GC/MS or HPLC/FLD analysis as described in EN 15549.

NOTE If sampling is on a weekly basis, 4 weekly extracts are combined to one sample. In this case only 0,25 µg of surrogate standard is added to each weekly sample. The 4 weeks sample contains 1 µg of surrogate standard, if extraction is complete.

B.4.3 Wet-only and funnel-bottle bulk collectors, treatment of funnel rinsing solution and wiping material

— Add e.g. 1 µg of surrogate standard to the collection bottle, if separate analysis of funnel and bottle is required. Place the opened bottle with the rinsing solution and the glass wool into an ultrasonic bath for 15 min, decant, refill the bottle with 100 ml of toluene or DCM, extract again in the ultrasonic bath for 15 min, repeat the procedure once.

— Dry the combined solutions with anhydrous sodium sulphate, filter, rinse the bottle and rinse the filter three times with toluene or DCM, evaporate (using a round bottom flask) in order to obtain a concentrated solution of 2 ml to 3 ml, finally fill this concentrated solution into a vial and complete the evaporation to dryness.

— If sampling is on a weekly basis combine 4 weekly extracts to one sample. Combine the extracts with those of the water samples, if separate analysis is not required.

NOTE If separate analysis of funnel and bottle is required, e.g. 1 µg of surrogate standard is added to the bottle with the rinsing solutions before the extraction.

B.4.4 Bergerhoff collectors: treatment of collected deposition using liquid–liquid extraction or SPE

— Add e.g. 0,25 µg of surrogate standard (e.g. 6-methylchrysene (for HPLC) or perylene-d12 (for GC/MS) in 1 ml of appropriate solvent) to each collector.

— Filter the water of all the four collectors as described for the funnel-bottle and wet-only collectors. Use one filter and one separation funnel for the 4 collectors.

— Rinse the collectors as described for the bottles of the funnel-bottle and wet-only collectors, use only ca. 5 ml of solvent per collector. Filter the rinsing solutions with the same filter as it was used for the rain water.

— For further work up, follow the procedure described for the wet-only and funnel-bottle bulk collectors.

B.4.5 Work-up in case of no wet deposition

— Add e.g. 1 µg of surrogate standard (e.g. 6-methylchrysene (for HPLC) or perylene-d12 (for GC/MS) in 1 ml of appropriate solvent) to the bottles or 0,25 µg of surrogate standard to each of the Bergerhoff collectors. Add 200 ml of water (50 ml to each of the Bergerhoff collectors) and treat the sample as usual.

Annex C
(normative)

Analytical conditions

C.1 HPLC/FLD method

— HPLC-column: e.g. RP-C18 250 mm; 4,6 mm

— Injector: e.g. 20 µl

— Oven temperature: e.g. 30 °C ± 1 °C

— Mobile phase: mixture of acetonitrile and water

— Flow rate: e.g. 1,5 ml/min

Table C.1 gives a list of PAH compounds and suitable wavelength pairs for excitation and emission.

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

Compounds	Excitation wavelength in nm	Emission wavelength in nm
BaA, 6-methylchrysene, CHR	275	390
BaP, BeP (suitable also for BbF and BkF)	260	415
DBahA	297	405
INP	250	500
BjF	382	517

NOTE The DAD wavelength is 290 nm or 385 nm.

C.2 GC/MS method

C.2.1 Parameters for GC operation

— GC-column: e.g. 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: e.g. 100 °C for 2 min
- rate: e.g. 5 °C/min to 300 °C, then hold for 25 min

- rate: e.g. 20 °C/min to 320°C then hold for 5 min

— Flow: constant flow, e.g. 1,2 ml/min

— Injection mode: splitless or on-column

C.2.2 Parameters for MS operation

C.2.2.1 Quadrupole MS

— Mode: Selected Ion Monitoring (SIM), see Table C.2

— Transfer line temperature: e.g. 300 °C

— Ion source temperature: approximately 180 °C

— Ion source energy 70 eV

C.2.2.2 Ion trap

— Ion source temperature: e.g. 250 °C

— Transfer line temperature: e.g. 250 °C

— Mode: SIM, see Table C.2

— Ion source energy: 70 eV

— Trap offset: 10

— Emission current: 250 µA

— Selected Ions: see Table C.2

C.2.2.3 List of ions for selection

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

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

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

C.3 Interferences

C.3.1 HPLC/FLD method

BjF is not or at least not completely separated from benzo[*e*]pyrene using reversed phase columns and acetonitrile/water eluents. For its determination, suitable excitation and emission wavelengths are 382 nm and 517 nm respectively: using these conditions co-elution of BjF and benzo[*e*]pyrene does not have an effect on the analytical results. At the wavelength pairs used for the determination of the benzopyrenes and the other benzofluoranthenes (see Table C.1) the fluorescence of BjF is very low.

C.3.2 GC/MS method

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

BaA

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

— If necessary, BaA may be resolved from CPP using a column with a phase equivalent to 50 % phenyl, polysiloxane, such as DB-17ms or BPX50.

BbF+BjF+BkF

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

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

DBahA and INP

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

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

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

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

Annex D
(informative)

Performance characteristics determined in laboratory and field tests

D.1 General

The performance characteristics are based upon the data of method validation. The method validation test included both laboratory and field tests with five participating laboratories. In the laboratory tests liquid calibration standards, real sample extracts, a sample of collected rain water and a sample of solid CRM suspended in water had been analysed. Some laboratories also reported their blank values. The results of the laboratory tests are used to calculate the detection limit, the within-laboratory standard deviation and the between-laboratory standard deviation.

The field validation tests were carried out at four measurement sites (one industrial, one urban, one remote southern and one remote alpine site). The test comprised all steps including sampling, sample preparation and analysis. The results from these tests are used to estimate the between-collector standard uncertainty. Table D.1 shows the range of the deposition rates measured in the field test. The upper and lower limits are the minimum and maximum values measured.

Table D.1 — Range of the deposition rates measured in the field test

	Lower limit ng/(m^2· d)	**Upper limit** ng/(m^2· d)
BaA	2	250
BbF	5	500
BjF	5	250
BkF	2	250
BaP	2	300
INP	4	550
DBahA	2	100

For the calculation of the uncertainty budget a combination of data of both tests was used.

D.2 Detection limit

D.2.1 General

The detection limit shall be calculated from laboratory blanks (see D.2.2). In some cases these are extremely low so that even no signal corresponding to the substance of interest can be observed. Then the detection limit shall be calculated based on the signal-to-noise ratio (see D.2.3).

D.2.2 Determination based on laboratory blanks

Determine the minimal detectable mass of the individual PAH compounds from the standard deviation of at least 10 laboratory blanks using Equations (D.1) and (D.2).

$$S_{\mathrm{lb,a}} = \sqrt{\frac{\sum_{i=1}^{n}(m_{\mathrm{a},i} - \overline{m}_{\mathrm{a}})^2}{n-1}} \qquad \text{(D.1)}$$

where

$S_{\mathrm{lb,a}}$ is the standard deviation of laboratory blank value in ng;

$\overline{m}_{\mathrm{a}}$ is the mean of laboratory blank values for compound a in ng;

$m_{\mathrm{a},i}$ is the individual laboratory blank value for compound a in ng;

n is the number of analysed laboratory blanks.

The minimal detectable mass of the individual PAH compounds is:

$$D_{\mathrm{M,a}} = t_{\mathrm{n-1;0,95}} \times S_{\mathrm{lb,a}} \qquad \text{(D.2)}$$

where

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

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

$S_{\mathrm{lb,a}}$ is the standard deviation of laboratory blanks for compound a in ng.

D.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 the PAH compounds. Calculate the detection limit as three times the average of the height of the noise at the retention time of the PAH compound ± 10 times the peak width at half peak height at the lowest calibration level.

D.2.4 Calculation of the detection limit

The detection limit $D_{\mathrm{L,a}}$, expressed in ng/(m^2·d), is calculated according to Equation (D.3) using the sampling duration and the area of the cross-section of the collector opening.

$$D_{\mathrm{L,a}} = \frac{D_{\mathrm{M,a}}}{A \times t} \qquad \text{(D.3)}$$

where

$D_{\mathrm{L,a}}$ is the detection limit in ng/(m^2·d);

$D_{\mathrm{M,a}}$ is the minimum detectable mass in ng;

A is the area of the cross-section of the collector opening in m^2;

t is the sampling duration in d.

Examples of detection limits, using laboratory blank data from a laboratory participating in the validation program, are shown in Table D.2.

Table D.2 — Examples of detection limits (HPLC/FLD analysis) for the tested PAH compounds (funnel-bottle bulk collector, funnel diameter 15,8 cm; sampling time: 28 days)

Substance	Detection limit in ng/(m²·d)
BaA	1,9
BbF	1,6
BkF	0,5
BaP	1,2
INP	1,4
DBahA	0,1
NOTE The detection limit of BjF was not determined.	

D.3 Within-laboratory and between-laboratory standard deviation using data of the laboratory test

D.3.1 General

The following samples have been analyzed in the laboratory test:

1) a calibration standard with known concentrations of PAH in dichloromethane and toluene;

2) a real sample extract at low PAH levels in DCM;

3) a real sample extract at high PAH levels in DCM;

4) rain water samples;

5) a sample of NIST SRM 1649a suspended in rain water + 1 % acetone + sodium chloride, with known concentrations of PAH (high amounts);

6) a sample of NIST SRM 1649a suspended in rain water + 1 % acetone + sodium chloride, with known concentrations of PAH (low amounts).

Participating laboratories have analysed the samples using their own methods based on EN 15549, ISO 12884 [5] and ISO 16362 [6]. The extraction of PAH was performed either by liquid-liquid extraction (see B.4.1) or by solid phase extraction (see B.4.2).

Statistical evaluation of the laboratory test was carried out in order to estimate uncertainty sources by assessment of within- and between-laboratory variances due to different approaches of individual laboratories, particularly in sample processing and calibration by applying ISO 5725 [7] statistics. It was also used to compare the two extraction methods described in B.4.1 and B.4.2.

Although strictly speaking ISO 5725 statistics are meant to be used for the evaluation of uncertainty of a single method, these statistics are useful to reveal potential ‘macro’ sources of measurement uncertainty and their magnitudes. In addition, these results can be used to evaluate whether between-laboratory contributions to uncertainty will be sufficiently low not to significantly influence the outcome of the field validation tests. Finally, the reproducibility standard deviations for samples 4, 5 and 7 are measures of the uncertainties to be expected when applying the method under validation.

D.3.2 Within-laboratory standard deviation

The results of repeated measurements of a sample extract in one laboratory are used to calculate the standard deviation for the individual laboratory according to Equation (D.4):

$$s_{\mathrm{ri}} = \sqrt{\frac{\sum_{j=1}^{n}(c_j - \bar{c}_i)^2}{n-1}} \tag{D.4}$$

where

s_{ri} is the standard deviation of repeated measurements of a solution by laboratory i;

c_{j} is the concentration of a compound in the solution of measurement j;

$\bar{c}_i$ is the mean value of the concentration of a compound in the solution measured by laboratory i;

n is the number of repeated measurements.

The individual standard deviations of the laboratories can be summarised to the within-laboratory standard deviation according to Equation (D.5):

$$s_{\mathrm{i}} = \sqrt{\frac{\sum_{i=1}^{m} s_{\mathrm{ri}}^2}{m}} \tag{D.5}$$

where

s_{i} is the within-laboratory standard deviation;

s_{ri} is the standard deviation of repeated measurements of a solution by laboratory i;

m is the number of participating laboratories.

D.3.3 Between-laboratory standard deviation and reproducibility standard deviation

The results for the extracts, which were analysed in the laboratory test, were used to calculate the between-laboratory standard deviation using Equation (D.6).

$$s_L = \sqrt{\frac{\sum_{i=1}^{m}(c_i - \bar{c})^2}{m-1}} \tag{D.6}$$

where

s_{L} is the between-laboratory standard deviation;

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

c_{i} is the concentration of a compound in the solution measured by laboratory i;

m is the number of participating laboratories.

The reproducibility standard deviation is obtained according to the rules of error propagation as shown in Equation (D.7).

$$s_R = \sqrt{s_r^2 + s_L^2} \tag{D.7}$$

where

s_R is the reproducibility standard deviation;

s_i is the within-laboratory standard deviation;

s_L is the between-laboratory standard deviation.

D.3.4 Results

Results of the laboratory test for real sample extracts and a CRM, suspended in water, worked up like a real sample, are summarised in Tables D.3 and D.4.

Table D.3 — Results of the laboratory test for a liquid extract of deposition samples

Component	Mean in ng/ml		s_r in %		s_L in %		s_R in %		m
	high	low	high	low	high	low	high	low	
BaP	227,9	56,4	4,8	2,8	18,3	12,2	18,9	12,5	6
BaA	240,9	62,3	4,6	3,9	14,9	7,4	15,6	8,4	6
BbF	245,5	64,3	5,4	2,8	9,7	3,1	11,1	4,2	4
BjF	146,4	35,5							2
BkF	120,6	33,9	4,5	2,1	11,4	20,9	12,2	21,0	4
(BF) [a]	526,8	133,6	1,0	2,4	13,2	6,4	13,2	6,9	4
INP	210,8	51,6	4,1	4,3	17,2	18,3	17,6	18,8	6
DBahA	28,3	8,4	6,2	9,8	31,1	44,3	31,7	45,4	6

[a] (BF) is the sum of BbF+BjF+BkF

Table D.4 — Results of the laboratory test for a CRM suspended in water

Component	Nominal level in ng		Mean in ng		Ratio		s_r in %		s_L in %		s_R in %		m
	high	low	high	low	high	low	high	low	high	low	high	low	
BaP	100,2	25,1	93,7	22,8	0,94	0,91	11,3	12,0	13,6	17,2	17,7	20,9	7
BaA	88,3	22,1	78,8	21,8	0,89	0,99	10,0	6,2	14,2	14,7	17,4	15,9	7
BbF	258,0	64,5	199,5	52,8	1,07	1,04	9,3	7,2	8,2	12,3	12,4	14,2	5
BjF			76,3	14,4			15,7	10,9	15,7	43,1	15,7	44,5	3
BkF	76,5	19,1	69,5	18,3	0,91	0,96	11,2	6,1	17,5	9,3	20,8	11,1	5
(BF) [a]	334,5	83,6	357,6	89,0	1,07	1,06	7,8	6,0	9,0	13,8	11,9	15,0	5
INP	127,2	31,8	136,0	33,4	1,07	1,05	7,7	8,1	19,0	16,4	20,5	18,3	7
DBahA	11,5	2,9	17,9	3,9	1,56	1,36	10,3	8,8	45,1	37,0	46,2	38,1	7

[a] (BF) is the sum of BbF+BjF+BkF

D.3.5 Overall conclusions

1) Analytical methods used are robust and lead to comparable results, with reproducibility standard deviations ranging from about 6 % to 10 %.

2) The determination of PAH in rain water with added suspended NIST SRM 1649a leads to results that are both consistent within and between laboratories, with reproducibility standard deviations ranging from 12 % to 20 % (with exception of that for DBahA).

3) No difference can be observed between results obtained by liquid/liquid extraction and solid-phase extraction. An additional quick scan, based on the comparison of the mean-of-means and standard deviations-of-means obtained by both techniques, confirmed this conclusion, although results for this scan are based on relatively few data.

D.4 Uncertainty budget using data of laboratory and field test experiments

D.4.1 General description of the field test

In the field test three different collector types were tested side-by-side at four different locations. The collector types were:

1) a funnel-bottle bulk collector (see A.2);

2) a cylindrical gauge (Bergerhoff collector, see A.3);

3) a wet-only collector (see A.4).

The four sampling sites were:

a) a remote site in Central Europe (Austria);

b) an industrial site in Central Europe (Germany);

c) a remote site in Southern Europe (France);

d) an urban site in Western Europe (Netherlands).

At each site two collectors of types (1) and (3) were exposed in parallel, while 2 × 4 collectors of type (2) were exposed. The contents of 4 collectors of type (2) were combined to one sample, yielding two parallel samples for collector type (2). All collectors were exposed for six consecutive four-week periods; collectors at site (1) were exposed for seven consecutive four-week periods.

Statistical evaluation serves two purposes, namely:

— estimation and comparison of the uncertainties associated with the use of the different collectors by assessment of between-collector variances;

— calculation of the combined uncertainty for the complete procedure of sampling and analysis by combining results from the laboratory tests with those of the field tests.

D.4.2 Results and data processing

D.4.2.1 Data submitted

For each of the four sites results were submitted of the mass of each PAH found in each of the collectors for each of the individual exposure periods 'by spreadsheet'. These results were converted into mass deposition rates in units of $ng \cdot m^{-2} \cdot d^{-1}$ by combination with relevant surface area dimensions of the collectors (in m^2) and exposure periods (in days).

The results for each site averaged over all periods are presented in Tables D.5 to D.8 (w_{bc} is the relative between-collector uncertainty).

Table D.5 — Results of the field tests (Austria)

	Funnel-bottle bulk collector		Wet-only collector		Bergerhoff collector (sum of 4 collectors)	
Component	**Mean deposition rate (all periods)** in $ng.m^{-2}.d^{-1}$	w_{bc} in %	**Mean deposition rate (all periods)** in $ng.m^{-2}.d^{-1}$	w_{bc} in %	**Mean deposition rate (all periods)** in $ng.m^{-2}.d^{-1}$	w_{bc} in %
BaA	38	11	38	15	27	120
BbF	61	11	61	16	44	41
BjF	74	8,8	68	10	40	33
BkF	28	12	34	12	17	26
BaP	34	16	37	13	19	58
INP	62	9,9	62	11	34	15
DBahA	6,5	22	7,1	16	4,1	39

Table D.6 — Results of the field tests (Germany)

	Funnel-bottle bulk collector		Wet-only collector		Bergerhoff collector (sum of 4 collectors)	
Component	**Mean deposition rate (all periods)** in $ng.m^{-2}.d^{-1}$	w_{bc} in %	**Mean deposition rate (all periods)** in $ng.m^{-2}.d^{-1}$	w_{bc} in %	**Mean deposition rate (all periods)** in $ng.m^{-2}.d^{-1}$	w_{bc} in %
BaA	288	5,2	119	7,7	264	45
BbF	369	6,4	159	7,7	340	22
BjF	164	7,9	66	9,3	133	25
BkF	192	5,1	80	6,7	162	26
BaP	212	6,3	78	9,2	251	49
INP	330	9,1	136	11	303	15
DBahA	53	2,3	14	14	30	16

Table D.7 — Results of the field tests (France)

	Funnel-bottle bulk collector		Wet-only collector		Bergerhoff collector (sum of 4 collectors)	
Component	**Mean deposition rate (all periods)** in $ng.m^{-2}.d^{-1}$	w_{bc} in %	**Mean deposition rate (all periods)** in $ng.m^{-2}.d^{-1}$	w_{bc} in %	**Mean deposition rate (all periods)** in $ng.m^{-2}.d^{-1}$	w_{bc} in %
BaA	7,6	27	6,3	41	3,6	33
BbF	23	13	16	18	6,8	41
BjF	11	16	6,3	22	4,0	30
BkF	7,0	15	4,7	15	2,7	15
BaP	7,7	14	5,0	16	2,6	14
INP	15	13	9,9	20	4,3	50
DBahA	3,0	17	1,9	14	1,7	4,3

Table D.8 — Results of the field tests (Netherlands)

	Funnel-bottle bulk collector		Wet-only collector		Bergerhoff collector (sum of 4 collectors)	
Component [a]	**Mean deposition rate (all periods)** in $ng.m^{-2}.d^{-1}$	w_{bc} in %	**Mean deposition rate (all periods)** in $ng.m^{-2}.d^{-1}$	w_{bc} in %	**Mean deposition rate (all periods)** in $ng.m^{-2}.d^{-1}$	w_{bc} in %
BaA	10	37	8,1	33	6,3	39
BbF	19	43	23	39	16	23
BkF	7,6	18	6,8	30	7,0	26
BaP	13	24	12	37	10	35
INP	7,7	*126* [b]	8,7	*120* [b]	10	33
DBahA	2,4	*129* [b]	1,3	*221* [b]	1,7	28

[a] BjF was not determined in this field test.
[b] Value treated as outlier in further calculations.

These results show that, in general, the funnel-bottle bulk collector yields the highest results. The mean ratios of the funnel-bottle bulk collector results to the other collector types are:

— 1,6 for the wet-only collector;

— 1,7 for the Bergerhoff collector.

D.4.2.2 Data treatment

For each site, each collector and each component the mean deposition rates observed during the consecutive sampling periods were calculated from the results for the individual periods. Further, for each collector type and each component the relative between-collector uncertainties were calculated of the results per component per pair of similar collectors exposed in parallel (or combinations of results for four Bergerhoff collectors). The between-collector uncertainty and the relative between-collector uncertainty were calculated according to Equations (D.8) and (D.9) as

$$u_{bc,j} = \sqrt{\frac{\sum_i (x_{i,j,1} - x_{i,j,2})^2}{2 \times n}} \tag{D.8}$$

$$w_{bc,j} = \frac{100 \times u_{bc,j}}{\overline{x}_j} \tag{D.9}$$

where

$u_{bc,j}$ is the between-collector uncertainty for collector type j;

$w_{bc,j}$ is the relative between-collector uncertainty for collector type j;

$x_{i,j,1}$, $x_{i,j,2}$ are the results for collectors 1 and 2 for each exposure period i for collector type j;

i is the individual exposure period;

j is the collector type;

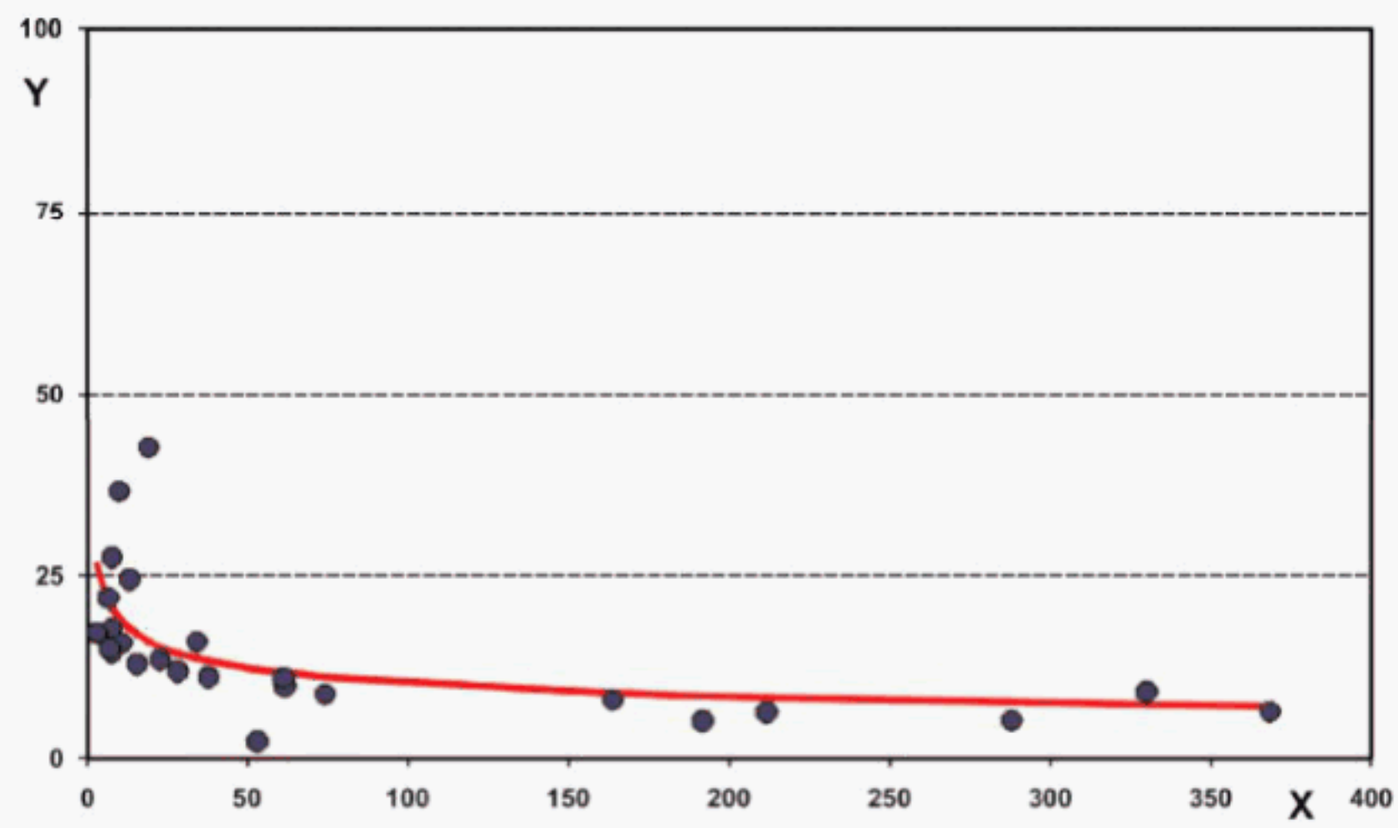
n is the number of exposure periods;

$\overline{x}_j$ is the mean of mean results over period i for collector j.

The results of the calculations are presented in Tables D.5 to D.8 above.

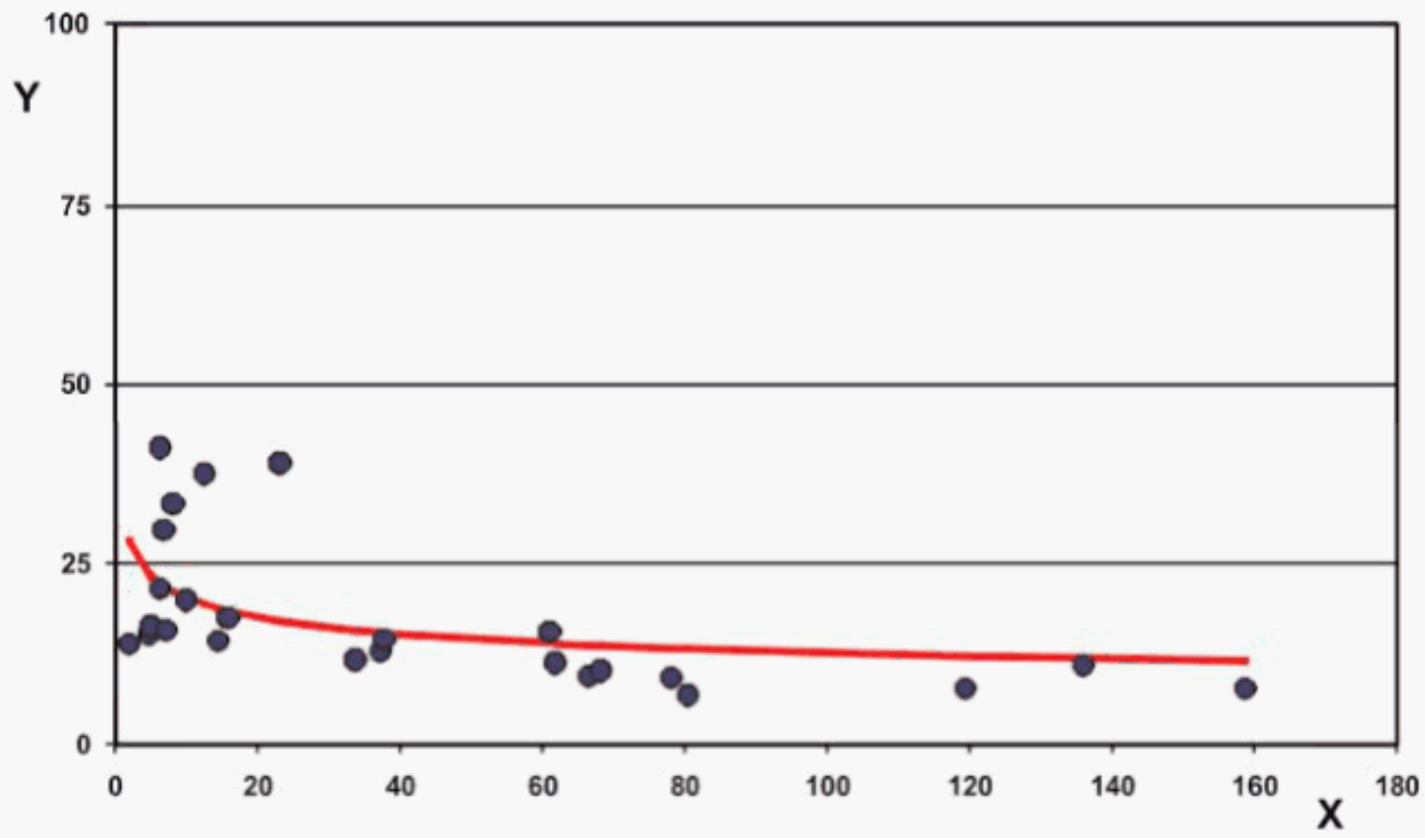
D.4.3 Uncertainty evaluations

First, values for $w_{bc,j}$ were plotted against the mean depositions reported for all components for each collector type in order to study the relationships between $w_{bc,j}$ and compound deposition. The plots are given in Figure D.1 to Figure D.3 below. From these figures it is apparent that particularly for the funnel-bottle bulk and wet-only collectors the relationships tend to have the shape of a "Horwitz-curve" [8], with $w_{bc,j}$ being constant at higher deposition levels and increasing exponentially at low concentrations. For the Bergerhoff collector this relationship is less apparent because of the high scatter observed at the low concentration range.



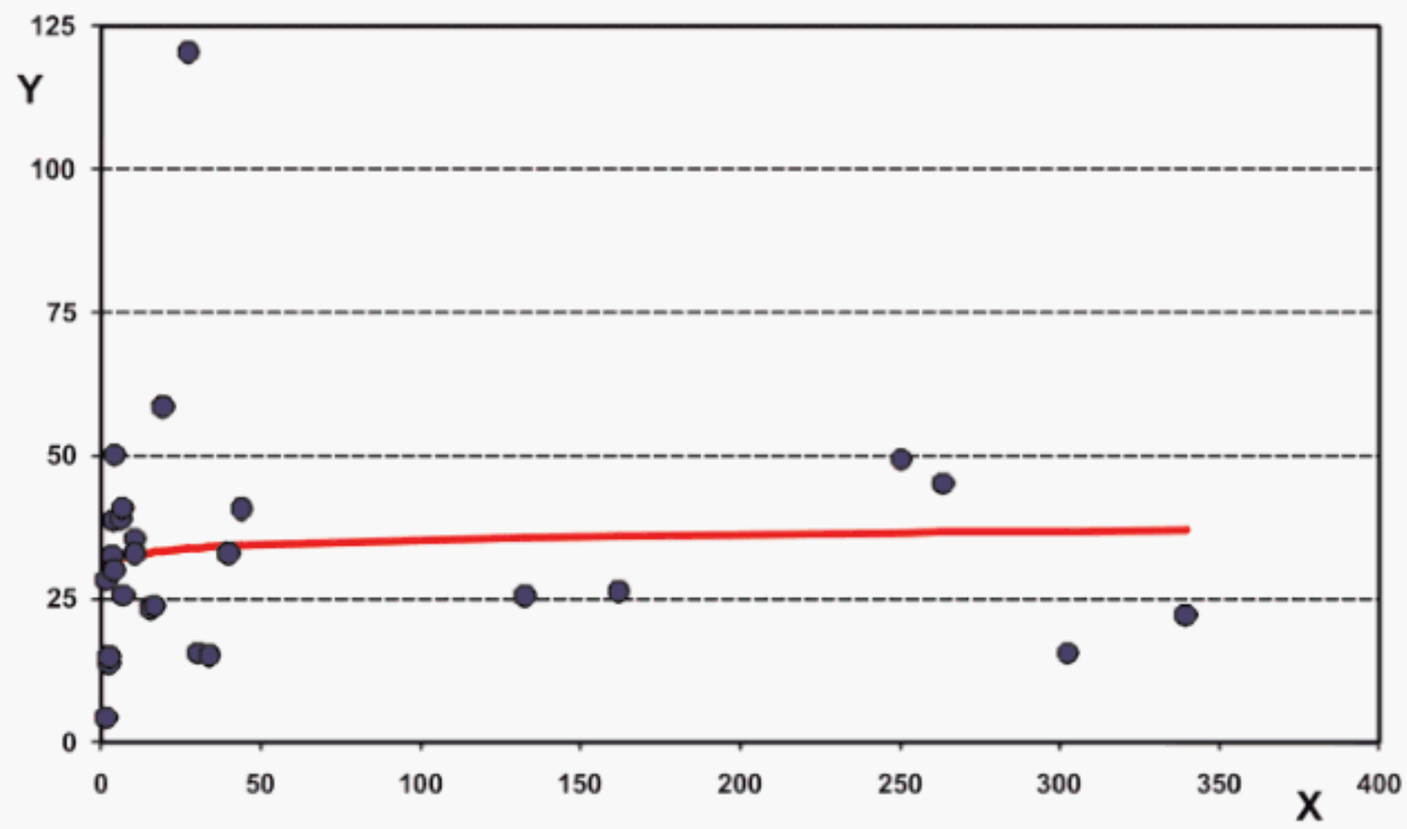
Key
X mean deposition in $ng.m^{-2}.d^{-1}$
Y relative between-collector uncertainty in %

Figure D.1 — Relative between-collector uncertainty vs. deposition: funnel-bottle bulk collector



Key
X mean deposition in $ng.m^{-2}.d^{-1}$
Y relative between-collector uncertainty in %

Figure D.2 — Relative between-collector uncertainty vs. deposition: wet-only collector



Key
X mean deposition in $ng.m^{-2}.d^{-1}$
Y relative between-collector uncertainty in %

Figure D.3 — Relative between-collector uncertainty vs. deposition: Bergerhoff collector

In order to express the relationship between $w_{bc,j}$ t and the deposition rate, an exponential function according to Equation (D.10) was established for each collector type.

$$w_{bc,j} = a \cdot \left(\overline{x_j}\right)^b \tag{D.10}$$

The appropriate values for coefficients a and b were obtained by minimizing the squares of the residuals resulting from the fitting procedure using Excel's solver function. The sum of the residues was defined as zero as a side condition. The random relative uncertainties of the fits were calculated from the residual sum-of-squares of the fits as (Equation D.11)

$$w_{fit} = \sqrt{\frac{rss}{p-2}} \qquad \text{(D.11)}$$

where

w_{fit} is the random relative uncertainty of the fits;

rss is the residual sum of squares from the fit;

p is the number of values for $w_{bc,j}$ used for the fitting procedure.

The following values for a, b and w_{fit} were obtained (see Table D.9).

Table D.9 — Results of exponential fits of $w_{bc,j}$ vs. mean deposition

	Coefficient a	Coefficient b	w_{fit}
Funnel-bottle bulk collector	35,5	-0,270	8,1
Wet-only collector	32,2	-0,203	9,1
Bergerhoff collector	30,0	0,036	21,9

The relationships obtained in this way may be used to estimate the between-collector uncertainty as a function of the deposition measured.

In order to estimate the total random uncertainty of results of the deposition measurements, the between-collector uncertainties obtained in the fields tests were combined with the between- laboratory uncertainties obtained in the laboratory tests. It should be born in mind that the between-collector uncertainties already contain contributions representing the within-laboratory analytical uncertainty for the component measured. Consequently, when estimating the total uncertainty for the field test results the between-collector uncertainty should be combined with estimates of between-laboratory uncertainty contributions for the analytical procedures used. The uncertainties calculated in this way represent “reproducibility uncertainties”.

A selection of results from the laboratory test analyses were used for this. In these tests two samples were analyzed that may be considered representative of real deposition samples (samples 5 and 6 – NIST SRM suspended in water). For the calculation of the total uncertainty the mean results of the analyses of samples 5 and 6 were converted to deposition rates by using the appropriate collector surface areas and an exposure period of 28 days. When combining the two contributions by summation in quadrature the following uncertainties resulted.

The between-laboratory analytical standard deviation s_L is listed in Table D.4, $s_{L,rel}$ the relative between-laboratory standard deviation w_c the combined relative uncertainty and W the expanded relative uncertainty (95 % confidence level) are listed in Tables D.10 to D.12, expressed in percent of the calculated deposition rates.

Table D.10 — Results for the funnel-bottle bulk collector

	Deposition rate in ng·m^{-2}·d^{-1}		$s_{L,rel}$		w_{bc}		w_c		W (95 % confidence level, k = 2)	
Amount of PAH	**high**	**low**	**high**	**Low**	**high**	**low**	**high**	**low**	**high**	**low**
BaA	161	40	14	15	9	13	17	20	34	39
BbF	340	92	8	12	7	10	11	16	22	32
BjF	130	25	16	43	10	15	18	46	37	*91*
BkF	139	35	18	9	9	14	20	16	40	33
BaP	183	46	14	17	9	13	16	21	32	43
INP	232	58	19	16	8	12	21	20	41	40
DBahA	21	5,3	45	37	16	23	48	43	*95*	*87*
(BF) [a]	610	152	9	14	6	9	11	17	22	33

[a] (BF) is the sum of BbF+BjF+BkF

Table D.11 — Results for the wet-only collector

	Deposition rate in ng·m^{-2}·d^{-1}		$s_{L,rel}$		w_{bc}		w_c		W (95 % confidence level, k = 2)	
Amount of PAH	**high**	**low**	**High**	**low**	**high**	**low**	**high**	**low**	**high**	**low**
BaA	64	16	14	15	14	18	20	24	40	47
BbF	136	37	8	12	12	15	14	20	29	40
BjF	52	10	16	43	14	20	21	48	43	*95*
BkF	56	14	18	9	14	19	23	21	45	42
BaP	73	18	14	17	13	18	19	25	38	50
INP	93	23	19	16	13	17	23	24	46	47
DBahA	8,4	2,1	45	37	21	28	50	46	*99*	*92*
(BF) [a]	243	61	9	14	11	14	14	20	28	39

[a] (BF) is the sum of BbF+BjF+BkF

Table D.12 — Results for the Bergerhoff collector

	Deposition rate in ng·m^{-2}·d^{-1}		$s_{L,rel}$		w_{bc}		w_c		W (95 % confidence level, k = 2)	
Amount of PAH	**high**	**low**	**High**	**low**	**high**	**low**	**high**	**low**	**high**	**low**
BaA	127	32	14	15	36	34	38	37	*77*	*74*
BbF	269	73	8	12	37	35	38	37	*75*	*74*
BjF	103	20	16	43	35	33	39	55	*78*	*109*
BkF	110	28	18	9	36	34	40	35	*79*	*70*
BaP	144	36	14	17	36	34	38	38	*77*	*76*
INP	183	46	19	16	36	34	41	38	*82*	*76*
DBahA	17	4,2	45	37	33	32	56	49	*112*	*97*
(BF) [a]	482	120	9	14	37	36	39	38	*77*	*76*

[a] (BF) is the sum of BbF+BjF+BkF

Subsequently, the calculated expanded relative uncertainties W can be compared with the data quality objective of 70 % given in Annex IV of Directive 2004/107/EC. Values for W exceeding the data quality objective are highlighted in italics.

These comparisons show that, generally, uncertainties obtained using the Bergerhoff collector do not meet the 70 % uncertainty criterion. This is due to the high relative between-collector uncertainty of 30 % to 35 %.

The uncertainties for funnel-bottle bulk collector and wet-only collector meet the 70 % criterion except for BjF and DBahA at low deposition values. However, the exceedances for these cases can be fully explained by the high analytical between-laboratory uncertainties for these components at the low levels of lab test sample 7.

NOTE Only 4 laboratories analysed BjF in the laboratory test. Interferences influencing the analysis of DBahA are described in C.3.2.

D.4.4 Conclusions

From the results of the field tests the between-collector uncertainties were calculated for the three collector types investigated. These were found to be described more or less by exponential functions of the depositions measured, independent of the components analyzed. The lowest uncertainties and best fits were found for the total-bulk collector and the wet-only collector. However, the latter collector generally yields substantially lower deposition values.

Through combination of the between-collector uncertainties with analytical between-laboratory uncertainties for samples from the laboratory validation tests the total uncertainties for the deposition measurement results may be obtained. For the funnel-bottle bulk collector and wet-only collector the uncertainties observed generally meet the 70 % uncertainty criterion given in Directive 2004/107/EC. Those cases in which the criterion is exceeded may simply be explained from the atypically high analytical uncertainties rather than from the performances of the collectors. The uncertainties for the Bergerhoff collector generally do not meet the 70 % criterion.

Annex E
(informative)

Relationship between this European Standard and the essential requirements of EU Directives

This European Standard has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association and supports essential requirements of the Council Directive 2004/107/EC relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air [2].

WARNING — Other requirements and other EU Directives may be applicable to the product(s) falling within the scope of this standard.

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