
Ambient air — Determination of total (gas and particle-phase) polycyclic aromatic hydrocarbons — Collection on sorbent-backed filters with gas chromatographic/mass spectrometric analyses

Air ambient — Détermination des hydrocarbures aromatiques polycycliques totales (phase gazeuse et particulaire) — Prélèvement sur filtres à sorption et analyses par chromatographie en phase gazeuse/spectrométrie en masse



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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 12884 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 3, *Ambient air*.

Annex A forms a normative part of this International Standard. Annexes B, C, D and E are for information only.

Introduction

This International Standard is applicable to polycyclic aromatic hydrocarbons (PAH) composed of two or more fused aromatic rings. It does not apply to polyphenyls or other compounds composed of aromatic rings linked by single bonds. Several PAH are considered to be potential human carcinogens. PAH are emitted into the atmosphere primarily through combustion of fossil fuel and wood. Two-ring and three-ring PAH are typically present in urban air at concentrations ranging from ten to several hundred nanograms per cubic metre (ng/m^3); those with four or more rings are usually found at concentrations of a few ng/m^3 or lower. PAH possess saturation vapour pressures at 25 °C that range from 10^{-2} kPa to less than 10^{-13} kPa. Those with vapour pressures above 10^{-8} kPa may be substantially distributed between phases depending on ambient temperature, humidity, types and concentrations of PAH and particulate matter, and residence time in the air. PAH, especially those having vapour pressures above 10^{-8} kPa, will tend to vaporize from particle filters during sampling. Consequently, a back-up vapour trap is included for efficient sampling. Except for PAH with vapour pressures below 10^{-9} kPa, separate analyses of the filter and vapour trap will not reflect the original atmospheric phase distributions at normal ambient temperature because of volatilization of compounds from the filter.

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Ambient air — Determination of total (gas and particle-phase) polycyclic aromatic hydrocarbons — Collection on sorbent-backed filters with gas chromatographic/mass spectrometric analyses

1 Scope

This International Standard specifies sampling, cleanup and analysis procedures for the determination of polycyclic aromatic hydrocarbons (PAH) in ambient air. It is designed to collect both gas-phase and particulate-phase PAH and to determine them collectively. It is a high-volume (100 l/min to 250 l/min) method capable of detecting 0,05 ng/m³ or lower concentrations of PAH with sampling volumes up to 350 m³. The method has been validated for sampling periods up to 24 h.

Precision under normal conditions can be expected to be $\pm 25\%$ or better and uncertainty $\pm 50\%$ or better (see annex A, Table A.1).

This International Standard describes a procedure for sampling and analysis for PAH that involves collection from air on a combination fine-particle filter and sorbent trap, and subsequent analysis by gas chromatography/mass spectrometry (GC/MS).

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 6879:1995, *Air quality — Performance characteristics and related concepts for air quality measuring methods*.

ISO 9169:1994, *Air quality — Determination of performance characteristics of measurement methods*.

ISO/TR 4227:1989, *Planning of ambient air quality monitoring*.

3 Terms and definitions

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

3.1 sampling efficiency

E_s
ability of the sampler to trap and retain PAH

NOTE The % E_s is the percentage of the analyte of interest collected and retained by the sampling medium when a known amount of analyte is introduced into the air sampler and the sampler is operated under normal conditions for a period of time equal to or greater than that required for the intended use.

3.2

dynamic retention efficiency

E_r

ability of the sampling medium to retain a given PAH that has been added to the sorbent trap in a spiking solution when air is drawn through the sampler under normal conditions for a period of time equal to or greater than that required for the intended use

4 Principle

4.1 Sampling

An air sample is collected directly from the ambient atmosphere by pulling air at a maximum flowrate of 225 l/min (16 m³/h) through first a fine-particle filter followed by a vapour trap containing polyurethane foam (PUF) or styrene/divinylbenzene polymer resin (XAD-2). Sampling times may be varied depending on monitoring needs and the detection limits required. The total volume of air sampled shall not exceed 350 m³ unless the appropriate deuterated PAH or other suitable standards are added as internal standards to the PUF or XAD-2 sorbent before sampling to validate retention efficiency.

4.2 Analysis

After sampling a fixed volume of air, the particle filter and sorbent cartridge are extracted together in a Soxhlet extractor. The sample extract is concentrated by means of a Kuderna-Danish concentrator (or other validated method), followed by a further concentration under a nitrogen stream if necessary, and an aliquot is analysed by gas chromatography/mass spectrometry. The results derived represent the combined gas-phase and particulate-phase air concentrations of each PAH analysed.

5 Limits and interferences

5.1 Limits

PAH span a broad spectrum of vapour pressures (e.g. from $1,1 \times 10^{-2}$ kPa for naphthalene to 2×10^{-13} kPa for coronene at 25 °C). Table B.1 in annex B lists some PAH that are frequently found in ambient air. Those with vapour pressures above about 10^{-8} kPa will be present in the ambient air, distributed between the gas and particulate phases. This method permits the collection of both phases. However, particulate-phase PAH may be lost from the particle filter during sampling due to desorption and volatilization [1] to [8]. During summer months, especially in warmer climates, volatilization from the filter may be as great as 90 % for PAH with vapour pressures above 10^{-6} kPa [3] and [8]. At ambient temperatures of 30 °C and above, as much as 20 % of benzo[a]pyrene and perylene (vapour pressure $\approx 7 \times 10^{-10}$ kPa) have been found in the vapour trap [1]. Therefore, separate analysis of the filter will not reflect the concentrations of the PAH originally associated with particles, nor will analysis of the sorbent provide an accurate measure of the gas phase. Consequently, this method requires coextraction of the filter and sorbent to permit accurate measure of total PAH air concentrations.

NOTE This method collects all airborne particulate matter up to at least 40 µm. Particulate-phase PAH are concentrated on fine particles in the ambient atmosphere. Therefore, the use of a particle size-limiting inlet (e.g. PM₁₀ or PM_{2,5}), if required, should have little effect on total PAH measurements.

This method has been evaluated for the PAH shown in annex B. Other PAH may be determined by this method, but the user shall demonstrate acceptable sampling and analysis efficiencies. Naphthalene and acenaphthene possess relatively high vapour pressures and may not be efficiently trapped by this method. The sampling efficiency for naphthalene has been determined to be about 35 % for PUF and about 60 % for XAD-2 [9]. The user may estimate the sampling efficiencies for PAH of interest by determining dynamic retention efficiency of the sorbent. The % E_r generally approximates the % E_s .

5.2 Interferences

Method interferences can be caused by contaminants in solvents, reagents, on glassware and other sample processing hardware that result in discrete artifacts and/or elevated baselines in the detector profiles. Glassware shall be scrupulously cleaned (e.g. by acid washing, followed by heating to 450 °C in a muffle furnace, and solvent-rinsed immediately prior to use). All solvents and other materials shall be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.

Matrix interferences can be caused by contaminants that are coextracted from the sample. Additional clean-up by column chromatography shall be required.

The extent of interferences that can be encountered using gas chromatographic techniques has not been fully assessed. Although the GC/MS conditions described allow for resolution of most PAH, some PAH isomers may not be chromatographically resolvable and therefore cannot be distinguished from each other by MS. Interferences from some non-PAH compounds, especially oils and polar organic species, may be reduced or eliminated by the use of column chromatography for sample clean-up prior to GC/MS analysis. The analytical system shall be routinely demonstrated to be free of internal contaminants such as contaminated solvents, glassware, or other reagents that may lead to method interferences. A laboratory reagent blank shall be analysed for each batch of reagents used to determine if reagents are contaminant-free.

Alkyl PAH, if present, may coelute with analytes of interest, but should rarely present problems. Methylacenaphthalene coelution with fluorene is the most likely potential problem, but the identity of fluorene can be confirmed by monitoring secondary ions.

Heteroatomic PAH (e.g. quinoline) should not cause interferences, even if co-elution occurs when the primary and secondary mass ions are used for identification.

Exposure to heat, ozone, nitrogen dioxide (NO₂) and ultraviolet (UV) light may cause PAH degradation during sampling, sample storage and processing. These problems shall be addressed as part of a standard operating procedure (SOP) prepared by the user. Where possible, incandescent or UV-filtered (excluding wavelengths below 365 nm) fluorescent lighting shall be used in the laboratory to avoid photodegradation during analysis.

NOTE Reactive gases, such as ozone and nitrogen oxides, should not significantly affect sample integrity when sampling typical ambient atmospheres. Whereas losses of up to 50 % of benzo[a]pyrene spiked onto air filters (with or without the presence of particulate matter) are likely to occur when ambient air is passed through such filters, especially in atmospheres with high ozone concentrations, studies have shown that reactive losses are insignificant during normal sampling or for benzo[a]pyrene spiked onto filters at near-ambient levels [3], [8], [10] and [11].

Smoking of tobacco products in the sample preparation or analytical laboratory or in adjoining areas may result in contamination of samples with PAH.

6 Safety measures

WARNING — Benzo[a]pyrene and several other PAH have been classified as carcinogens. Care shall be exercised when working with these substances.

This method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this method to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. The user shall be thoroughly familiar with the chemical and physical properties of targeted substances.

All PAH shall be treated as carcinogens. Pure compounds shall be weighed in a glove box. Unused samples and standards are considered to be toxic waste and shall be properly disposed of according to regulations. Laboratory benchtops and equipment shall be regularly checked with a hand-held long wavelength UV lamp (365 nm) for fluorescence indicative of contamination.

Some solvents specified in this International Standard may present health hazards if breathed or absorbed through the skin. Hexane is of particular concern. Special care should be exercised when using this solvent. All operations that require working with this solvent should be performed in a fume hood.

7 Apparatus

7.1 Sampling

7.1.1 Sampling module

A typical collection system consisting of a particle filter backed up by a sorbent trap is shown as an example in Figure 1 [12]. It consists of a metal filter holder (Part 2) capable of holding a 102 mm circular particle filter supported by a 1,2 mm stainless steel screen with 50 % open area and attaching to a metal cylinder (Part 1) capable of holding a 64 mm o.d. (58 mm i.d.) $\times$ 125 mm borosilicate glass sorbent cartridge. The filter holder is equipped with inert sealing gaskets [e.g. polytetrafluoroethylene (PTFE)] placed on either side of the filter. Likewise, inert, pliable gaskets (e.g. silicone rubber) are used to provide an air-tight seal at each end of the sorbent cartridge. The glass sorbent cartridge is indented 20 mm from the lower end to provide a support for a 1,2 mm stainless steel screen that holds the sorbent. The glass sorbent cartridge fits into Part 1, which is screwed onto Part 2 until the sorbent cartridge is sealed between the gaskets. The sampling module is described in [12]. Similar sampling modules are commercially available.

7.1.2 High-volume pumping system

Any air sampler pumping system capable of providing a constant air flow of up to 250 l/min (15 m³/h) through the sampling module may be used. It shall be equipped with an appropriate flow-control device, a vacuum gauge to measure pressure drop across the sampling module or other suitable flow monitoring device, an interval timer, and an exhaust hose to carry exhausted air at least 3 m away from the sampler. The inlet of the sampler may be oriented upward or downward. If oriented upward, a rain and dust shelter shall be provided.

NOTE The choice of inlets is at the discretion of the user. Particulate-associated PAH are principally concentrated on fine particles; therefore, the particle-size cut-point of the inlet will have little, if any, effect on total PAH measurements.

7.1.3 Flow calibrator

A calibrated manometer or other suitable flow-measuring device capable of being attached to the inlet of the sampling module.

7.1.4 Particle filters

Micro-quartz-fibre, 102 mm diameter binderless, acid-washed, with a filtration efficiency of 99,99 % mass fraction or better for particles below 0,5 μ m in diameter, or other appropriate size filter depending on the specific sampling module used.

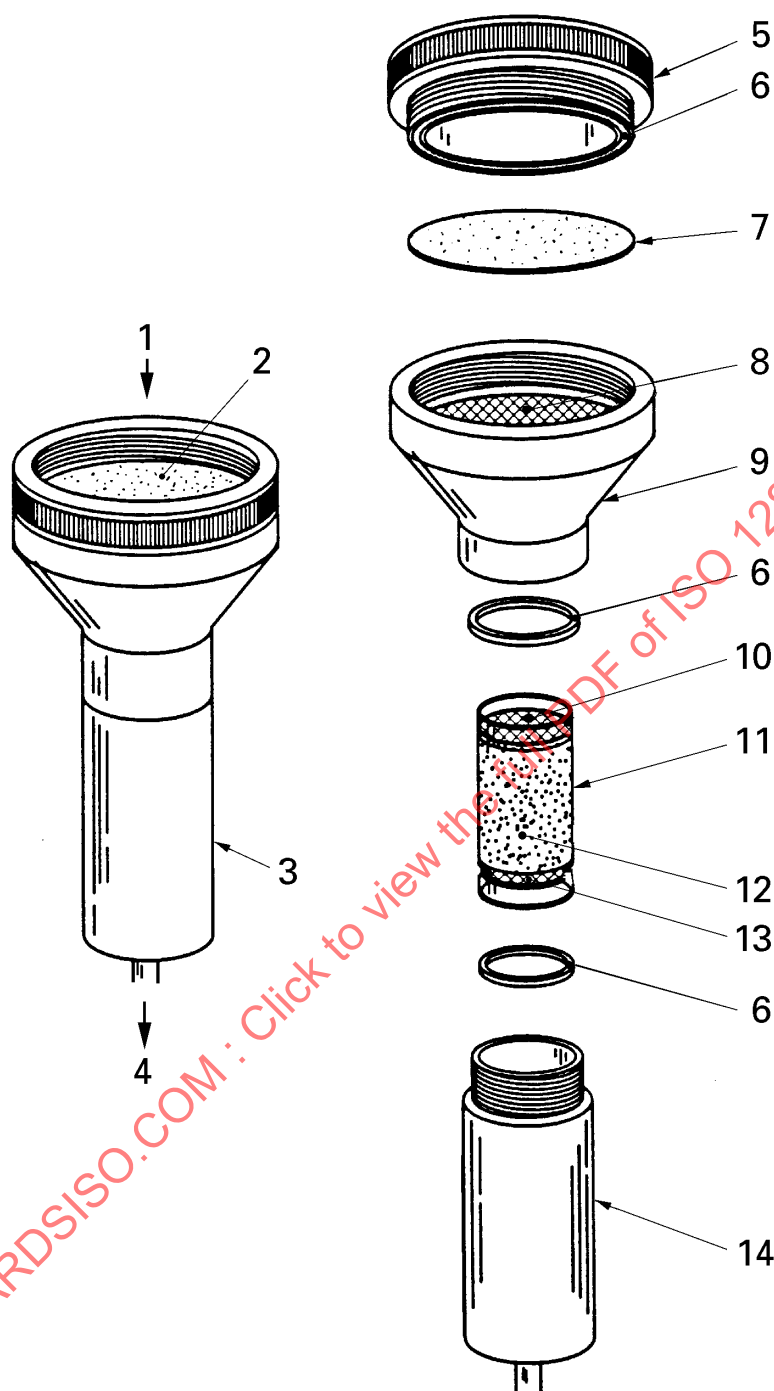
NOTE Glass-fibre or quartz-fibre filters coated or impregnated with PTFE have been used for collection of particulate-associated PAH [13]. Use of these filters in lieu of those specified requires validation of performance by the user.

7.1.5 Polyurethane foam, polyether type, density 22 mg/cm³, cut into cylinders 76 mm long $\times$ 62 mm diameter or other appropriate size depending on the specific sampling module used.

7.1.6 Adsorbent resin, of styrene/divinylbenzene polymer (XAD-2), spherical beads, 500 μ m diameter, precleaned.

NOTE The sampling system described in 7.1.1 to 7.1.6 has been shown to efficiently trap PAH with three or more rings at a sampling rate of 225 l/min and sample volumes of 350 m³ and lower [4], [6], [9], [14] to [20]. Other samplers utilizing larger filters (e.g. 200 mm $\times$ 250 mm) and higher capacity sorbent traps (e.g. tandem 77 mm $\times$ 62 mm PUF plugs) have been used to collect PAH from larger air volumes (e.g. 700 m³) [1], [2], [5], [7], [21] to [28].

7.1.7 Gloves, polyester or latex rubber, for handling cartridges and filters.



Key

- | | | |
|-----------------------------|--------------------------------------|------------------------------|
| 1 Air flow inlet | 6 Sealing gasket | 11 Glass cartridge |
| 2 Particle filter | 7 102-mm quartz-fibre filter | 12 Sorbent (XAD-2 or PUF) |
| 3 Assembled sampling module | 8 Filter support screen | 13 Retaining screen |
| 4 Air flow exhaust | 9 Filter holder (Part 2) | 14 Cartridge holder (Part 1) |
| 5 Filter retaining ring | 10 Retaining screen (if using XAD-2) | |

Figure 1 — Example of sampling module

7.1.8 Sample containers, airtight, labelled and screw-capped (wide-mouth, preferably glass jars with PTFE-lined lids), to hold filters and sorbent cartridges during transport to the analytical laboratory.

7.1.9 Ice chest, to hold samples at a temperature of 0 °C or below during transport to the laboratory after collection.

7.1.10 Data sheets, for each sample, for recording the location and sampling time, duration of sampling, starting time, and volume of air sampled.

7.2 Sample preparation

7.2.1 Soxhlet extractor system, of volume 200 ml, with 500 ml flask and appropriate condenser. If glass sorbent cartridge is extracted without unloading, a 500 ml extractor and 1 000 ml flask are required.

7.2.2 Kuderna-Danish (KD) concentrators, of volume 500 ml, 10 ml graduated tubes with ground-glass stoppers, and 3-ball macro-Snyder column.

7.2.3 Evaporative concentrators, including microevaporator tubes of 1 ml capacity, micro-Snyder columns (optional), water bath with ± 5 °C temperature control, nitrogen blow-down apparatus with adjustable flow control.

7.2.4 Cleanup columns

Chromatography columns of e.g. length 60 mm, inner diameter 11,5 mm.

7.2.5 Vacuum oven

Drying oven system capable of maintaining a vacuum at 30 kPa to 35 kPa (flushed with nitrogen) overnight.

7.2.6 Laboratory refrigerator/freezer, capable of cooling from 4 °C to –20 °C.

7.2.7 Glove box or high-efficiency hood, for handling highly toxic standards, with UV-filtered light source.

7.2.8 Vials, of volume 40 ml, borosilicate glass.

7.2.9 Minivials, of volume 2 ml, borosilicate glass, with conical reservoir and screw caps lined with PTFE-faced silicone disks, and a vial holder.

7.2.10 Erlenmeyer flasks, of volume 50 ml, borosilicate glass.

7.2.11 Boiling chips, solvent-extracted, silicon carbide or equivalent, grain diameter 0,3 mm to 0,9 mm.

7.2.12 Spatulas, PTFE-coated or of stainless steel.

7.2.13 Tweezers and forceps, PTFE-coated or of stainless steel.

7.3 Sample analysis

7.3.1 Gas chromatograph/mass spectrometer

Analytical system complete with gas chromatograph coupled with a mass spectrometer and data processor, suitable for splitless injection, and all required accessories, including temperature programmer, column supplies, recorders, gases and syringes.

7.3.2 GC columns, fused silica capillary column of length 30 m to 50 m, inner diameter 0,25 mm, coated with crosslinked 5 % phenyl methylsilicone of 0,25 μ m film thickness, or other suitable columns.

Ferrules made up of no more than 40 % mass fraction of graphite (e.g. 60 % polyimide and 40 % graphite by mass fraction) shall be used at the GC column injection inlet to avoid possible absorption of PAH.

7.3.3 Syringes, of volumes 10 µl, 50 µl, 100 µl and 250 µl, for injecting samples into GC and making calibration, reference standard, and spiking solutions.

8 Reagents and materials

- 8.1 Acetone**, glass-distilled, chromatographic quality.
- 8.2 *n*-Hexane**, glass-distilled, chromatographic quality.
- 8.3 Diethyl ether**, reagent grade, preserved with 2 % volume fraction of ethanol.
- 8.4 Dichloromethane**, glass-distilled, chromatographic quality.
- 8.5 Cyclohexane** (optional), glass-distilled, chromatographic quality.
- 8.6 Toluene** (optional), glass-distilled, chromatographic quality.
- 8.7 Pentane**, glass-distilled, chromatographic quality.
- 8.8 Silica gel**, high purity grade, type 60, grain diameter 75 µm to 200 µm (purified by extraction with dichloromethane as described in 11.1.1).
- 8.9 Sodium sulfate**, anhydrous, reagent grade (purified by washing with dichloromethane followed by heating at 450 °C for 4 h in a shallow tray).
- 8.10 Extraction efficiency standards**, fluorene-d₁₀, pyrene-d₁₀, benzo[*k*]fluoranthene-d₁₂, or other appropriate deuterated standards, of purity 98 % mass fraction or better. Spiking solutions of the standards are made up in *n*-hexane or dichloromethane, as appropriate, to a concentration of 50 ng/µl. Alternatively or additionally, 2,2'-dibromobiphenyl and 2,2',3,3',4,4',5,5',6,6'-decafluorobiphenyl or ¹³C-labelled PAH may be used as extraction efficiency standards.
- 8.11 Internal standards**, naphthalene-d₈, acenaphthene-d₁₀, perylene-d₁₂, chrysene-d₁₂, of purity 98 % mass fraction or better.
- 8.12 Compressed gases**, helium carrier gas, ultra-high purity, and nitrogen for sample concentration, high purity.

9 Preparation of sampling media

9.1 Polyurethane foam

For initial cleanup, the PUF plug is placed in a Soxhlet apparatus and first extracted with acetone for 14 h to 24 h at approximately 4 cycles per hour. This is followed by a second Soxhlet extraction for 14 h to 24 h at approximately 4 cycles per hour with a mixture of 10 % volume fraction of diethyl ether in *n*-hexane (or other appropriate to solvent to be used in the sample extraction step described in 11).

The PUF plug may be reused if properly cleaned after each use. The number of possible uses before significant deterioration of performance occurs has not been determined, but it should not be used more than six times without verifying that the performance is unchanged.

NOTE If the PUF plug is reused, 10 % volume fraction of diethyl ether in *n*-hexane (or the optional extraction solvent, if appropriate) may be used as the solvent for cleanup.

The extracted PUF plug is placed in a vacuum oven connected to an ultra-pure nitrogen gas stream and dried at room temperature for approximately 2 h to 4 h (until the plug is no longer swollen).

The cleaned and dried PUF plug is placed in the glass sampling cartridge using polyester or latex rubber gloves and PTFE-coated forceps.

9.2 Styrene/divinylbenzene resin (XAD-2)

For initial cleanup of the XAD-2, a batch of XAD-2 (60 g to 100 g) is placed in a Soxhlet apparatus and extracted with dichloromethane for 16 h at approximately 4 cycles per hour. At the end of the initial Soxhlet extraction, the used dichloromethane is discarded and replaced with fresh reagent. The XAD-2 resin is once again extracted for 16 h at approximately 4 cycles per hour. The XAD-2 resin is removed from the Soxhlet apparatus, placed in a vacuum oven connected to an ultra-pure nitrogen gas stream and dried at room temperature for approximately 4 h to 8 h (until the resin particles flow freely).

NOTE The XAD resin may be dried more quickly using a fluidized-bed suspension system with dry nitrogen [29].

The XAD may be reused if properly cleaned after each use. The number of possible uses before significant deterioration of performance occurs has not been determined, but it should not be used more than six times without verifying that the performance is unchanged.

A stainless steel screen (75 µm) or 1 cm thick plug of pre-extracted PUF is placed at the bottom of the hexane-rinsed glass cartridge to retain the XAD-2 resin.

When dry, the XAD-2 resin is poured into the sampling cartridge to a depth of approximately 5 cm. This will require 55 g to 60 g of sorbent. Another 75 µm screen or a 1 cm PUF plug is placed on top of the XAD bed to retain the sorbent.

9.3 Storage

The loaded sampling cartridge is wrapped with hexane-rinsed aluminium foil, placed in a clean container and tightly sealed.

NOTE In lieu of solvent rinsing, the aluminium foil may be heated for 1 h at 450 °C in a muffle furnace.

9.4 Blank check

At least one assembled cartridge from each batch shall be analysed as a laboratory blank, using the procedures described in clause 11, before the batch is considered acceptable for field use. A blank level of < 10 ng per sorbent cartridge for single compounds is considered to be acceptable. The blank level for a given PAH shall be less than 10 % of the mass anticipated to be collected for analysis.

NOTE Blank levels of < 10 ng may not be achievable for naphthalene or phenanthrene. However, since these compounds are typically present in ambient at relatively high concentrations, a blank level of < 50 ng is usually acceptable.

10 Sampling

10.1 Calibration of the sampler flow control system

The airflow through the sampling system shall be monitored by a flow-control device or devices. A multi-point calibration of the flow-control system shall be conducted every six months using a standard audit calibration orifice, which is temporally attached to the inlet of the sampler. A single-point calibration shall be performed before and after each sample collection. Alternatively, a high-flow dry gas metre may be used if it has been validated as a transfer standard.

The sampler shall be calibrated:

- a) when new;
- b) after major repairs or maintenance;

- c) whenever any audit point deviates from the calibration curve by more than 7 %;
- d) when using a different collection medium (PUF vs. XAD) than that for which the sampler was originally calibrated; or
- e) at the frequency specified in the user's manual.

Calibration of the air sampler in the field is performed using a calibrated orifice flowrate transfer standard. The flowrate transfer standard shall be certified in the laboratory against a positive displacement roots metre. Once certified, the recertification shall be performed once a year, if the orifice is protected from damage.

10.2 Determination of sampling efficiency or dynamic retention efficiency

The efficiency of the sampler for the targeted PAH shall be confirmed under the conditions anticipated in the field prior to the initiation of any sampling programme. Determination of the efficiency is particularly important if sampling periods exceeding 24 h are planned. Acceptable performance may be established by determining sampling efficiency directly or estimating it from the dynamic retention efficiency.

Sampling efficiency (E_s) is determined by spiking a solution of the compounds of interest (or a representative selection that includes the most volatile PAH) onto a clean particle filter backed with the vapour cartridge, then pulling through the assembled sampling module a volume of air equivalent to the maximum volume that will be sampled. Retention efficiency (E_r) is determined by spiking the sorbent directly, placing it behind a clean filter in the sampling module, and otherwise following the same procedure.

For E_s determinations, add the spiking solution dropwise to the filter, so as to uniformly load it and avoid oversaturation. For E_r determinations, carefully inject the spiking solution into the inlet face of the sorbent bed in a manner that will apply the solution uniformly across the face and to a depth of no more than 1 cm. The spiking solution shall be in a volatile solvent, such as hexane or dichloromethane. Spiking levels shall correspond to at least 3 times but no more than 10 times the anticipated concentrations of the targeted compounds in the air to be pulled through the sampling medium. Allow the spiked filter or sorbent to dry for about 1 h in a clean, light-protected area prior to pulling air through the system.

The sampling rate and sampling period shall be the same as that planned for the programme. Ambient temperatures during the test shall also approximate those expected in the field, especially when warm-weather conditions are anticipated.

For determination of sampling efficiencies, analyse the sorbent and spiked filter separately and subtract any residue retained by the filter from the initial spike quantity for calculation of sampling efficiencies. For determination of dynamic retention efficiencies, only the sorbent is analysed.

The sampling efficiency E_s for a given PAH, in percent, is calculated using the following equation:

$$E_s = \frac{W}{W_0 - W_R} \times 100$$

where

W is the quantity of PAH extracted from the sorbent after air is pulled through it;

W_0 is the quantity of PAH initially applied to the filter;

W_R is the quantity of PAH remaining on the filter after air is pulled through it.

Sampling efficiencies shall fall between 75 % and 125 %, except for naphthalene and acenaphthylene, which may exhibit lower efficiencies, especially with PUF. In no case shall sampling efficiencies below 50 % or above 150 % be accepted.

The dynamic retention efficiency E_r , in percent, is calculated from the following equation:

$$E_r = \frac{W}{W_0} \times 100$$

where W_0 is the quantity of PAH initially applied to the sorbent bed.

The % E_r has generally been found to be approximately equal to or slightly lower than the % E_s for semivolatile organic compounds. The same range of acceptability applies to % E_r as to % E_s .

10.3 Sample collection

Clean the interior surfaces and gaskets of the sampling module prior to sampling. Load and unload the sampling cartridge in a controlled clean environment or at a centralized sample processing area, so that the sample handling variables can be minimized.

Load the sorbent-filled glass sampling cartridge into the lower part (Part 1) of the sampling head and attach the filter holder (Part 2) tightly to it (see Figure 1). With clean PTFE-tipped forceps, carefully place the particle filter on top of the filter support and secure the filter holder ring over the filter. Tightly assembled all module connections.

NOTE Failure to properly tighten connections may result in air leaks and affect sample representativeness.

Locate the sampler in an unobstructed area, at least 2 m from any obstruction of air flow. Stretch out the exhaust hose in the predominant downwind direction to inhibit recycling of air into the sampler.

With the sampling head removed from the sampler and the flow control valve fully open, turn on the pump and allow it to warm up for 5 min to 10 min.

Load a test sampling module with the same type of filter and sorbent collection cartridge as will be used for sample collection and attach to the inlet of the air sampler pump. Turn on the pump and open the flow control valve fully. Adjust the flow regulator (e.g. voltage variator) so that a sample flowrate corresponding to approximately 110 % of the desired flow rate is indicated on the vacuum gauge (based on the previously obtained multipoint calibration curve).

Then remove the test sampling module and place the calibration orifice on the air sampling pump. Attach a manometer to the tap on the calibration orifice. Turn off the pump momentarily to set the zero level of the manometer. Then switch on the pump and record the manometer reading, once a stable reading is achieved. Then shut off the pump.

Use the calibration curve for the orifice to calculate sample flow from the data obtained in the previous step, and use the calibration curve for the flow control assembly to calculate sample flow from the data obtained with the test sampling module. Record the calibration data on an appropriate data sheet. If the two values do not agree within 10 %, inspect the sampler for damage, flow blockage, etc. If no obvious problems are found, recalibrate the sampler.

Turned off the air sampling pump again and check the zero reading of the vacuum gauge. Record ambient temperature, barometric pressure, elapsed-time meter setting, sampler serial number, filter number and sample number.

Now attach the loaded sampling module to the sampler and begin the sampling cycle. Activate the elapsed-time meter and record the start time. Adjust the flow, if necessary, using the flow control valve. Read and record the flowrate at least once a day during the sampling period. Record ambient temperature, barometric pressure and flowrates at the beginning and end of the sampling period (see example field data sheet shown in annex C).

At the end of the desired sampling period, carefully remove the sampling module and take to a clean area. Then perform a final flow check using the test sampling module. If calibration deviates by more than 10 % from the initial reading, mark the flow data for that sample as suspect, inspect the sampler and/or remove from service.

While wearing polyester or latex gloves, carefully remove the sorbent cartridge from the lower sampling module chamber and place on solvent-rinsed aluminium foil (the foil in which it was originally wrapped may be used). Then carefully remove the particle filter from its holder with clean PTFE-tipped forceps, fold in half twice (sample-side inward), and place inside the glass cartridge on top of the sorbent. Then return the cartridge to its original transportation container and write the appropriate information on the label. Keep the sealed sample containers refrigerated and protected from light for transport to the laboratory. Store the samples at 4 °C or below and for no longer than two weeks prior to extraction.

10.4 Field blank

At least 10 % of the samples, or a minimum of one per sampling site, shall be field blanks. If sampling is periodic or large numbers of samples are involved, take at least one blank at each site on each day of sampling.

11 Sample preparation

11.1 General

Set up the Soxhlet extractor in normal fashion in a fume hood and add the appropriate amount and volume of extraction solvent to the boiling flask. If the glass sorbent cartridge is to be extracted without first removing the sorbent, a 500 ml Soxhlet extractor and 1 000 ml boiling flask are required and the extraction solvent volume is 600 ml. If the sorbent is removed from the cartridge for extraction, a 200 ml extractor and 500 ml flask are adequate and only 300 ml of extraction solvent is required.

If PUF is the sorbent, the extraction solvent shall be 10 % volume fraction of diethyl ether in *n*-hexane. Alternatively, cyclohexane or toluene may be used for extraction of PUF [9], [13], [17], [21] and [30].

If XAD-2 resin is the sorbent, the extraction solvent may be either 10 % volume fraction of diethyl ether in *n*-hexane or 100 % dichloromethane. Alternatively, cyclohexane or toluene may be used if first validated by the user.

NOTE Some studies have suggested that dichloromethane is less efficient than toluene for extraction of PAH from carbonaceous particulate matter [30].

Remove the sampling cartridge from the sealed transportation containers using gloved hands and place on solvent-rinsed aluminium foil. Remove the folded particle filter from the cartridge with hexane-rinsed tweezers and place in the bottom of the Soxhlet extractor. If the glass sorbent cartridge is to be extracted, carefully rinse the outside walls with hexane before placing it into the extractor on top of the filter. If the sorbent is to be removed for extraction, it may be placed in a pre-extracted Soxhlet thimble for insertion into the extractor, or it may be placed directly into the extractor.

When PUF is used, it is recommended that the PUF plug be removed from the sampling cartridge with tweezers or tongs and compressed into a 200 ml Soxhlet extractor for extraction. Rinse the inside walls of the glass sampling cartridge with 10 ml to 20 ml of hexane into the extractor. Immediately prior to extraction, add 20 µl of the surrogate standard solution to the sorbent in the Soxhlet extractor to monitor recovery.

Add the surrogate standard solution containing dibromobiphenyl, decafluorobiphenyl, or selected deuterated PAH at 50 ng/µl of each in *n*-hexane or dichloromethane, as appropriate, to every sample and field blank.

Operate the Soxhlet extractors for 14 h to 24 h (typically overnight) at a reflux rate of about 4 cycles per hour. When the extract has cooled, pass it through a drying column containing about 10 g of pre-cleaned anhydrous sodium sulfate (see 8.9) and collect in a Kuderna-Danish (K-D) concentrator. Wash the extractor flask and drying column with 100 ml to 125 ml of *n*-hexane or dichloromethane, as appropriate, to complete the quantitative transfer. Carefully concentrate the extract in the K-D apparatus to 5 ml or less on a water bath at 60 °C to 65 °C.

Exercise care to prevent the K-D concentrator tube from going dry. If total evaporation occurs, discard the sample.

Drying with sodium sulfate should not be necessary for samples collected during dry weather. However, if XAD-2 is used as the sorbent and drying is not indicated, filter the extract through a clean particle filter to remove fine particles of the resin.

A vacuum rotary evaporator may be used to concentrate the extract to about 5 ml, if it can be demonstrated that acceptable recoveries of internal standards and targeted PAH are achieved. Exercise care to prevent all of the solvent from evaporating. If total evaporation occurs, discard the sample.

Carefully rinse the insides of the K-D concentrator flask and Snyder column with *n*-hexane or dichloromethane, as appropriate, into the 10-ml concentrator tube. Then place the concentrator in a water bath held at 30 °C to 40 °C and concentrate the extract to 1 ml or less under a gentle stream of nitrogen. (Alternatively, a micro-K-D concentrator fitted with a micro-Snyder column may be used for concentration.) Add the internal standards at this point (see 11.3) and adjust the final volume to 1,0 ml.

When dichloromethane is used, the water bath temperature shall not exceed 30 °C.

Exercise care to prevent the concentrator tube from going dry. If total evaporation occurs, discard the sample.

Volumetrically adjust concentrated sample extracts to 1,0 ml and add the internal standard. Mix the sample well and transfer to sealed brown vials for storage at 4 °C or lower until analysed.

Analyse final extracts within 30 days.

11.2 Sample cleanup

11.2.1 Column preparation

Extract silica gel, type 60, in a Soxhlet extractor with dichloromethane for 6 h (minimum rate, 3 cycles/h) and then activate by heating in a foil-covered glass container for 16 h at 150 °C.

Pack a small piece of glass wool into the bottom of a glass chromatography column of 15-ml to 25-ml capacity (e.g. 11,5 mm i.d. × 160 mm long) and slurry 10 g of activated silica gel into the column with pentane. Tap the column gently as the slurry is settling to assure proper packing. Finally, add 1 g of anhydrous sodium sulfate to the top of the silica gel. Prior to use, pre-elute the column with 40 ml of pentane and discard the eluate.

NOTE Cleanup procedures may not be needed for relatively clean matrix samples.

11.2.2 Column chromatography

While the pentane pre-eluant covers the top of the column, transfer 1 ml of sample extract in *n*-hexane to the column, and wash on with 2 ml of *n*-hexane to complete the transfer. Allow to elute through the column. Immediately prior to exposure of the sodium sulfate layer to the air, add 25 ml of pentane and continue elution. The pentane eluate may be discarded.

NOTE 1 This pentane fraction contains the aliphatic hydrocarbons collected on the filter/adsorbent combination. If desired, this fraction may be analysed for specific aliphatic organics.

If dichloromethane is used for extraction of the sample, it shall be solvent-exchanged with *n*-hexane. This can be accomplished by diluting the extract at least 2-fold with hexane and concentrating to 1 ml at 30 °C under a purified nitrogen stream. The dilution and concentration process should be repeated at least twice. Alternatively, a micro-K-D concentrator fitted with a micro-Snyder column may be used for concentration.

Finally, elute the column at 2 ml/min with 25 ml of dichloromethane in pentane (4:6 volume fraction) and collect in a 50 ml K-D flask equipped with a 5-ml concentrator tube for concentration to less than 5 ml. Concentrate further to 1 ml or less under a gentle stream of nitrogen as previously described.

NOTE 2 An additional elution of the column with 25 ml of methanol will elute polar (oxygenated, nitrated and sulfonated) PAH. This fraction may be analysed for specific polar PAH.

11.3 Internal reference standards addition

To use this approach, the analyst shall select one or more internal reference standards that are similar in chromatographic behaviour to the compounds of interest. For PAH, these are typically the deuterated analogs. The analyst shall further demonstrate that the measurement of the internal reference standard is not affected by method or matrix interferences. The following internal reference standards are suggested for the specific PAH as listed below:

Naphthalene-d₈	Perylene-d₁₂
Naphthalene	Perylene
	Benzo[a]pyrene
	Benzo[b]fluoranthene
	Benzo[k]fluoranthene
	Benzo[ghi]perylene
	Dibenz[a,h]anthracene
	Indeno[1,2,3-cd]pyrene
	Coronene
Acenaphthene-d₁₀	
Acenaphthene	
Acenaphthalene	
Fluorene	
Phenanthrene-d₁₀	Chrysene-d₁₂
Anthracene	Benz[a]anthracene
Fluoranthene	Chrysene
Phenanthrene	Cyclopenta[cd]pyrene
Pyrene	

Stock solutions of the appropriate deuterated internal standards are typically made up to concentrations of 50 ng/μl. They are added to sample extracts to achieve concentrations similar to those expected for the PAH in the samples to be analysed (e.g. 20 μl of stock solution would be added to the 1-ml sample extract to achieve a 1 ng/μl concentration corresponding to a 3 ng/m³ air concentration if 325 m³ of air is sampled). The final sample volume after addition of the internal standards is adjusted to 1,0 ml. The internal standards should be added immediately after sample cleanup (if any) and prior to storage in the freezer pending analysis.

NOTE Deuterated PAH standards contain traces of natural (undeuterated) PAH. If too much deuterated PAH standard is added, possible contamination of the sample from natural PAH in the deuterated standard may interfere with accurate quantification. Typically, air concentrations of PAH decrease with increasing ring number. Therefore, the concentrations of internal standards added should be lower for the larger PAH (e.g. 1 ng/μl for naphthalene-d₈, acenaphthalene-d₁₀ and phenanthrene-d₁₀, and 0,1 ng/μl for chrysene-d₁₂ and perylene-d₁₂).

12 Sample analysis

12.1 Instrumentation

Analyses are typically performed on a 70-eV electron impact ionization MS operated in the selected-ion monitoring mode (SIM). However, other types of mass spectrometers (e.g. ion trap), ionization modes (e.g. negative-ion chemical ionization), and ion monitoring modes (e.g. full scan) may be used if the user can demonstrate equivalent performance. A 30-m to 50-m × 0,25-mm capillary GC column coated with crosslinked 5 % phenyl methylsilicone (0,25 μm film thickness) or equivalent is recommended. Typical instrument parameters are:

- initial column temperature and hold time: 60 °C for 2 min;
- column temperature programme: 60 °C to 290 °C at 8 °C/min;

- final hold time (at 290 °C): 12 min;
- injector: Grob-type, splitless (for 0,5 min to 1 min);
- injector temperature: 275 °C to 300 °C;
- transfer line temperature: 275 °C to 300 °C;
- source temperature: According to manufacturer 's specifications;
- injection volume: 1 µl to 3 µl;
- carrier gas: Helium at a flow velocity of 30 cm/s to 40 cm/s.

A typical gas chromatogram of PAH standards obtained under these conditions is shown in Figure D.1 in annex D.

NOTE 1 Alternative mass spectrometric instruments, such as ion traps and tandem MS (MS-MS), as well as other ionization techniques or ion monitoring modes, may be used and provide equal or better analytical sensitivity. On-column injection may also provide better sensitivity, but this technique requires careful maintenance to assure optimal column performance.

NOTE 2 When dichloromethane is used, the initial column temperature can be lowered to 40 °C; however, little, if any improvement in column performance is expected.

NOTE 3 For higher resolution (e.g. partial separation of benzo[b]fluoranthene and benzo[k]fluoranthene), a 4 °C/min to 5 °C/min column temperature programme may be used, with resultant increase in analysis time.

12.2 Instrument calibration

Calibration standards of native PAH are prepared at a minimum of three concentration levels for each PAH of interest. This is accomplished by adding appropriate volumes of one or more stock standards to a volumetric flask. One of the calibration standards shall be at a concentration near, but above, the minimum detection limit (MDL) and the other concentrations shall correspond to the expected range of concentrations found in real samples or shall define the working range of the GC/MS system.

The minimum acceptable ion intensity is instrument-dependent. However, quantitative results shall not be reported below the lowest calibration level. The lowest calibration level shall be sufficiently above the instrument noise level to provide precision between replicate analyses of 20 % relative standard deviation or better. Typically a signal-to-noise ratio of 3:1 is acceptable for compound identification. For quantification, the signal-to-noise ratio shall be at least 7:1.

Each of the calibration standards shall contain the appropriate deuterated internal standards at the specified concentration.

Analyse injections (1 µl to 3 µl) of each standard solution and plot the area ratio of the primary ions of the analyte and the corresponding internal standard against the concentration for each compound and internal standard. The response factor (R_f) for each analyte is calculated using the following equation:

$$R_f = \frac{A_s \rho_{is}}{A_{is} \rho_s}$$

where

A_s is the peak area of the primary ion for the analyte to be measured;

A_{is} is the peak area of the primary ion for the internal standard;

ρ_s is the mass concentration of the analyte to be measured, in nanograms per microlitre;

ρ_{is} is the mass concentration of the internal standard, in nanograms per microlitre.

The base peak ion is usually selected as the primary ion for quantification of the standards. If interferences are noted, use the next two most intense ions as the secondary ions. Table E.1 in annex E lists key ions for selected deuterated internal standards. These standards may also serve as retention-time standards. The internal standards are added to all calibration standards and all sample extracts analysed by GC/MS.

If the R_f is constant over the working range ($< 20\%$ RSD), the R_f can be assumed to be invariant and the average R_f can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_S/A_{IS} , vs. R_f .

Verify the working calibration curve or R_f on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than $\pm 20\%$, repeat the test using a fresh calibration standard. Alternatively, prepare a new calibration curve. The relative retention times for each compound in each calibration run shall agree within 0,03 relative retention time units.

12.3 Analysis

Remove the sample extracts from cold storage (if appropriate) and allow to warm to room temperature. Once the GC and MS are properly set up, make 1 μ l to 3 μ l injections of each sample extract and note the MS response. Select a minimum of two ions per compound for monitoring. A minimum dwell time of 100 ms per peak is recommended. Typical characteristic ions for selected PAH are outlined in annex E.

In SIM analysis, analyte identification is based on retention times and qualifier ion ratios. There are no mass spectra to compare. If secondary ions are included for monitoring, method detection limits will be significantly reduced since relative abundances of these ions are low for PAH. Therefore, presence of the primary ion coupled with the relative retention time or index (relative to the corresponding deuterated internal standard) may be more a practical approach to identification when a low detection limit is required. When the ratio (r) of the retention time (t_R) of the unknown analyte u to that of the corresponding internal standard I (where $r = t_{R,u}/t_{R,I}$) is used to identify the analyte, the ratio of retention times r_s from the sample chromatogram shall not be greater than 0,4 % of the retention time ratio r_c from the chromatogram of the calibration standard. The value of r shall not be larger than 2 or smaller than 0,5. The retention index of the sample analyte and corresponding standard shall agree within $\pm 2\%$.

The abundance ratio of the major characteristic ions of the analyte and corresponding calibration standard shall agree within $\pm 30\%$. If the response for any quantification ion exceeds the initial calibration curve range of the GC/MS system, dilute the extract. Add additional internal standard solution to the diluted extract to maintain the required concentration (e.g. 1 ng/ μ l to 10 ng/ μ l) of each internal standard in the extract. Reanalyse the diluted extract.

When an analyte has been identified, the quantification of that analyte will be based on the integrated abundance from the monitoring of the primary characteristic ion. Quantification is accomplished by the internal standard technique. The internal standard used is that having a retention time nearest that of a given analyte. The peak maxima of specified characteristic ions of the analyte shall be coincident, within $\pm 0,03$ relative retention-time units, to the retention-time maxima of the designated internal standard.

Carry-over contamination may occur when a sample containing low concentrations of PAH is analysed immediately after a sample containing high concentrations of PAH or PAH standard solutions. A solvent rinse shall be used to verify that there is no carry-over.

13 Calculations

The mass concentration, in nanograms per microlitre (ng/ μ l), of each identified analyte in the sample extract is calculated as follows:

$$\rho_{PAH} = \frac{A_x \rho_{IS}}{A_{XS} R_f}$$

where

A_x is the peak area of characteristic ion(s) for analyte being measured;

A_{xs} is the peak area of characteristic ion(s) for internal standard;

R_f is the response factor.

The air volume is calculated from the periodic flow readings taken during sampling using the following equation:

$$V_m = \frac{q_1 + q_2 \dots q_n}{n} \times \frac{t}{1\,000}$$

where

V_m is the total sample volume under ambient conditions, in cubic metres;

$q_1, q_2 \dots q_n$ are the flowrates determined at the beginning, end, and intermediate points during sampling, in litres per minute;

n is the number of data points;

t is the elapsed sampling time, in minutes.

The volume of air sampled may optionally be converted to reference conditions of temperature and pressure (25 °C and 101,3 kPa) using the following equation:

$$V_s = V_m \times \frac{p_A}{101,3} \times \frac{298}{273 + T_A}$$

where

V_s is the total sample volume at reference conditions (25 °C; 101,3 kPa), in cubic metres;

V_m is the total sample volume under ambient conditions, in cubic metres;

p_A is the ambient pressure, in kilopascals;

T_A is the ambient temperature, in degrees Centigrade.

The mass concentration, in nanograms per cubic metre, of each analyte in the air sampled is given by:

$$\rho_a = \frac{\rho_e V_e}{V_s}$$

where V_e is final volume of extract, in microlitres.

14 Quality assurance

Users shall generate standard operating procedures (SOPs) describing the following activities in their laboratory: assembly, calibration, and operation of the sampling system, mentioning the manufacturer and model of equipment used; preparation, purification, storage, and handling of sampling reagent and samples; assembly, calibration, and operation of the GC/MS system, mentioning make and model of equipment used; and all aspects of data recording and processing, including lists of computer hardware and software used.

The SOPs shall provide specific stepwise instructions and shall be readily available to and understood by the laboratory personnel conducting the work. The SOPs shall be consistent with this International Standard.

Calibration standards shall be freshly prepared every one to two months, and checked for accuracy against commercially available PAH standard mixtures.

NOTE Standard reference materials of PAH mixtures are commercially available.

Calibration standards shall be analysed before and after each set of samples that are injected into the GC/MS.

A performance standard such as fluoranthene-d₁₀ or other suitable surrogate may be added to the purified sample extract prior to analysis to monitor instrument/operator variability.

Recovery efficiencies of the isotopically-labelled PAH surrogates added to the samples prior to extraction and analysis shall be closely monitored to assure the effectiveness of sample work-up and analytical procedures. The surrogate recoveries should fall between 75 % to 125 % mass fraction. Samples for which surrogate recoveries are less than 50 % or more than 150 % mass fraction shall be discarded.

Approximately 10 % of the sample extracts shall be subjected to duplicate GC/MS analysis to assure acceptable analytical precision.

To assure acceptable analytical accuracy, periodic analyses shall be made of a known standard reference material.

15 Method detection limit, uncertainty and precision

The detection limit of this method is proportional to sample volume. A 350 m³ sample will afford method detection limits of less than 0,05 ng/m³. Concentration of sample extracts to less than 1 ml in volume prior to analysis will lower the detection limit, but introduce the risk of analyte losses, particularly of two-ring and three-ring PAH. High-resolution mass spectrometry can also improve sensitivity.

Precision and uncertainty will vary with sample volume and analyte concentration. Precision should be at least ± 25 % and uncertainty ± 50 %.

Analysis of collocated samples of 150 m³ of ambient air collected in two U.S. cities over a one-year period have yielded an overall mean standard deviation of 13 % (range 0,03 % to 45,3 %) for 18 PAH (naphthalene through coronene) [6]. The performance characteristics of the analytical method described here are summarized in Table A.1.

Annex A (normative)

Performance characteristics

Table A.1 — Summary of performance characteristics of the analytical method

Range of method	Naphthalene to coronene at 0,05 ng/m ³ to 1 000 ng/m ³
Detection limit	≤ 0,05 ng/m ³ for 350 m ³ sample volume
Sampling rate	≤ 250 l/min
Air sampler flow control	± 10 %
Sampling efficiency	Goal: 75 % to 125 %; acceptable: 50 % to 150 %
Surrogate recovery	Goal: 75 % to 125 %; acceptable: 50 % to 150 %
Media blanks	< 10 ng (< 50 ng for naphthalene and phenanthrene)
Reference standards	98 % mass fraction purity or better
Replicate samples	10 % or more (at least one)
GC retention times	Ratio of the retention times of the analyte to those of the corresponding internal standard shall fall between 0,5 and 2. Peak maxima shall agree within 0,03 relative retention-time units.
Precision	± 25 % or better
Overall uncertainty	± 50 % or better

Annex B (informative)

Physical properties of selected PAH

Table B.1 — Formulae and physical properties of selected PAH [8]

Compound (common name)	Formula	Molecular weight	Melting point °C	Boiling point ^a °C	Vapour pressure kPa at 25 °C
Naphthalene	C ₁₀ H ₈	128,18	80,2	218	1,1 × 10 ⁻²
Acenaphthylene	C ₁₂ H ₈	152,20	92 to 93	265 to 280	3,9 × 10 ⁻³
Acenaphthene	C ₁₂ H ₁₀	154,20	90 to 96	278 to 279	2,1 × 10 ⁻³
Fluorene	C ₁₃ H ₁₀	166,23	116 to 118	293 to 295	8,7 × 10 ⁻⁵
9-Fluorenone	C ₁₃ H ₈ O	180,21	84	341,5	ca. 10 ⁻⁵
Anthracene	C ₁₄ H ₁₀	178,24	216 to 219	340	3,6 × 10 ⁻⁶
Phenanthrene	C ₁₄ H ₁₀	178,24	96 to 101	339 to 340	2,3 × 10 ⁻⁵
Fluoranthene	C ₁₆ H ₁₀	202,26	107 to 111	375 to 393	6,5 × 10 ⁻⁷
Pyrene	C ₁₆ H ₁₀	202,26	150 to 156	360 to 404	3,1 × 10 ⁻⁶
Cyclopenta[<i>cd</i>]pyrene	C ₁₈ H ₁₀	226,28	ca. 275?	—	ca. 10 ⁻⁷
Benz[<i>a</i>]anthracene	C ₁₈ H ₁₂	228,30	157 to 167	435	1,5 × 10 ⁻⁸
Chrysene	C ₁₈ H ₁₂	228,30	252 to 256	441 to 448	5,7 × 10 ⁻¹⁰
Retene	C ₁₈ H ₁₈	234,34	101	390	ca. 10 ⁻⁶
Benzo[<i>b</i>]fluoranthene	C ₂₀ H ₁₂	252,32	167 to 168	481	6,7 × 10 ⁻⁸
Benzo[<i>k</i>]fluoranthene	C ₂₀ H ₁₂	252,32	198 to 217	480 to 481	2,1 × 10 ⁻⁸
Perylene	C ₂₀ H ₁₂	252,32	273 to 278	500 to 503	7,0 × 10 ⁻¹⁰
Benzo[<i>a</i>]pyrene	C ₂₀ H ₁₂	252,32	177 to 179	493 to 496	7,3 × 10 ⁻¹⁰
Benzo[<i>e</i>]pyrene	C ₂₀ H ₁₂	252,32	178 to 179	493	7,4 × 10 ⁻¹⁰
Benzo[<i>ghi</i>]perylene	C ₂₂ H ₁₂	276,34	275 to 278	525	1,3 × 10 ⁻¹¹
Indeno[1,2,3- <i>cd</i>]pyrene	C ₂₂ H ₁₂	276,34	162 to 163	—	ca. 10 ⁻¹¹
Dibenz[<i>a,h</i>]anthracene	C ₂₂ H ₁₄	278,35	266 to 270	524	1,3 × 10 ⁻¹¹
Coronene	C ₂₄ H ₁₂	300,36	438 to 440	525	2,0 × 10 ⁻¹³

^a Many of these compounds sublime at temperatures below the boiling point.