BRITISH STANDARD

BS ISO
11338-2:2003

Stationary source emissions — Determination of gas and particle-phase polycyclic aromatic hydrocarbons —

Part 2: Sample preparation, clean-up and determination

ICS 13.040.40

National foreword

This British Standard reproduces verbatim ISO 11338-2:2003 and implements it as the UK national standard.

The UK participation in its preparation was entrusted by Technical Committee EH/2, Air quality, to Subcommittee EH/2/1, Stationary source emissions, which has the responsibility to:

— aid enquirers to understand the text;

— present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;

— monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this subcommittee can be obtained on request to its secretary.

Cross-references

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Stationary source emissions — Determination of gas and particle-phase polycyclic aromatic hydrocarbons —

Part 2: Sample preparation, clean-up and determination

Émissions de sources fixes — Détermination des hydrocarbures aromatiques polycycliques sous forme gazeuse et particulaire —

Partie 2: Préparation des échantillons, purification et détermination

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Contents

Page

Foreword ... iv

Introduction ... v

1 Scope ... 1

2 Normative references ... 1

3 Terms and definitions ... 1

4 Principle ... 2
4.1 Sampling ... 2
4.2 Analysis ... 2

5 Safety measures ... 2

6 Procedures ... 2
6.1 HPLC method ... 2
6.2 GC-MS method ... 9

7 Limitations and interferences ... 16
7.1 Limitations ... 16
7.2 Interferences ... 17

Annex A (informative) **Maximum UV absorption wavelength and recommended combinations of excitation-emission wavelengths for HPLC** ... 18

Annex B (informative) **Formulae and physical properties of selected PAH** ... 19

Annex C (informative) **Characteristic ions for GC-MS detection of selected PAH, recovery, and surrogate recovery standards** ... 20

Annex D (informative) **Applicability of internal standards for GC-MS detection of selected PAH** ... 21

Annex E (normative) **Summary of performance characteristics of the HPLC method** ... 22

Bibliography ... 23

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 2.

The main task of technical committees is to prepare International Standards. 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 document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 11338-2 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 1, *Stationary source emissions*.

ISO 11338 consists of the following parts, under the general title *Stationary source emissions — Determination of gas and particle-phase polycyclic aromatic hydrocarbons*:

— *Part 1: Sampling*

— *Part 2: Sample preparation, clean-up and determination*

Introduction

This part of ISO 11338 describes procedures for sample preparation, clean-up and analysis of polycyclic aromatic hydrocarbons (PAHs) (collected from stack and waste gases), based on either high performance liquid chromatography (HPLC) (see Annexes A and E) or gas chromatography-mass spectrometry (GC-MS) (see Annexes B, C and D).

PAHs are emitted to the atmosphere primarily by the combustion of fossil fuels and wood. PAHs are considered to be an important class of environmental carcinogens. The identification and quantification of PAHs emitted from stationary sources represent a critical aspect in the assessment of air quality.

Stack and waste gases emitted from stationary sources often contain solid particles. Because of the range of their vapour pressures, PAHs are distributed between gas and particle phases. In the atmosphere, PAHs containing four or more rings tend to adsorb onto particles, while PAHs containing two to four rings tend to be present in gaseous form. However in stack and waste gases, the distribution of PAHs between gas and particle phases depends on the temperature, the mass of emitted particles, particle size, humidity, type and concentration of PAH.

During sampling, sample storage and preparation of the sample, losses of PAH can occur and prevent quantitative analysis. These losses can be the result of the volatility of two- and three-ring PAHs, the physical-chemical instability of PAHs in the presence of light, O_3, NO_x, SO_2, HCl and certain heavy metals.

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Stationary source emissions — Determination of gas and particle-phase polycyclic aromatic hydrocarbons —

Part 2:
Sample preparation, clean-up and determination

1 Scope

This part of ISO 11338 specifies procedures for sample preparation, clean-up and analysis for the determination of gas and particle-phase polycyclic aromatic hydrocarbons (PAH) in stack and waste gases. The analytical methods are capable of detecting sub-microgram concentrations of PAH per cubic metre of sample, depending on the type of PAH and the flue gas volume sampled.

The methods described in this part of ISO 11338 are based on either high performance liquid chromatography (HPLC) or gas chromatography-mass spectrometry (GC-MS).

NOTE ISO 11338-1 describes three methods and specifies minimum requirements for the sampling of PAH in stack and waste gases.

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.

ISO 4225:1994, *Air quality — General aspects — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 4225 and the following apply.

3.1
polycyclic aromatic hydrocarbon
PAH
compound that contains two or more fused aromatic rings made up of carbon and hydrogen atoms

3.2
stationary source emission
gas emitted by a stationary plant or process and transported to a chimney for dispersion into the atmosphere

3.3
accelerated solvent extractor
ASE
equipment that accelerates the traditional extraction process by using solvent at elevated temperatures

NOTE Pressure is applied to the sample extraction cell to maintain the heated solvent in a liquid state during the extraction.

4 Principle

4.1 Sampling

A representative sample is collected from the gas passing through a duct under isokinetic conditions with the use of a suitable sampling device. The particulate phase is collected on a suitable filter and the gas phase is trapped by condensation onto an adsorbent [e.g. styrene-divinylbenzene polymer resin (XAD-2), polyurethane foam or other adsorbent of comparable efficiency].

4.2 Analysis

After sampling, the sample is removed from the sampling equipment. The parts of the sampling equipment which have been in contact with the sample are washed with solvent. The washings are then combined with the filter(s) and adsorbent and then extracted with a suitable organic solvent, with the use of a Soxhlet extractor [or other validated method, e.g. accelerated solvent extractor (ASE)]. The extract is concentrated by means of a rotary evaporator, followed by further concentration under nitrogen if necessary. Sample clean-up may be necessary before quantification.

An aliquot of the concentrated sample is analysed either by reversed phase high performance liquid chromatography (HPLC) or by gas chromatography-mass-spectrometry (GC-MS). The concentration of each PAH is calculated from the mass of PAH (particle- and gas-phase) determined during analysis and the volume of flue gas sampled corrected to appropriate reference conditions.

5 Safety measures

All PAH should be treated as potential carcinogens. The user should be familiar with the chemical and physical properties of PAH. Measures shall be taken to prevent PAH in solid form, extract or solution coming into contact with the body. PAH can co-distil with the solvent and may cling to the outside of glassware with ground glass stoppers.

Owing in particular to the risks associated with working with PAH in solid form, self-preparation of standard solutions is ill-advised. The use of commercially available standard solutions[1)] minimizes the risk of exposure.

All glassware containing PAH solutions shall therefore be handled with solvent-resistant gloves. Any contamination can be revealed in ultraviolet light by fluorescence. PAH are most dangerous in solid form, becoming electrostatically charged. Therefore PAH should be weighed in a glove box. Unused samples and contaminated equipment, glassware and clothing shall be disposed of properly, taking into account the relevant regulations.

6 Procedures

6.1 HPLC method

6.1.1 General

This subclause describes the preparation, sample clean-up and analytical method for determining the concentration of polycyclic aromatic hydrocarbons (PAH) in stack and waste gases using high pressure liquid chromatography (HPLC).

1) Standard Reference Material (SRM) 1647: Priority Pollutant Polynuclear Aromatic Hydrocarbons, a certified solution of 16 PAH in acetonitrile. This solution is an example of a suitable product available commercially from The National Institute of Standards and Technology (NIST), US Department of Commerce, Gaithersburg, MD, USA. This information is given for the convenience of users of this part of ISO 11338 and does not constitute an endorsement by ISO of this product.

6.1.2 Reagents and materials

6.1.2.1 **Acetonitrile**, HPLC grade.

6.1.2.2 **n-Hexane**, HPLC grade.

6.1.2.3 **Methanol**, HPLC grade.

6.1.2.4 **Pentane**, HPLC grade.

6.1.2.5 **Diethyl ether**, reagent grade, preserved with 2 % ethanol, HPLC grade.

6.1.2.6 **Silica gel**, high purity grade, type 60, 70 mesh to 23 mesh.

6.1.2.7 **Sodium sulfate**, anhydrous, reagent grade, dried by heating at 300 °C for at least 4 h.

6.1.2.8 **Recovery standards for HPLC**: 2-methylchrysene or 6-methylchrysene, purity at least 98 %.

6.1.2.9 **Compressed gases**: high purity helium for degassing the mobile phase and high purity nitrogen for sample concentration.

6.1.2.10 **Aluminium foil**.

6.1.2.11 **Glass wool.**

6.1.3 Apparatus

6.1.3.1 **Soxhlet extractor**, capacity 100 ml to 200 ml, and appropriate condenser.

6.1.3.2 **Glass-fibre filter**, precleaned by heating for 3 h at 200 °C or to an acceptable blank level.

6.1.3.3 **Round-bottom flasks**, capacity 100 ml and either 250 ml or 500 ml depending on the capacity of the Soxhlet extractor.

6.1.3.4 **Rotary evaporator system**, capable of producing a maximum vacuum of 0,1 MPa (1,0 bar), and with a water bath that can be heated to 50 °C.

6.1.3.5 **Kuderna Danish concentrators**, capacity 500 ml, including 10 ml graduated concentrator tubes with ground-glass stoppers, and a 3-ball macro-Snyder column.

6.1.3.6 **Nitrogen evaporative concentrator**: nitrogen blow-down apparatus with flowrate control and temperature-controlled water bath, evaporator tubes of volume 1 ml to 10 ml.

6.1.3.7 **Separation funnels**, of capacity 100 ml and 250 ml.

6.1.3.8 **Glass chromatography column**.

6.1.3.9 **Conical tubes**, of 10 ml capacity.

6.1.3.10 **Extraction thimbles**, pre-extracted with methanol.

6.1.3.11 **Laboratory refrigerator**, capable of cooling to less than 4 °C or **freezer**, capable of cooling to less than −15 °C.

6.1.3.12 **Bumping granules**, solvent extract.

6.1.3.13 **Oven**, capable of maintaining 500 °C.

6.1.3.14 High Performance Liquid Chromatography (HPLC) system, consisting of constant-flow pumps adjusted with gradient controller, an injector capable of injecting sample volumes up to 20 µl, a means of controlling the column temperature within the range 29 °C to 40 °C ± 1 °C, a fluorescence detector with programmable excitation and emission wavelengths and a UV detector adjusted to a wavelength of 229 nm, and accessories including column supplies, recorders and gases.

6.1.3.15 HPLC separation column, of glass or stainless steel [20 mm to 250 mm long and 3 mm to 4,6 mm internal diameter (ID)], based on silica, derivatized with C18 alkyl chains, of particle size 3 µm to 5 µm.

6.1.3.16 HPLC guard column, stainless steel column for use in reversed phase chromatography (10 mm long by 2 mm ID, screen mesh < 1 µm, frit 0,5 µm) or other suitable columns**.**

Guard columns should always be used, because sample and eluent contamination can result in excessive column pressures leading to altered selectivity.

6.1.3.17 Degassing system for HPLC, helium

Eluents should be degassed to avoid quenching of the fluorescence signal.

6.1.3.18 Filtration system, including filter of pore size 45 µm for filtration of mobile phase.

6.1.3.19 Syringes, 10 µl, 25 µl, 50 µl, 100 µl, 250 µl, 500 µl and 1 000 µl for preparing calibration, reference standard and spiking solutions.

6.1.4 Sample preparation

6.1.4.1 Storage conditions of samples

Owing to possible reactions of PAH with light and components present in air, all sampling parts containing PAH should be stored until required for laboratory preparation, in sealed containers protected from light and at temperatures either between 0 °C to 4 °C or below –15 °C. Samples stored between 0 °C to 4 °C shall be extracted within one week after sampling has been completed. If samples are stored at a temperature of −15 °C or below, extraction shall take place within one month. Any condensate shall be acidified with hydrochloric acid to pH ≈ 2, and may then be stored for up to 14 days.

6.1.4.2 Extraction of filters and solid sorbents

Remove the filter and solid sorbents from their sealed containers and place in the pre-extracted Soxhlet thimble. Immediately prior to extraction add 500 µl of the recovery standard, 2- or 6-methylchrysene (6.1.2.8) in acetonitrile (mass concentration of ≈ 1 µg/ml), to the sorbent or filter in order to determine the recovery of the extraction procedure. If separate analyses of the sorbent and filter are required, both shall be spiked.

Carry out the extraction with 10 % diethyl ether (6.1.2.5) in n-hexane (6.1.2.2) for approximately 20 h, at a reflux rate of 4 cycles per hour.

Add the recovery standard to all related samples, including field and method blanks.

Alternatively, other extraction techniques (e.g. ASE) or other solvents or solvent mixtures may be used if validated by the user.

6.1.4.3 Extraction of condensate

Transfer the condensate into the separation funnel. Rinse the impingers or condensate flasks with n-hexane (6.1.2.2) and transfer the n-hexane to the separation funnel. Shake for at least 5 min. Allow to settle and then separate the n-hexane from the condensate. Carry out a further extraction on the condensate under the same conditions and combine the n-hexane fractions. Dry the combined n-hexane fractions over sodium sulfate (6.1.2.7).

The volume of n-hexane used in each of the two extractions shall be at least 20 % of the volume of the condensate.

6.1.4.4 Concentration of the extract

Combine the dried n-hexane extracts of the condensate with the extract of the filter and solid sorbent. Filter the combined extracts over a pre-cleaned glass-fibre filter (6.1.3.2) and transfer to the rotary evaporator. Concentrate the extract to a volume of approximately 2 ml. Transfer the extract quantitatively with n-hexane to a calibrated 10 ml conical tube. Add 1 ml of acetonitrile (6.1.2.1) to the tube. Then place the tube in a water bath at 25 °C and concentrate the extract under a gentle stream of nitrogen until the hexane (upper layer) and a small part of the acetonitrile is evaporated. Adjust the volume of the concentrated sample extracts to 1,0 ml with acetonitrile.

Mix the sample well and transfer to sealed brown vials for storage at less than 4 °C, protected from light, until analysed. Concentrated extracts should be analysed within 30 days.

A rotary evaporator (6.1.3.4) may be used with a vacuum of approximately 0,1 MPa pressure and a water bath at a temperature not exceeding 45 °C. If validated by the user, other evaporation systems may be used to concentrate the extract. If the extract is concentrated to dryness, substantial losses of PAH may occur; therefore the sample should be discarded where this has occurred.

Other evaporation systems to concentrate the extract may be used if validated by the user.

NOTE 1 Concentrating the sample extract to a volume of 1 ml may not be needed, depending on the target detection limits, the sensitivity of the detector and the flue gas volume sampled.

NOTE 2 The last evaporation step with the use of nitrogen is the most critical aspect in sample preparation. Losses of volatile PAH due to the final concentration step of sample extracts can lead to losses up to 10 % for 2- to 4-ring PAH if n-hexane is the extraction solvent. If toluene is used as extraction solvent, losses up to 10 % to 40 % for 2- to 4-ring PAH can be expected.

6.1.4.5 Sample clean-up

6.1.4.5.1 General

Clean-up procedures may not be necessary for relative clean matrices. Complex matrices require a purification stage, to eliminate interferences caused by the presence of polar and non-polar compounds.

If dichloromethane is used for extraction of the sample, it should be solvent-exchanged with n-hexane prior to the clean-up procedure.

6.1.4.5.2 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 450 °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. 160 mm long × 11,5 mm ID). Slurry 10 g of the activated silica gel with pentane and pour into the column. 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.

6.1.4.5.3 Column chromatography

Prior to use, pre-elute the column with 40 ml of pentane and discard the eluate. While the pentane pre-eluent still covers the top of the column, quantitatively transfer 1 ml of sample extract in n-hexane to the column, and wash on with a further 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.

Finally, elute the column with 25 ml of dichloromethane in pentane (4:6 volume ratio) at 2 ml/min and collect in a 100 ml round-bottomed flask (6.1.3.3). Further concentrate the extract to a volume of ~2 ml to 5 ml. Transfer the extract quantitatively to a 10 ml conical tube (6.1.3.9). Transfer the tube to a water bath at 25 °C and concentrate the extract to near dryness under a gentle stream of nitrogen. Then solvent-exchange the sample extracts with acetonitrile and adjust the volume to 1,0 ml.

Clean-up columns are commercially available and may be used, if validated.

NOTE 1 The pentane fraction contains the aliphatic hydrocarbons. If required, this fraction can be analysed for specific aliphatic hydrocarbons.

NOTE 2 An additional elution of the column with 25 ml of methanol will elute polar compounds (e.g. oxygenated, nitrated and sulfonated PAH).

6.1.5 Sample analysis

6.1.5.1 Instrumentation

HPLC analysis is performed on an analytical system consisting of constant-flow pumps adjusted with a gradient controller, injector, column heater, fluorescence detector with programmable excitation and emission wavelengths, and a UV detector adjusted to a wavelength of 229 nm.

Typical instrument parameters are:

— Column: glass or stainless steel, 200 mm long, 4,6 mm ID;

— Stationary phase: silica derivatized with C18 alkyl chains, particle size 5 µm;

— Mobile phase: solvent A acetonitrile/water (50 % volume fraction)
solvent B acetonitrile (100 % volume fraction)
linear gradient, with respect to time, changing from 100 % solvent A to 100 % solvent B;

— Flowrate: 0,8 ml/min;

— Injection volume: 20 µl;

— Column temperature: (29 ± 1) °C.

A fluorescence detector with programmable wavelengths should be used for more selectivity in complex matrices. The excitation and emission wavelength combinations can be optimized for each component. An example is given in Annex A. Acenaphthylene is determined by UV (at 229 nm) because this component does not exhibit fluorescence.

A minimum column length of 20 cm is desirable for sufficient peak separation. In order to achieve proper results, injection volumes of 100 µl or more, column lengths of 15 cm or less and gradients of 25 min or less should be avoided. Typical gradient time is about 40 min to 60 min.

NOTE 1 Choice of mobile phase, injection volume and flowrate depends on manufacturer's column specifications.

NOTE 2 Diode-array detectors provide an opportunity to improve selectivity by using the entire UV spectrum of a compound in order to identify false positives.

6.1.5.2 Instrument calibration

Prepare calibration standards of individual PAH at a minimum of five concentration levels by adding appropriate volumes of stock standards to a volumetric flask. The lowest concentration shall be at a level near the quantification limit.

The standard solutions are directly injected and analysed, and the heights of the analyte peaks are plotted against the concentration for each compound.

Determine the linear range for each compound by using linear regression, with peak height as a function of concentration, and calculate the linear best-fit straight line. Determine the residuals of the measured values against the fitted straight line. If the individual residuals are all less than 5 % of the fitted value, the instrument is taken to be linear over the entire concentration range used. If any of the residuals is more than 5 %, the concentration area is reduced by eliminating the measured value of the highest concentration and once again, via linear regression, a straight line is calculated and checked.

If the linearity of the system has been established over the range of concentration of interest, a one-point calibration can be used for daily quantification. In case any significant part of the instrument is replaced, repeat linearity checks should take place.

NOTE With chromatographic techniques, it is customary to use peak areas; however in view of the resolution capability of HPLC columns and the complexity of the resulting chromatogram from emission samples, peak heights are used for calculations.

6.1.5.3 Analysis

If the sample extracts are removed from cold storage, allow them to warm to room temperature before analysis. Once the HPLC system is set up, make 20 µl injections of each sample extract. Determine the retention times of the individual peaks and identify them against the chromatogram of the calibration standards.

The retention times of the sample analyte and corresponding calibration standard should not differ by more than 0,2 min. In case of greater retention time shifts with regard to the calibration standard, an extra identification can be made by using a diode-array detector or by GC-MS.

Measure the peak height of individual peaks, using a correctly positioned baseline. Each sample is, in principle, analysed undiluted. If compounds fall outside the linear field of the detector, dilute the sample and re-analyse.

During HPLC analysis of PAH, both UV and fluorescence detections shall be used. Acenaphthylene shall be analysed with UV detection. The other 15 PAH should be analysed with fluorescence detection.

Carry-over contamination can occur when a sample containing low concentrations of PAH is analysed immediately after a sample containing high concentrations of PAH. A solvent injection between samples can be used to verify that there is no carry-over between samples.

6.1.6 Calculation

Starting from the measured peak heights, and using the calibration data from the standard solution(s) analysed and the quantity of PAH present in the sample extract, calculate as follows:

$$m = \frac{F \cdot \rho \cdot V \cdot d_{\mathrm{f}}}{F_{\mathrm{s}}} \qquad (1)$$

where

m is the mass of the PAH compound in the sample extract, in nanograms;

F is the peak height of the relevant PAH in the sample extract;

ρ is the mass concentration of the respective PAH in the standard solution, in nanograms per millilitre;

F_{s} is the peak height of the respective PAH in the standard solution;

V is the final volume of the sample extract, in millilitres;

d_{f} is the factor resulting from possible concentration or dilution of the sample extract.

PAH emission levels are expressed as the mass of PAH per dry standard cubic metre of waste gas and reference oxygen (or carbon dioxide) content.

Taking the volume referred to standard conditions (273,15 K, 1013,25 kPa dry), calculate the gas sample entrained in terms of the PAH concentration in the gas stream, expressed in micrograms per cubic metre (dry).

The mass concentration of each PAH in the waste gas is calculated as follows:

$$\rho_i = \frac{m_{\mathrm{a},i}}{V_{\mathrm{nr}}} \tag{2}$$

where

ρ_i is the mass concentration of analyte i in the waste gas, in micrograms per cubic metre;

$m_{\mathrm{a},i}$ is the mass of analyte i found in the extract, in micrograms;

V_{nr} is the volume, in cubic metres, of the waste gas sample, under standard dry and reference conditions.

Calculate the recovery efficiency, E_{rec} (%), from the recovery standard using:

$$E_{\mathrm{rec}} = \frac{c_{x,y} \cdot V_y}{c_{x,\mathrm{add}} \cdot V_{x,\mathrm{add}}} \times 100 \tag{3}$$

where

$c_{x,y}$ is the concentration of recovery standard x in the injection extract;

V_y is the volume of injection extract y;

$c_{x,\mathrm{add}}$ is the concentration of recovery standard x added to the sample;

$V_{x,\mathrm{add}}$ is the volume of recovery standard solution added to the sample.

6.1.7 Quality assurance

Calibration standards shall be prepared at least every six months. The accuracy shall be determined by comparing the calibration standard to a commercially available reference material[1)]. Calibration standards shall be analysed immediately before and after every tenth sample that is injected into the HPLC.

Recovery efficiencies of the 2- or 6-methylchrysene 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 recoveries should fall between 50 % and 150 %. Results from samples for which surrogate recoveries are less than 50 % or more than 150 % shall be discarded.

PAHs analyte concentrations should not be corrected for the recovery efficiency.

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

To assure acceptable analytical accuracy, periodic analyses shall be made of a known standard reference material[2)].

A field blank shall be taken with each set of emission measurements and a laboratory blank shall be processed with each batch of samples. In order to reduce the frequency of rejection of samples, it is suggested that at least one set of the reagents and matrices to be used during sampling be analysed, using the procedures described below, before the batch is considered acceptable for use.

A blank level of < 10 ng/sample for single compounds is considered to be acceptable. Blank levels of < 10 ng/sample may not be achievable for naphthalene or phenanthrene. However, since these compounds are typically present at relatively high concentrations, a blank level of < 50 ng/sample is usually acceptable. For the results to be acceptable, the amount of a given PAH in the field blank shall be less than 10 % of the amount of that compound measured in the sample.

At least one set of sampling reagents and matrices similar to that used during sampling shall be analysed, using the procedures described above.

In parallel with each batch of analyses, a blank sample taken from an extraction without sample but with recovery standard should be processed.

NOTE The external recovery standard (2- or 6- methylchrysene) is used to check the method performance and sample preparation. However, the recovery of this standard cannot be used as a correction factor because this standard is in a matrix other than the PAH present in the sample and does not cover the broad spectra of vapour pressures of all 16 PAH.

6.1.8 Method sensitivity, accuracy and precision

The sensitivity of this method depends on the sample volume taken. A sample of 6 m^3 will afford method detection limits of less than 1 $\mu g/m^3$. Concentration of sample extracts to less than 1 ml in volume prior to analysis will increase sensitivity, but introduce the risk of analyte losses, particularly of 2- to 3-ring PAH.

The accuracy of the method (sample preparation and analysis) has been determined using NIST SRM 1649 (urban dust, with certified values for five PAH) and varies between 76 % (benzo[a]pyrene) and 100 % (indeno[123-cd]pyrene). The repeatability varies between 3 % (fluoranthene) and 9 % (indeno[123-cd]pyrene).

The performance characteristics of the HPLC-method are given in Annex E.

6.2 GC-MS method

6.2.1 General

This subclause describes the sample preparation, extraction, clean-up and instrumental analyses for the determination of the concentration of polycyclic aromatic hydrocarbons (PAH) in stack and waste gases using gas chromatography in combination with mass spectrometry.

6.2.2 Reagents and materials

6.2.2.1 **Acetone**, glass-distilled, chromatographic quality.

6.2.2.2 **Dichloromethane**, glass-distilled, chromatographic quality.

6.2.2.3 **n-Hexane**, glass-distilled, chromatographic quality.

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2) NIST SRM 1649 (urban dust, with certified values for five PAH) is an example of a suitable product available commercially from the National Institute for Standards and Technology (NIST), U.S. Department of Commerce, Gaithersburg, Maryland, U.S.A. This information is given for the convenience of users of this part of ISO 11338 and does not constitute an endorsement by ISO of this product.

6.2.2.4 **Pentane**, glass-distilled, chromatographic quality.

6.2.2.5 **Diethyl ether**, reagent grade, preserved with 2 % ethanol.

6.2.2.6 **Silica gel**, high purity grade, type 60, 70 mesh to 230 mesh.

6.2.2.7 **Sodium sulfate,** anhydrous, reagent grade, dried by heating at 300 °C for 4 h.

6.2.2.8 **Recovery standards**, either deuterated or carbon-13 labelled PAH, with a purity of 98 % or higher.

A complete set of recovery standards for each PAH of interest may be used or a selected number of recovery standards may be used, for example one recovery standard for each 2-ring, 3-ring, 4-ring and 5-ring PAH. Solutions of the appropriate recovery standards are typically made up to mass concentrations of 50 ng/µl.

6.2.2.9 **Syringe standards**.

2,2'-dibromobiphenyl, 2,2',3,3',4,4',5,5',6,6'-decafluorobiphenyl, or a deuterated or carbon-13 labelled PAH, if not used as recovery standard, may be used as a syringe standard. Fluorene-d10, pyrene-d10, and benzo[k]fluorene-d12 are good choices. Their purity should be 98 % or better. Solutions of the appropriate syringe standard are typically made up to mass concentrations of 50 ng/µl.

6.2.2.10 **Compressed gases**, ultra-high purity helium carrier gas, and high purity nitrogen for sample concentration.

6.2.2.11 **Aluminium foil**.

6.2.2.12 **Glass wool**.

6.2.3 Apparatus

6.2.3.1 Sample preparation

The apparatus for sample preparation shall be as described in 6.1.3.1.

6.2.3.2 Sample analysis

6.2.3.2.1 **Gas chromatograph-mass spectrometer,** consisting of a gas chromatograph coupled with a mass spectrometer and data station, suitable for splitless injection, and all required accessories, including temperature programmer, column supplies, recorders, gases and syringes.

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

6.2.3.2.2 **Fused silica GC capillary column** (30 m to 50 m × 0,25 mm ID) coated with crosslinked 5 % phenyl methylsiloxane film of 0,25 µm thickness, or other suitable columns.

6.2.3.2.3 **Syringes,** of capacity 1 µl, 5 µl, 10 µl, 25 µl, 50 µl, 100 µl and 250 µl for injecting samples into GC and making calibration and internal standard solutions.

6.2.4 Sample preparation

6.2.4.1 Storage conditions for samples

Owing to possible reactions of PAH with light and components present in air, all sampling parts containing PAH should be stored until required for laboratory preparation in sealed containers, protected from light, at temperatures either between 0 °C to 4 °C or below –15 °C. Samples stored between 0 °C to 4 °C shall be extracted within one week after sampling has been completed. If samples are stored at a temperature of

−15 °C or below, extraction shall take place within one month. Any condensate shall be acidified with hydrochloric acid to pH ≈ 2, and may then be stored for up to 14 days.

6.2.4.2 Addition of recovery standards

Prior to extraction, a recovery standard mixture is added to the samples. To use the isotope dilution approach the analyst must select one or more recovery standards that are similar in chromatographic behaviour to the compounds of interest. For PAHs, these are typically the deuterated PAH analogues or the carbon-13 labelled PAHs. The analyst shall demonstrate that the measurement of the recovery standard is not affected by method or matrix interferences.

Stock solutions of the appropriate recovery standards are typically made up to concentrations of 50 ng/µl. A known volume of this solution is added to that part of the sample that is expected to contain the largest amount of PAHs, most often the sorbent. The solvent should be allowed to evaporate before extraction.

The amount of recovery standard added to the sample should be comparable to the amount of PAH expected in the sample (e.g. if concentrations are expected to be in the order of 200 ng/m^3 and the sampled volume was 5 m^3, 20 µl of a stock solution with a mass concentration of 50 ng/µl should be added to the sample).

6.2.4.3 Extraction of filters and solid sorbents

Remove the filter and solid sorbents from their sealed containers and place in the pre-extracted Soxhlet thimble. Immediately prior to extraction, add the required volume of the recovery standard solution to the sample in order to determine the recovery of the procedure.

Carry out extraction with 10 % diethyl ether (6.2.2.5) in n-hexane (6.2.2.3) for approximately 20 h, at a reflux rate of 4 cycles per hour.

The recovery standard shall be added to all related samples, including field and method blanks.

Alternatively, extraction techniques (e.g. ASE) or other solvents or solvent mixtures may be used, if validated by the user.

6.2.4.4 Extraction of condensate

Transfer the condensate into the separation funnel. Rinse the impingers or condensate flasks with n-hexane (6.2.2.3) and transfer the n-hexane to the separation funnel. Shake for at least 5 min. Allow to settle and then separate the n-hexane from the condensate. Carry out a further extraction on the condensate under the same conditions and combine the n-hexane fractions. Dry the combined n-hexane fractions over sodium sulfate (6.2.2.7).

The volume of n-hexane used in each of the two extractions shall be at least 20 % of the volume of the condensate.

6.2.4.5 Concentration of the extract

Combine the dried n-hexane extracts of the condensate with the extract of the filter and solid. Filter the combined extracts over a pre-cleaned glass fibre filter (6.1.3.2) and transfer to the rotary evaporator. The temperature of the water bath shall not exceed 45 °C. Concentrate the extract to a volume of approximately 5 ml. Transfer the extract quantitatively with n-hexane to a calibrated 10 ml conical tube. Then place the tube in a water bath at 25 °C and concentrate the extract under a gentle stream of nitrogen, until the hexane is evaporated to 1 ml or less.

Mix the sample well and transfer to sealed brown vials for storage at less than 4 °C, protected from light until analysed. Concentrated extracts should be analysed within 30 days.

Clean-up procedures may not be needed for relatively clean matrices. If no clean-up procedure is being used, add the syringe standard at this point and adjust the final volume of the extract to 1,0 ml with n-hexane. If clean-up is required, see 6.2.4.6.

A rotary evaporator (6.1.3.4) may be used with a vacuum of approximately 0,1 MPa pressure and a water bath at a temperature not exceeding 45 °C. If validated by the user, other evaporation systems may be used to concentrate the extract. If the extract is concentrated to dryness, substantial losses of PAH may occur; therefore the sample should be discarded where this has occurred.

NOTE 1 Concentrating the sample to a volume of 1 ml extract may not be needed, depending on the target detection limits, the sensitivity of the detector and the flue gas volume sampled.

NOTE 2 The last evaporation step with the use of nitrogen is the most critical aspect in sample preparation. Losses of volatile PAH due to the final concentration step of sample extracts can lead to losses up to 10 % for 2- to 4-ring PAH if n-hexane is the extraction solvent. If toluene is used as extraction solvent, losses of 10 % to 40 % for 2- to 4-ring PAH can be expected.

6.2.4.6 Sample clean-up

6.2.4.6.1 General

Clean-up procedures may not be needed for relatively clean matrices. Complex matrices may require a purification stage to eliminate interferences caused by the presence of polar compounds or other hydrocarbons, e.g. oil.

If dichloromethane is used for extraction of the sample, it should be solvent-exchanged with n-hexane prior to the clean-up procedure.

6.2.4.6.2 Column preparation

Carry out column preparation in accordance with 6.1.4.5.2.

6.2.4.6.3 Column chromatography

Prior to use, the column is pre-eluted with 40 ml of pentane and the eluate discarded. While the pentane pre-eluent still covers the top of the column, 1 ml of sample extract in n-hexane is quantitatively transferred to the column, and washed on with a further 2 ml of n-hexane to complete the transfer. Allow to eluate through the column. Immediately prior to exposure of the sodium sulfate layer to the air, 25 ml of pentane is added and elution continued. The pentane eluate may be discarded.

Finally elute the column with 25 ml of dichloromethane in pentane (4:6 volume ratio) at 2 ml/min and collect in a 100 ml round-bottomed flask. Further concentrate the extract to 1 ml or less under a gentle stream of nitrogen as previously described. Add the syringe standard; the final volume of the extract should be adjusted to 1,0 ml with n-hexane.

Clean-up columns are commercially available and may be used, if validated.

NOTE 1 The pentane fraction contains the aliphatic hydrocarbons. If necessary, this fraction may be analysed for specific aliphatic organic compounds.

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

6.2.5 Sample analysis

6.2.5.1 Instrumentation

Analyses are typically performed using a 70 eV electron impact ionization mass spectrometer (MS), operated in the selected-ion monitoring mode (SIM). However, other types of mass spectrometer (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 long by 0,25 mm ID capillary GC column coated with crosslinked 5 % phenyl methylsiloxane (0,25 µm film thickness) or equivalent is recommended.

Typical gas chromatograph 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;

— 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 40 cm/s.

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

For the identification of the PAH compounds a primary ion (target ion) and at least one secondary ion (qualifier ion) are selected for monitoring. A minimum dwell time of 50 ms per peak is recommended. Annex C shows key ions for PAH and a selected number of deuterated PAH.

6.2.5.2 Instrument calibration

External calibration standards of native PAH shall be prepared at a minimum of five 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 the quantification limit, and the other concentrations shall correspond to the range of concentrations expected in the samples or shall define the working range of the GC-MS system.

If the linearity of the system has been established over the range of concentration of interest, a one-point calibration can be used for daily quantification. If any significant part of the instrument is replaced, repeat linearity checks should take place.

The minimum acceptable ion intensity is instrument-dependent. The lowest calibration level shall be sufficiently above the instrument noise level to a relative standard deviation of less than 20 % between replicate analyses. Typically, a signal-to-noise ratio of 3:1 is acceptable for compound identification, a 10:1 ratio for compound quantification.

Each of the calibration standards shall contain the appropriate recovery standards at the specified concentration level. The standards are used to determine the relative retention times of the PAH, the relative response factors of the PAH relative to the corresponding internal standard, and the qualifier ion ratio relative to the target ion.

The relative retention time ($R_{\mathrm{t},i,j}$) for each analyte is calculated using the following equation:

$$R_{\mathrm{t},i,j} = \frac{t_{\mathrm{a},i}}{t_{\mathrm{rs},j}} \tag{4}$$

where

$R_{\mathrm{t},i,j}$ is the relative retention time of analyte i relative to the corresponding recovery standard j;

$t_{a,i}$ is the retention time of analyte i in the calibration standard;

$t_{rs,j}$ is the retention time of recovery standard j in the calibration standard.

The ratio of the amount of qualifier ion relative to the amount of target ion is calculated using the following equation:

$$Q = \frac{A_{\text{qualifier}}}{A_{\text{target}}} \tag{5}$$

where

Q is the ratio of the amount of qualifier ion relative to the amount of target ion;

$A_{\text{qualifier}}$ is the peak area of the qualifier (or secondary) ion;

A_{target} is the peak area of the target (or primary) ion.

NOTE Qualifier ion ratios can be obtained from reference mass spectra, but can vary depending on the type of mass spectrometer used, e.g. quadrupole versus ion-trap.

The relative response factor ($R_{RF,i,j}$) for each analyte is calculated using the following equation:

$$R_{RF,i,j} = \frac{A_{a,i}}{A_{rs,j}} \cdot \frac{m_{rs,j}}{m_{a,i}} \tag{6}$$

where

$R_{RF,i,j}$ is the relative response factor of analyte i relative to the corresponding recovery standard j;

$A_{a,i}$ is the area of the primary target ion of the analyte i in the calibration standard;

$A_{rs,j}$ is the area of the primary target ion of the corresponding recovery standard j in the calibration standard;

$m_{a,i}$ is the mass of the analyte i added to the calibration standard, in nanograms;

$m_{rs,j}$ is the mass of the corresponding recovery standard j in the calibration standard, in nanograms.

If the $R_{RF,i,j}$ is found to be constant over the working range (<20 % RSD), the $R_{RF,i,j}$ can be assumed to be invariant and the average $R_{RF,i,j}$ shall be used for calculations.

On each working day the $R_{t,i,j}$ and $R_{RF,i,j}$ shall be verified by the measurement of one or more calibration standards. If the $R_{t,i,j}$ varies from the expected $R_{t,i,j}$ by more than ± 3 %, the $R_{t,i,j}$ values of all analytes shall be determined. If the $R_{RF,i,j}$ varies from the expected $R_{RF,i,j}$ by more than ± 20 %, the calibration shall be repeated using a fresh calibration standard.

6.2.5.3 Analysis

6.2.5.3.1 GC-MS analysis

Remove the sample extracts from cold storage and allow to warm to room temperature (if appropriate). Once the GC and MS are properly set up, determine the performance of the system by analysis of a calibration

standard. Next, inject 1 µl to 3 µl of each sample extract and note the MS response. For each ten sample extracts, at least one calibration standard and one solvent blank shall be analysed, the latter to verify that no carry-over of contamination occurs between samples.

6.2.5.3.2 Identification

Correct identification of the analytes is based on:

— relative retention time: the relative retention time of the analyte shall be within ± 3 % of the expected relative retention time of the analyte;

— qualifier ion ratio: the ratio Q of the qualifier ion to target ion [see Equation (5)] shall be within ± 30 % of the expected ratio.

6.2.6 Calculation

Analytes are quantified using the area of the primary target ion peak of the analyte and the area of the primary target ion peak of the internal standard. The concentrations of the analytes in the extracts are calculated using the following equation:

$$m_{\mathrm{a}i} = \frac{m_{\mathrm{is},j}}{R_{\mathrm{F},i,j}} \cdot \frac{A_{\mathrm{a}i}}{A_{\mathrm{is},j}} \tag{7}$$

where

$m_{\mathrm{a}i}$ is the mass of analyte i in the sample extract;

$m_{\mathrm{is},j}$ is the mass of the corresponding internal standard j added to the sample;

$R_{\mathrm{RF},i,j}$ is the response factor of analyte i relative to the corresponding external standard j;

$A_{\mathrm{a}i}$ is the peak area of the target ion of the analyte i in the sample extract;

$A_{\mathrm{is},j}$ is the peak area of the target ion of the internal standard j in the sample extract.

If the response of the target ion of any analyte exceeds the linear calibration curve range of the GC-MS system, dilute the extract and analyse again. Carry out dilution by addition of solvent. No additional syringe standard shall be added.

The recovery efficiencies of the internal standards are quantified against the syringe standard using the following equation:

$$Rec_{\mathrm{is},j} = \frac{100}{m_{\mathrm{is},j}} \cdot \frac{m_{\mathrm{ss}}}{R_{\mathrm{F},j,\mathrm{s}}} \cdot \frac{A_{\mathrm{is},j}}{A_{\mathrm{ss}}} \tag{8}$$

where

$Rec_{\mathrm{is},j}$ is the recovery of internal standard j, in percent;

$m_{\mathrm{is},j}$ is the mass of the internal standard j added to the sample;

m_{ss} is the mass of the syringe standard added to the sample extract;

$R_{\mathrm{F},j,\mathrm{s}}$ is the response factor of internal standard j relative to the syringe standard;

$A_{\mathrm{is},j}$ is the peak area of the primary target ion of internal standard j in the sample extract;

A_{ss} is the peak area of the primary target ion of the syringe standard in the sample extract.

The recoveries of the internal standards added to the samples prior to extraction and analysis shall be closely monitored to assure the performance of the procedure. The recoveries should fall between 50 % to 150 %. Samples for which the recoveries of the internal standard are less than 50 % or more than 150 % shall be discarded.

PAH emissions are expressed as the mass of PAH per dry standard cubic metre of waste gas and reference oxygen (or carbon dioxide) content. The concentration of each PAH in the waste gas is calculated as follows:

$$\rho_i = \frac{m_{ai}}{V_{nr}} \quad (9)$$

where

ρ_i is the mass concentration of analyte i in the waste gas, in nanograms per cubic metre;

$m_{a,i}$ is the mass of analyte i found in the sample, in nanograms;

V_{nr} is the volume, in cubic metres, of the gas sample under standard conditions.

6.2.7 Quality assurance

Calibration standards shall be analysed immediately after each tenth sample that is injected into the GC-MS.

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

Field blanks and a laboratory blank shall be taken and analysed with each set of emission measurements.

It is recommended to analyse at least one set of sampling materials using the procedure to assure that acceptable blank levels can be obtained. A blank level of < 10 ng/sample for a single analyte is considered to be acceptable. Blank levels of < 10 ng/sample may not be achievable for naphthalene or phenanthrene. However, since these compounds are typically present at relatively high concentrations, a blank level of < 50 ng/sample is usually acceptable. For the results to be acceptable, the amount of a given PAH in the field blank shall be less than 10 % of the amount of that compound measured in the sample.

Calibration standards shall be prepared at least every six months. The accuracy shall be determined by comparing the calibration standard to a commercially available reference material[1)].

To assure acceptable analytical accuracy, periodic analyses shall be made of a known standard reference material[2)] with certified values.

6.2.8 Method sensitivity, accuracy and precision

The sensitivity of this method depends on sample volume taken. A sample volume of 6 m^3 will afford method detection limits in the range of 0,1 µg/m^3 to 1 µg/m^3. Concentration of sample extracts to less than 1 ml in volume prior to analysis will increase sensitivity, but introduce the risk of analyte losses, particularly of 2- to 3-ring PAH.

7 Limitations and interferences

7.1 Limitations

The HPLC method has been evaluated for the PAH shown in Annex A, and the GC-MS method has been evaluated for the PAH shown in Annex B. Other PAH may be determined by both methods, but the user must demonstrate acceptable analysis efficiencies. Losses of naphthalene, acenaphthylene and acenaphthene may

occur during evaporation and concentration of the sample extract because these compounds possess relative high vapour pressures.

7.2 Interferences

Interferences caused by contaminants in solvents, reagents or glassware and other sample processing equipment can result in discrete artefacts and/or elevated baselines in the detector profiles. Matrix interferences can be caused by contaminants that are co-extracted from the sample. If significant interferences are detected (e.g. by unacceptable qualifier ion ratios), additional clean-up by column chromatography shall be carried out.

The analytical system shall be routinely demonstrated to be free of internal contaminants from contaminated solvents, glassware, or other reagents that can lead to method interferences. A laboratory reagent blank shall be analysed for each batch of reagents used to determine whether reagents are contaminant-free.

With HPLC analysis, mobile phases shall be degassed, because dissolved oxygen interferes with the response of the fluorescence detector.

Glassware shall be cleaned (e.g. by acid washing, followed by heating to 300 °C for 12 h in a muffle furnace, and solvent-rinsed immediately prior to use).

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 co-elute and not give good resolution (e.g. benzo[b]fluoranthene and benzo[k]fluoranthene, chrysene and triphenylene).

Interferences from some non-PAH compounds, especially oils and polar organic species, can be reduced or eliminated by the use of column chromatography for sample clean-up prior to HPLC or GC-MS analysis.

Exposure to heat, ozone, nitrogen dioxide (NO_2) and ultraviolet (UV) light can cause PAH degradation during sampling, sample storage, and processing. These problems shall be addressed as part of a standard operating procedure prepared by the user. Where possible, incandescent or UV-filtered fluorescent lighting may be used in the laboratory to avoid photodegradation during analysis.

Annex A
(informative)

Maximum UV absorption wavelength and recommended combinations of excitation-emission wavelengths for HPLC

Compound	λ_{max} for UV abs. nm	Recommended $\lambda_{ex}/\lambda_{em}$ nm	Optimal $\lambda_{ex}/\lambda_{em}$ nm
Naphthalene	220	254/350	280/334
Acenaphthylene	229	not applicable	not applicable
Acenaphthene	229	254/350	280/324
Fluorene	261	254/350	268/308
Phenanthrene	251	254/350	292/366
Anthracene	252	254/420	253/402
Fluoranthene	236	254/420	360/460
Pyrene	240	254/420	336/376
Benz[a]anthracene	287	254/420	288/390
Chrysene	267	254/420	268/383
Benz[b]fluoranthene	256	305/430	300/436
Benz[k]fluoranthene	307	305/430	308/414
Benzo[a]pyrene	296	305/430	296/408
Benzo[ghi]perylene	300	305/430	300/410
Dibenz [a,h] anthracene	297	305/430	297/398
Indeno [1,2,3-cd] pyrene	250	305/500	302/506

Annex B
(informative)

Formulae and physical properties of selected PAH for GC-MS

Compound	Molecular formula	Molecular mass	Melting point °C	Boiling point °C	Vapour pressure kPa at 25 °C
Naphthalene	$C_{10}H_8$	128,18	80,2	218	$1{,}1 \times 10^{-2}$
Acenaphthylene	$C_{12}H_8$	152,20	92 to 93	265 to 280	$3{,}9 \times 10^{-3}$
Acenaphthene	$C_{12}H_{10}$	154,20	90 to 96	278 to 279	$2{,}1 \times 10^{-3}$
Fluorene	$C_{13}H_{10}$	166,23	116 to 118	293 to 295	$8{,}7 \times 10^{-5}$
Anthracene	$C_{14}H_{10}$	178,24	216 to 219	340	$3{,}6 \times 10^{-6}$
Phenanthrene	$C_{14}H_{10}$	178,24	96 to 101	339 to 340	$2{,}3 \times 10^{-5}$
Fluoranthene	$C_{16}H_{10}$	202,26	107 to 111	375 to 393	$6{,}5 \times 10^{-7}$
Pyrene	$C_{16}H_{10}$	202,26	150 to 156	360 to 404	$3{,}1 \times 10^{-6}$
Cyclopenta[cd]pyrene	$C_{18}H_{10}$	226,28	174 to 176	—	ca. 10^{-7}
Benz[a]anthracene	$C_{18}H_{12}$	228,30	157 to 167	435	$1{,}5 \times 10^{-8}$
Chrysene	$C_{18}H_{12}$	228,30	252 to 256	441 to 448	$5{,}7 \times 10^{-10}$
Retene	$C_{18}H_{18}$	234,34	101	390	ca. 10^{-6}
Benzo[b]fluoranthene	$C_{20}H_{12}$	252,32	167 to 168	481	$6{,}7 \times 10^{-8}$
Benzo[k]fluoranthene	$C_{20}H_{12}$	252,32	198 to 217	480 to 481	$2{,}1 \times 10^{-8}$
Perylene	$C_{20}H_{12}$	252,32	273 to 278	500 to 503	$7{,}0 \times 10^{-10}$
Benzo[a]pyrene	$C_{20}H_{12}$	252,32	177 to 179	493 to 496	$7{,}3 \times 10^{-10}$
Benzo[e]pyrene	$C_{20}H_{12}$	252,32	178 to 179	493	$7{,}4 \times 10^{-10}$
Benzo[ghi]perylene	$C_{22}H_{12}$	276,34	275 to 278	525	$1{,}3 \times 10^{-11}$
Indeno[1,2,3-cd]pyrene	$C_{22}H_{12}$	276,34	162 to 163	—	ca. 10^{-11}
Dibenz[ah]anthracene	$C_{22}H_{14}$	278,35	266 to 270	524	$1{,}3 \times 10^{-11}$
Coronene	$C_{24}H_{12}$	300,36	438 to 440	525	$2{,}0 \times 10^{-13}$

Annex C
(informative)

Characteristic ions for GC-MS detection of selected PAH, recovery, and surrogate recovery standards

Compound	Primary ion	Secondary ion	Secondary ion
Acenaphthene	154	153	152
Acenaphthene-d_{10}	164	163	162
Acenaphthylene	152	151	153
Anthracene	178	89	179
Benz[a]anthracene	228	114	229
Benzo[a]pyrene	252	253	126
Benzo[e]pyrene	252	253	126
Benzo[b]fluoranthene	252	253	126
Benzo[ghi]perylene	276	138	277
Benzo[k]fluoranthene	252	253	125
Chrysene	228	114	229
Chrysene-d_{12}	240	126	241
Coronene	300	150	301
Cyclopenta[cd]pyrene	226	113	228
Dibenz[ah]anthracene	278	139	279
Fluoranthene	202	101	203
Fluorene	166	165	167
Indeno[1,2,3-cd]pyrene	276	138	227
Naphthalene	128	129	127
Naphthalene-d_8	136	137	134
Perylene	252	253	126
Perylene-d_{12}	264	265	138
Phenanthrene	178	179	176
Phenanthrene-d_{10}	188	189	186
Pyrene	202	101	203
Retene	219	234	205
Dibromobiphenyl	312	310	314
Decafluorobiphenyl	334	335	265

Annex D
(informative)

Applicability of internal standards for GC-MS detection of selected PAH

Analyte	Ring system	Internal standard	Syringe standard
Naphthalene	2	naphthalene-d_8	decafluorobiphenyl
Acenaphthylene		acenaphthene-d_{10}	
Acenaphthene			
Fluorene			
Phenanthrene	3	phenanthrene-d_{10}	
Anthracene			
Retene			
Fluoranthene	3+		
Benz[a]anthracene	4	chrysene-d_{12}	
Chrysene			
Pyrene			
Cyclopenta[cd]pyrene	4+	perylene-d_{12}	
Benzo[k]fluoranthene			
Benzo[b]fluoranthene			
Perylene			
Benzo[a]pyrene	5	benzo[a]pyrene-d_{12}	
Benzo[e]pyrene			
Dibenz[ah]anthracene			
Indeno[123-cd]pyrene	5+		
Benzo[ghi]perylene			
Coronene	6		

Annex E
(normative)

Summary of performance characteristics of the HPLC method

Limit of detection (16 EPA-PAH):	0,1 µg/m^3 to 1 µg/m^3 for 6 m^3 (standardized conditions) sample size and dilution factor of 100
Relative standard deviation (repeatability):	2,5 % to 17 %
Relative standard deviation (reproducibility):	6,9 % to 37 %
Number of replicates:	30
Number of participants:	6

The statistical results above were obtained from analysis of real stack gas sample extracts.

Relative standard deviation (repeatability):	5,1 % to 22 %
Relative standard deviation (reproducibility):	15 % to 62 %
Number of replicates:	30
Number of participants:	6

The statistical results above were obtained from both extraction and analysis of real stack gas samples.

The samples used for the interlaboratory comparison programme whose results are given above were obtained from a source under the following conditions:

Stack gas temperature:	66 °C
Pressure:	60 Pa
Particle concentration:	100 mg/m^3 (standardized conditions)
Oxygen concentration:	17,1 %
Stack gas velocity:	14 m/s
Sample volume:	6 m^3 (standardized conditions)

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