भारतीय मानक

Indian Standard

IS 16197 (Part 10) : 2024
IEC 62321-10 : 2020

विद्युत तकनीकी उत्पादों में कुछ पदार्थों का निर्धारण

भाग 10 गैस क्रोमैटोग्राफी-मास स्पेक्ट्रोमेट्री (जीसी-एमएस) द्वारा पॉलिमर और इलेक्ट्रॉनिक्स में पॉलीसाइक्लिक एरोमैटिक हाइड्रोकार्बन (पीएएच)

Determination of Certain Substances in Electrotechnical Products

Part 10 Polycyclic Aromatic Hydrocarbons (PAHs) in Polymers and Electronics by Gas Chromatography-Mass Spectrometry (GC-MS)

ICS 13.020.01; 43.040.10

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NATIONAL FOREWORD

This Indian Standard (Part 10) which is identical to IEC 62321-10 : 2020 'Determination of certain substances in electrotechnical products — Part 10: Polycyclic aromatic hydrocarbons (PAHs) in polymers and electronics by gas chromatography-mass spectrometry (GC-MS)' issued by the International Electrotechnical Commission (IEC) was adopted by the Bureau of Indian Standards on the recommendation of the Standardization of Environmental Aspects for Electrical and Electronics Products Sectional Committee and approval of the Electrotechnical Division Council.

The text of IEC standard has been approved as suitable for publication as an Indian Standard without deviations. Certain terminologies and conventions are, however, not identical to those used in Indian Standards. Attention is particularly drawn to the following:

a) Wherever the words 'International Standard' appear referring to this standard, they should be read as 'Indian Standard'; and

b) Comma (,) has been used as a decimal marker, while in Indian Standards the current practice is to use a point (.) as the decimal marker.

In this standard, reference appears to International Standards for which Indian Standards also exists. The corresponding Indian Standards, which are to be substituted, are listed below along with their degree of equivalence for the editions indicated:

International Standard	*Corresponding Indian Standard*	*Degree of Equivalence*
IEC 62321-1 Determination of certain substances in electrotechnical products — Part 1: Introduction and overview	IS 16197 (Part 1) : 2014/IEC 62321-1 : 2013 Determination of certain substances in electrotechnical products: Part 1 Introduction and overview	Identical
IEC 62321-2 Determination of certain substances in electrotechnical products — Part 2: Disassembly, disjointment and mechanical sample preparation	IS 16197 (Part 2) : 2014/IEC 62321-2 : 2013 Determination of certain substances in electrotechnical products: Part 2 Disassembly, disjointment and mechanical sample preparation	Identical

The Committee has reviewed the provisions of the following International Standards referred in this adopted standard and decided that they are acceptable for use in conjunction with this standard.

International Standard	*Title*
ISO 3696	Water for analytical laboratory use — Specification and test methods

Only the English language text has been retained while adopting it in this Indian Standard, and as such, the page numbers given here are not the same as in the IEC publication.

For the purpose of deciding whether a particular requirement of this standard is complied with the final value, observed or calculated expressing the result of a test or analysis shall be rounded off in accordance with IS 2 : 2022 'Rules for rounding of numerical values (*second revision*)'. The number of significant places retained in the rounded off value should be the same as that of the specified value in this standard.

CONTENTS

INTRODUCTION

The widespread use of electrotechnical products has drawn increased attention to their impact on the environment. In many countries this has resulted in the adoption of regulations affecting wastes, substances and energy use of electrotechnical products.

The use of certain substances (e.g. lead (Pb), cadmium (Cd) and polybrominated diphenyl ethers (PBDEs)) in electrotechnical products is a source of concern in current and proposed regional legislation.

The purpose of the IEC 62321 series is therefore to provide test methods that will allow the electrotechnical industry to determine the levels of certain substances of concern in electrotechnical products on a consistent global basis.

This first edition of IEC 62321-10 introduces a new subject covering polycyclic aromatic hydrocarbons (PAHs) in the IEC 62321 series.

WARNING – Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

Indian Standard

DETERMINATION OF CERTAIN SUBSTANCES IN ELECTROTECHNICAL PRODUCTS

PART 10 POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN POLYMERS AND ELECTRONICS BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GC-MS)

1 Scope

This part of IEC 62321 specifies one normative technique for the determination of polycyclic aromatic hydrocarbons (PAHs) in polymers of electrotechnical products. These PAHs can especially be found in the plastic and rubber parts of a wide range of consumer articles. They are present as impurities in some of the raw materials used in the production of such articles, in particular in extender oils and in carbon black. They are not added intentionally to the articles and do not perform any specific function as constituents of the plastic or rubber parts.

The gas chromatography-mass spectrometry (GC-MS) test method is suitable for the determination of polycyclic aromatic hydrocarbons (PAHs).

These test methods have been evaluated for use with plastics and rubbers. These test methods have been evaluated for use with ABS (acrylonitrile butadiene styrene) containing individual PAHs ranging from 37,2 mg/kg to 119 mg/kg and rubbers containing individual PAHs ranging from 1 mg/kg to 221,2 mg/kg.

WARNING – This document does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this document to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

This horizontal standard is primarily intended for use by technical committees in the preparation of standards in accordance with the principles laid down in IEC Guide 108.

One of the responsibilities of a technical committee is, wherever applicable, to make use of horizontal standards in the preparation of its publications. The contents of this horizontal standard will not apply unless specifically referred to or included in the relevant publications.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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.

IEC 62321-1:2013, *Determination of certain substances in electrotechnical products – Part 1: Introduction and overview*

IEC 62321-2, *Determination of certain substances in electrotechnical products – Part 2: Disassembly, disjointment and mechanical sample preparation*

ISO 3696, *Water for analytical laboratory use – Specification and test methods*

3 Terms, definitions and abbreviated terms

3.1 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

3.2 Abbreviated terms

ABS	acrylonitrile butadiene styrene
CCC	continuing calibration check standard
EI	electron ionization
GC-MS	gas chromatography-mass spectrometry
IS	internal standard
IUPAC	International Union of Pure and Applied Chemistry
LOD	limit of detection
LOQ	limit of quantification
MDL	method detection limit
PAH	polycyclic aromatic hydrocarbon
PBDE	polybrominated diphenyl ether
QC	quality control
RSD	relative standard deviation
SIM	selected ion monitoring
TICS	tentatively identified compounds
US EPA	United States Environmental Protection Agency

4 Principle

PAH compounds are quantitatively determined using ultrasonic extraction or Soxhlet extraction followed by gas chromatography-mass spectrometry (GC-MS) using single (or "selected") ion monitoring (SIM).

5 Reagents and materials

Use, as far as available, reagents of analytical quality, or better. Use only reagents with negligibly low concentrations of PAH and verify by blank determinations and, if necessary, apply additional cleaning steps (for calibrants, see 8.4):

a) Dichloromethane (GC grade or higher).

b) Helium (purity of greater than a volume fraction of 99,999 %).

c) Silica gel (purity of greater than a mass fraction of 99 %).

d) Toluene (GC grade or higher).

NOTE 1 The standards are acceptable when using a quadrupole-type mass spectrometer. A high-resolution mass spectrometer will require the use of other suitable standard substances having a mass and elution time similar to that of the analyte (see 8.4). Other stock solution concentrations can be utilized providing the standard solution concentrations given in 8.5.2 can be achieved.

e) Sodium sulphate (purity of greater than a mass fraction of 99 %).

f) Surrogate and internal standards:

- internal standard (to correct for injection errors, according to 8.4.2 a)), (e.g. naphthalene-d8, pyrene-d10, anthracene-d10, phenanthrene-d10, benzo(a)pyrene-d12, perylene-d12 or triphenylbenzene);

NOTE 2 At least three internal standards are preferably used to be mixed with toluene as extraction agent.

- surrogate standard (to monitor analyte recovery according to 8.4.2 b), (e.g. chrysene-d12 or p-terphenyl-d14).

g) Petroleum ether (purity of greater than a mass fraction of 99 %).

h) Water (Grade 1 specified in ISO 3696 used for preparation of labware and others).

6 Apparatus

The following items shall be used for the analysis:

a) 0,45 µm PTFE filter membrane.

b) 1 ml, 5 ml, 10 ml, 100 ml volumetric flasks.

c) Aluminium foil.

d) Analytical balance capable of measuring accurately to 0,000 1 g.

e) 40 ml brown or amber vessel.

f) Cryogenic grinding with liquid N_2 cooling.

g) Dry oven.

h) Furnace.

i) Extraction thimble (cellulose 30 ml, ID 22 mm, height 80 mm).

j) Funnel.

k) Glass column (size: 220 mm × 15 mm).

l) Glass wool (for extraction thimble).

m) Heating jackets.

n) Microlitre syringe or automatic pipettes.

o) Mini-shaker (also known as vortexer or vortex mixer).

p) Pasteur pipette.

q) Rotary evaporator.

r) Soxhlet extractors:

- 30 ml Soxhlet extractors,
- 250 ml round-bottomed flasks,
- ground-in stopper NS 29/32,
- Dimroth condenser NS 29/32,
- boiling stones (e.g. glass pearls or Raschig rings).

s) Ultrasonic extractors:

Ultrasonic bath with a minimum power of 200 W and a bath area of 706 cm^2, corresponding to 0,28 W/cm^2, without a basket and with an internal or external thermostat.

t) Vial for GC-MS:

2 ml sample vials with 100 µl glass insert and a screw cap with polytetrafluoroethylene (PTFE) gasket or depending on the analytical system, a comparable sample receptacle. Brown or amber vessels shall be used as indicated in the text of the procedure.

u) GC-MS:

A gas chromatograph with a capillary column coupled to a mass spectrometric detector (electron ionization, EI) is used for the analysis. The mass spectrometric detector shall be able to perform selective ion monitoring and have an upper mass range of at least 550 m/z. The use of an autosampler is strongly recommended to ensure repeatability. Ferrules used shall not contain more than 40 % graphite (a suitable ferrule is made of 60 % polyimide and 40 % graphite) to decrease the risk that PAHs are absorbed.

v) GC column for PAH analysis:

A column length of 20 m or longer has sufficient separation efficiency for PAH compounds. An example of suitable column and its separation results is given in Annex A, see Table A.2, Table A.3 and Figure A.1.

For the capillary column, 5 % phenyl, 95 % methyl polysiloxane (e.g. such as HT8, DB-EUPAH and ZB-PAH) is recommended. The preferred dimensions are 20 m in length, 0,25 mm or 0,18 mm in internal diameter, and 0,25 µm or 0,14 µm in film thickness.

NOTE Based on the AfPS-GS-2014-01-PAK method, a nonpolar DB-5MS column is not suited for a separation of the different benzofluoranthenes listed in Table 1.

7 Sampling

As described in IEC 62321-2, unless indicated otherwise (e.g. "using a knife"), cryogenic grinding with liquid nitrogen cooling is recommended and the samples shall be ground to pass through a 500 µm sieve before extraction.

If samples are not tested immediately, they shall be stored in tightly sealed glass vessels and in a cool and dark place.

It shall be confirmed that glassware is thoroughly cleaned and that all new materials that may come into contact with the sample are checked by blank analysis that they give no interference.

NOTE Interferences which can affect the results can occur due to contaminations from glassware, solvents and other materials that can come into contact with the sample. Such interferences will form an artifact or will increase the detector baseline. Interferences can also come from components in samples that co-elute with the specific PAHs of interest.

8 Procedure

8.1 General instructions for the analysis

The following general instructions shall be followed:

The validation of the instrumentation shall include testing of potential cross contaminations between sequential samples. Additional blanks or an inverted sequence of testing will help to identify cross contaminations.

See Annex C for guidance regarding labware cleaning procedures for PAH testing.

To avoid decomposition of PAHs by UV light during extraction and analysis, glass equipment made from brown or amber glass shall be used.

NOTE If no brown or amber glass is available, aluminium foil can be used for protection from light.

8.2 Sample preparation

8.2.1 Ultrasonic extraction

The following steps shall be followed for sample extraction:

The samples shall be pre-cut less than 5 mm × 5 mm and/or milled by cryogenic grinding with liquid N_2 cooling or cut sample materials to 2 mm to 3 mm. Quantitatively transfer 500 mg ± 10 mg of the sample into the vessel (Clause 6 e)).

a) Weigh 500 mg ± 10 mg of the sample into a 40 ml amber vessel (Clause 6 e)). Record the mass to the nearest 0,1 mg.

b) Add 20 µl of the surrogate standard (Clause 5 f)) (100 µg/ml) into the 40 ml amber vessel.

c) Transfer 20 ml of toluene (Clause 5 d)) and 20 µl of internal standard (8.4.4 c)) (100 µg/ml) to the 40 ml amber vessels (Clause 6 e)).

d) Place it in an ultrasonic extractor (Clause 6 s)) and sonicate it for about 1 h at 60 °C and then allow to cool at room temperature after the extraction of the sample.

e) Allow the polymer to settle or filter the mixture through a 0,45 µm PTFE membrane.

8.2.2 Soxhlet extraction

For the Soxhlet extraction step the following procedure is applied:

a) Quantitatively transfer 500 mg ± 10 mg of the sample into a cellulose extraction thimble for Soxhlet extraction. Record the mass to the nearest 0,1 mg.

b) Allow the sample to be transferred through a funnel into the extraction thimble. To ensure a quantitative transfer, the funnel should be rinsed with approximately 10 ml of toluene.

c) 10 µl of the surrogate standard (8.4.5 d)) (50 µg/ml) is added.

d) Cover the thimble with glass wool to prevent the sample from floating.

e) Approximately 120 ml of toluene is used for extraction under reflux. Allow the sample to be extracted for at least 6 h with 6 to 8 cycles per hour. Shorter extraction times may result in lower recoveries of the analyses.

f) After six hours of reflux, the extract is concentrated to about 2 ml using a vacuum rotary evaporator. 10 µl of the internal standard (8.4.4 d)) (50 µg/ml) is then added and the extract is diluted with toluene to 5 ml.

g) The diluted sample is transferred into a 2 ml GC sample/auto sample vial with a PTFE coated seal.

8.2.3 Sample clean-up

If the interference is caused by relatively polar compounds of the same boiling range as the analytes, then multiple column or cartridge clean-ups may be required.

a) The silica gel (Clause 5 c)) is deactivated beforehand by adding 10 % water (the corresponding volume of water is added to the silica gel in a glass flask, and the mixture is homogenized on the rotary evaporator for 1 h at standard pressure and room temperature. The silica gel can then be stored in the sealed glass flask at room temperature).

b) The packed column is conditioned with 10 ml of petroleum ether (Clause 5 g)).

c) The aliquot of toluene extract is then evaporated to a volume of approximately 1 ml on the rotary evaporator and poured into the column.

d) The pointed flask is rinsed out with approximately 20 ml of eluent, which is then also transferred to the clean-up column.

e) Elution is performed with 50 ml of petroleum ether.

f) The collected petroleum ether eluent is amended with 1 ml of toluene and evaporated to a volume of approximately 1 ml under a nitrogen stream (e.g. on the TurboVap).

g) This is then made up to a defined volume with toluene, and the extract is analysed by GC-MS.

8.3 Instrumental parameters

Different conditions might be necessary to optimize a specific GC-MS system to achieve effective separation of all calibration congeners and meet the QC and limits of detection (LOD) requirements. The following parameters have been found suitable and are provided as an example:

a) GC column: a column length of approximately 20 m or longer has sufficient separation efficiency for PAH compounds (see Clause A.2 for an example of suitable column and its separation results). For the capillary column, 5 % phenyl, 95 % methyl polysiloxane (e.g. such as HT8, DB-EUPAH and ZB-PAH) is recommended. The preferred dimensions are length 20 m, internal diameter 0,25 mm or 0,18 mm, and film thickness 0,25 µm or 0,14 µm.

b) Carrier: helium (see Clause 5 b)), 1,0 ml/min, constant flow.

c) Oven: 50 °C (initial temperature), 300 °C (final temperature), 10 °C/min ramp to 300 °C.

d) Injection temperature: 280 °C.

e) Injection volume: 1 µl.

A full scan run using a total ion current ("full scan") MS method for each sample is also recommended for checking for the existence of peaks/congeners not present in the calibration (tentatively identified compounds or "TICS") or not seen in the SIM window. If present, identify the peak and determine the class of compound (e.g. benzo[e]pyrene, benzo[a]pyrene) by evaluation of the total ion spectra.

Table 1 lists GC-MS parameters related to reference masses for the quantification of PAHs. Additional detailed GC-MS instrument parameters are described in Table A.1.

Table 1 – List of reference masses for the quantification of PAHs

Type of PAHs	Ions (m/z) monitored in the extract		
	Target ions (m/z)	Qualifier ions (m/z)	
Internal standard			
Naphthalene-d8	136	108	137
Anthracene-d10	188	178	187
Benzo[a]pyrene-d12	264	260	265
Substances			
Naphthalene	128	102	129
Acenaphthylene	152	76	151
Acenaphthene	154	76	153
Fluorene	166	83	165
Phenanthrene	178	76	179
Anthracene	178	89	176
Fluoranthene	202	101	200
Pyrene	202	101	200
Benzo[a]anthracene	228	114	226
Chrysene	228	114	226
Benzo[b]fluoranthene	252	126	253
Benzo[j]fluoranthene	252	126	253
Benzo[k]fluoranthene	252	126	253
Benzo[e]pyrene	252	126	253
Benzo[a]pyrene	252	126	253
Indeno[1,2,3cd]pyrene	276	138	274
Dibenzo[a,h]anthracene	278	139	276
Benzo[ghi]perylene	276	138	274

8.4 Calibrants

8.4.1 General

All PAH species from naphthalene- to benzo(g,h,i)perylene shall be included in the calibration. The availability of calibration standards for a particular PAH (e.g. benzo(a)pyrene) may vary from region to region. The following Table 2 is an example list of typically available calibration chemicals which are suitable for this analysis.

8.4.2 Stock solution

The following stock solutions shall be prepared:

a) Internal standard (to correct for injection error): 50 µg/ml, 100 µg/ml in toluene (e.g. naphthalene-d8, anthracene-d10 and benzo[a]pyrene-d12).

b) Surrogate standard (to monitor analyte recovery): 50 µg/ml, 100 µg/ml in toluene (e.g. chrysene-d12).

c) A PAH solution can be utilized providing the standard solution concentrations given in 8.5.2 can be achieved.

8.4.3 Preparation of calibration standard

Table 2 – Example list of commercially available calibration chemicals considered suitable for this analysis

Abbreviation	Compound name	CAS number	Formula	Molecular mass (g/mol)
ACE	Acenaphthene	83-32-9	$C_{12}H_{10}$	154,20
ACY	Acenaphthylene	208-96-8	$C_{12}H_{8}$	152,20
ANT	Anthracene	120-12-7	$C_{14}H_{10}$	178,24
BaA	Benzo[a]anthracene	56-55-3	$C_{18}H_{12}$	228,30
BaP	Benzo[a]pyrene	50-32-8	$C_{20}H_{12}$	252,32
BeP	Benzo[e]pyrene	192-97-2	$C_{20}H_{12}$	252,32
BbF	Benzo[b]fluoranthene	205-99-2	$C_{20}H_{12}$	252,32
BjF	Benzo[j]fluoranthene	205-82-3	$C_{20}H_{12}$	252,32
BkF	Benzo[k]fluoranthene	207-08-9	$C_{20}H_{12}$	252,32
BghiP	Benzo[ghi]perylene	191-24-2	$C_{22}H_{12}$	276,34
CHR	Chrysene	218-01-9	$C_{18}H_{12}$	228,30
DBahA	Dibenzo[a,h]anthracene	53-70-3	$C_{22}H_{14}$	278,35
FLU	Fluoranthene	206-44-0	$C_{16}H_{10}$	202,26
FLN	Fluorene	86-73-7	$C_{13}H_{10}$	166,23
IcdP	Indeno[1,2,3cd]pyrene	193-39-5	$C_{22}H_{12}$	276,34
NP	Naphthalene	91-20-3	$C_{10}H_{8}$	128,18
PHE	Phenanthrene	85-01-8	$C_{14}H_{10}$	178,24
PYR	Pyrene	129-00-0	$C_{16}H_{10}$	202,26

a) 1 000 mg/l each standard mixed stock solution:

The standards of Table 2 are respectively weighed to 0,1 g (100 mg) with an accuracy of 0,001 g, then placed in a 100 ml beaker, dissolved in a small amount of dichloromethane (Clause 5 a)), and measuring the volume of 100 ml after they are filled up with dichloromethane graduated to the mark and transferred to a flask (Clause 6 b)) in order to well shake the mix. (If necessary, it may be shaked ultrasonically.)

b) Intermediate standard mixed solution of 20 mg/l for GC-MS analysis:

Pipet 2 ml from each stock standard solution (8.4.3 a)) and 2 ml surrogate standard solution (8.4.5 b)) into a 100 ml volumetric flask and fill with dichloromethane up to the mark.

c) Intermediate standard mixed solution of 10 mg/l for GC-MS analysis:

Pipet 1 ml from each stock standard solution (8.4.3 a)) and 1 ml surrogate standard solution (8.4.5 b)) into a 100 ml volumetric flask and fill with dichloromethane up to the mark.

d) For low concentration samples, test standard solutions for GC-MS analysis:

For the preparation of low concentrations of the calibration standard solution (8.4.3 e) to 8.4.3 h)), PAH standard solutions are prepared for GC-MS analysis as shown in Table 3. These standard solutions each contain (20, 50, 100, 200) µg/l of one of the 18 PAH compounds. Internal standards each contain 50 µg/l of substance (such as naphthalene-d8, anthracene-d10 and benzo[a]pyrene-d12).

e) 20 µg/l calibration standard solution:

Pipet 0,02 ml from the 10 mg/l standard solution and 0,1 ml from the 5 mg/l working internal standard solution into a 10 ml volumetric flask and fill with dichloromethane up to the mark.

f) 50 µg/l calibration standard solution:

Pipet 0,05 ml from the 10 mg/l standard solution and 0,1 ml from the 5 mg/l working internal standard solution into a 10 ml volumetric flask and fill with dichloromethane up to the mark.

g) 100 µg/l calibration standard solution:

Pipet 0,1 ml from the 10 mg/l standard solution and 0,1 ml from the 5 mg/l working internal standard solution into a 10 ml volumetric flask and fill with dichloromethane up to the mark.

h) 200 µg/l calibration standard solution:

Pipet 0,2 ml from the 10 mg/l standard solution and 0,1 ml from the 5 mg/l working internal standard solution into a 10 ml volumetric flask and fill with dichloromethane up to the mark.

i) For high concentration samples, test standard solutions for GC-MS analysis:

For the preparation of high concentrations of the calibration standard solution (8.4.3 e) to 8.4.3 h)), PAH standard solutions are prepared for GC-MS analysis as shown in Table 4. These standard solutions each contain (0,5, 1, 2, 4, 10) mg/l of one of the 18 PAH compounds. Internal standards each contain 2 mg/l of substance (such as naphthalene-d8, anthracene-d10 and benzo[a]pyrene-d12).

j) 0,5 mg/l calibration standard solution:

Pipet 0,25 ml from the 20 mg/l standard solution and 1 ml from the 20 mg/l working internal standard solution into a 10 ml volumetric flask and fill with dichloromethane up to the mark.

k) 1 mg/l calibration standard solution:

Pipet 0,5 ml from the 20 mg/l standard solution and 1 ml from the 20 mg/l working internal standard solution into a 10 ml volumetric flask and fill with dichloromethane up to the mark.

l) 2 mg/l calibration standard solution:

Pipet 1 ml from the 20 mg/l standard solution and 1 ml from the 20 mg/l working internal standard solution into a 10 ml volumetric flask and fill with dichloromethane up to the mark.

m) 4 mg/l calibration standard solution:

Pipet 2 ml from the 20 mg/l standard solution and 1 ml from the 20 mg/l working internal standard solution into a 10 ml volumetric flask and fill with dichloromethane up to the mark.

n) 10 mg/l calibration standard solution:

Pipet 5 ml from the 20 mg/l standard solution and 1 ml from the 20 mg/l working internal standard solution into a 10 ml volumetric flask and fill with dichloromethane up to the mark.

8.4.4 Internal standard

a) Working internal standard mixed solution:

To analyse by GC-MS methods, using a naphthalene-d8, anthracene-d10 and benzo[a]pyrene-d12 as an internal standard.

b) 1 000 mg/l working internal standard mixed solution:

Put 0,1 g (100 mg) of three internal standards (naphthalene-d8, anthracene-d10 and benzo[a]pyrene-d12) into a 100 ml volumetric flask and fill with dichloromethane up to the mark. (If necessary, ultrasonic shaking may be used).

c) 100 mg/l working internal standard mixed solution:

Pipet 10 ml from the 1 000 mg/l working internal standard mixed solution into a 100 ml volumetric flask and fill with dichloromethane up to the mark.

d) 50 mg/l working internal standard mixed solution:

Pipet 5 ml from the 1 000 mg/l working internal standard mixed solution into a 100 ml volumetric flask and fill with dichloromethane up to the mark.

8.4.5 Surrogate standard

a) Working surrogate standard solution:

To monitor analyte recovery, using a chrysene-d12 as a surrogate standard.

b) 1 000 mg/l working internal standard mixed solution:

A quantity of 0,1 g (100 mg) of surrogate standard (chrysene-d12) is placed in a 100 ml beaker and dissolved in a small amount of dichloromethane (Clause 5 a)), and then filled with dichloromethane (Clause 5 a)) up to the mark of the 100 ml volumetric flask. (If necessary, ultrasonic extraction may be used).

c) 100 mg/l working surrogate standard solution:

10 ml of a 1 000 mg/l of working surrogate standard solution (8.4.5 b)) is taken , and placed in a 100 ml volumetric flask for measurement, then filled with dichloromethane (Clause 5 a)) up to the mark.

d) 50 mg/l working surrogate standard solution:

5 ml of a 1 000 mg/l of working surrogate standard solution (8.4.5 b)) is taken and placed in a 100 ml volumetric flask for measurement, then filled with dichloromethane (Clause 5 a)) up to the mark.

8.5 Calibration

8.5.1 General

Wherever possible, the solvent used for the sample and standard solutions shall be the same to avoid any potential solvent effects. A calibration curve shall be developed for quantitative analysis. At least five calibration solutions shall be prepared in equidistant concentration steps. Quantification is made on the basis of the measurement of the specified peak areas taken from the GC chromatogram. The linear regression fit of each calibration curve is required to have a relative standard deviation (RSD) of less than or equal to 15 % of the linear calibration function.

NOTE If the limiting value of the RSD of 15 % is exceeded, from the point of view of quality assurance, second-order curve fitting does not guarantee any significantly better adjustment. Only statistical tests such as the F-test fulfil these requirements by comparing linear/2^{nd} order. That means that although the RSD value is exceeded, the calibration is linear.

8.5.2 Calibration standard solutions of PAHs

A PAH standard solution (20 µg/ml of each chemical for high concentration samples and 10 µg/ml of each chemical for low concentration samples) and a surrogate standard (20 µg/ml for high concentration samples and 5 µg/ml for low concentration samples) stock solution are prepared.

For PAHs, the calibration range suggested in Table 3 and Table 4 may have to be modified. When establishing a calibration curve for PAHs, the lower range should be set according to the instrument's sensitivity. A higher concentration may be used for the upper range to account for the generally high levels of PAHs normally found in samples.

Table 3 – Preparation of low concentrations of the calibration standard solution for GC-MS analysis

No.	Volume PAHs + surrogate ml (see 8.4.3 c))	Volume internal standard ml (see 8.4.4 c))	Final volume ml	c (PAHs) µg/l	c (surrogate) µg/l
1	0,02	0,01	10	20	20
2	0,05	0,01	10	50	50
3	0,1	0,01	10	100	100
4	0,2	0,01	10	200	200

Table 4 – Preparation of high concentrations of the calibration standard solution for GC-MS analysis

No.	Volume PAHs + surrogate ml (see 8.4.3 b))	Volume internal standard ml (see 8.4.4 c))	Final volume ml	c (PAHs) µg/ml	c (surrogate) µg/ml
1	0,25	0,01	10	0,5	0,5
2	0,5	0,01	10	1	1
3	1,0	0,01	10	2	2
4	2,0	0,01	10	4	5
5	5,0	0,01	10	10	10

The internal standard is used for the correction of the injection error. Therefore, the evaluation of the response factor or ratio is carried out by A/A_{IS}.

To produce the calibration straight lines, the response A/A_{IS} is plotted against the concentration ratio c/c_{IS}.

A linear regression is carried out using Equation (1):

$$\frac{A}{A_{IS}} = a \times \frac{c}{c_{IS}} + b \quad (1)$$

where

A is the peak area of PAHs or the surrogate in the calibration solution;

A_{IS} is the peak area of the internal standard;

c is the concentration of PAHs or the surrogate per congener (ng/ml);

c_{IS} is the concentration of the internal standard (ng/ml);

NOTE 1 It is common practice to set the internal standard concentration to 1 ng/ml for the internal standard methods when the amount and concentration of the internal standard added to the sample and calibrants prior to injection are the same.

a is the slope of the calibration curve;

b is the intercept on the y-axis of the calibration curve.

NOTE 2 A polynomial (e.g. second-order) regression can be utilized in the event that the relative standard deviation curve requirements cannot be achieved using linear regression. All quality control requirements are still in effect when using polynomial regression.

9 Calculation of PAH concentration

9.1 General

Only detected PAH compounds shall be included in a total summation.

When there are no PAHs detected in the sample, the total PAHs shall be reported as a function of the chemicals with the highest method detection limits. For example, if the method detection limit is 20 µg/kg for BaP, and no PAHs are found in the sample, the total PAHs shall be reported as less than 20 µg/kg.

Analytes detected below the limit of quantification (and above the limit of detection) shall be summed using the limit of quantification for the analyte detected. For example, if BaP is found above the limit of detection but below the limit of quantification, and if the limit of quantification is 100 µg/kg for BaP and no other PAHs are found above the limit of detection in the sample, the total PAHs shall be reported as 100 µg/kg.

9.2 Calculation

Quantify the samples using the calibration curve. The sum of each PAH concentration in the sample is calculated by Equation 2.

$$C_{total} = \frac{C_i \times V}{W} \times DF \quad (2)$$

where

C_{total} is the sum of each PAH concentration in the sample (µg/g);

C_i is the concentration of PAHs (ng/ml);

V is the final sample volume (ml);

W is the sample weight (g);

DF is the dilution factor.

10 Precision: repeatability and reproducibility

When the values of two independent single test results, obtained using the same method on identical test material in the same laboratory by the same operator using the same equipment within a short interval of time, lie within the range of the mean values cited in Table 5 below, the absolute difference between the two test results obtained should not exceed the repeatability limit r deduced by statistical analysis of the international interlaboratory study PAHs (IIS10-PAHs) results in more than 5 % of cases.

When the values of two single test results, obtained using the same method on identical test material in different laboratories by different operators using different equipment, lie within the range of the values cited in Table 5 below, the absolute difference between the two results should not be greater than the reproducibility limit R by statistical analysis of interlaboratory study PAHs (IIS10-PAHs) results in more than 5 % of cases.

Table 5 – IIS10-PAHs repeatability and reproducibility

Parameter	Number of test result (N)	Mean value (m) mg/kg	r mg/kg	R mg/kg
Total PAHs	21	656	77,2	276,25
Total PAHs	27	270	23,4	180,54
Total PAHs	24	1 041	102,9	359,26
Total PAHs	20	89,07	19,96	54,80
Naphthalene	27	1,1	0,15	6,20
Naphthalene	27	0,8	0,16	5,98
Acenaphthylene	24	8,5	1,54	6,96
Acenaphthylene	24	2,5	0,36	8,22
Acenaphthene	24	72,0	9,79	44,58
Acenaphthene	24	29,4	4,22	16,26
Acenaphthene	23	8,2	1,32	6,36
Acenaphthene	27	1,8	0,77	3,19
Fluorene	24	65,3	7,81	37,03
Fluorene	24	29,6	4,26	15,05
Fluorene	24	30,6	8,30	12,25
Fluorene	24	6,1	2,89	13,13
Phenanthrene	24	72,1	8,67	45,58
Phenanthrene	27	31,7	3,06	20,41
Phenanthrene	21	196,1	14,95	84,32
Phenanthrene	27	16,0	14,98	31,43
Anthracene	24	71,7	7,96	50,14
Anthracene	24	33,0	3,37	20,18
Anthracene	27	57,5	6,91	30,62
Anthracene	27	5,2	3,31	11,98
Fluoranthene	24	76,5	9,02	53,44
Fluoranthene	24	33,8	4,31	23,64
Fluoranthene	21	185,1	13,57	95,51
Fluoranthene	24	14,9	3,74	13,22
Pyrene	24	73,2	8,56	50,65
Pyrene	24	33,5	3,54	25,20
Pyrene	24	139,8	12,57	77,23
Pyrene	24	31,4	5,05	20,16

Parameter	Number of test result (N)	Mean value (m) mg/kg	r mg/kg	R mg/kg
Benzo[a]anthracene	18	78,0	11,34	34,13
Benzo[a]anthracene	21	28,5	5,35	22,72
Benzo[a]anthracene	24	71,9	8,86	15,50
Benzo[a]anthracene	21	1,6	0,39	0,86
Chrysene	25	2,3	2,86	18,86
Chrysene	25	1,1	1,04	8,62
Chrysene	24	74,6	10,01	24,37
Chrysene	24	2,5	0,55	3,18
Benzo[b]fluoranthene	20	58,3	9,72	11,73
Benzo[b]fluoranthene	20	2,9	0,48	8,15
Benzo[j]fluoranthene	20	0,1	0,00	0,82
Benzo[j]fluoranthene	20	0,1	0,00	0,82
Benzo[j]fluoranthene	20	22,8	6,49	12,81
Benzo[j]fluoranthene	20	0,5	0,15	1,13
Benzo[k]fluoranthene	23	0,1	0,00	1,08
Benzo[k]fluoranthene	23	0,1	0,00	1,06
Benzo[k]fluoranthene	23	25,3	4,11	6,25
Benzo[k]fluoranthene	23	0,6	0,32	1,39
Benzo[e]pyrene	24	0,0	0,00	0,00
Benzo[e]pyrene	24	0,0	0,00	0,00
Benzo[e]pyrene	22	48,3	6,26	21,37
Benzo[e]pyrene	19	3,1	0,80	2,72
Benzo[a]pyrene	27	66,5	12,43	39,57
Benzo[a]pyrene	24	30,4	4,97	19,24
Benzo[a]pyrene	24	51,7	7,44	15,60
Benzo[a]pyrene	24	2,3	0,69	1,85
Indeno[1,2,3cd]pyrene	27	0,1	0,00	1,47
Indeno[1,2,3cd]pyrene	27	0,1	0,01	1,45
Indeno[1,2,3cd]pyrene	23	35,6	6,80	21,34
Indeno[1,2,3cd]pyrene	23	2,6	0,44	7,83
Dibenzo[a,h]anthracene	24	0,2	0,09	2,19
Dibenzo[a,h]anthracene	24	0,3	0,12	2,59
Dibenzo[a,h]anthracene	23	9,9	2,07	5,85
Dibenzo[a,h]anthracene	24	0,3	0,24	1,83
Benzo[ghi]perylene	27	0,1	0,00	1,20
Benzo[ghi]perylene	27	0,1	0,00	1,17
Benzo[ghi]perylene	24	39,7	9,24	18,51
Benzo[ghi]perylene	27	7,3	1,88	7,66

Key

N: number of test results taken into calculation

m: mean value in mg/kg

r: repeatability

R: reproducibility

See Annex B (Table B.1) for supporting data.

11 Quality assurance and control

11.1 Performance

The following steps are taken for the quality control:

One reagent blank shall be extracted with each sequence of samples. The reagent blank is 20 ml (40 ml amber vessel for ultrasonic extraction) or 5 ml (250 ml round-bottomed flask for Soxhlet extraction) of only solvent taken through the entire extraction procedure according to 8.2.1 or 8.2.2. The concentration of any PAH compounds found in the method blank shall be less than the method detection limits (see 11.2) for each compound.

a) After every tenth sample run and at the end of each sample set, analyse a continuing calibration check standard (CCC). A CCC is an unextracted mid-range calibrant that is analysed as a sample. The percent recovery for each congener shall be between 70 % and 130 %. If the percent recovery for any congener in the CCC standard falls outside of this range, the CCC standard should be reinjected within 12 h. If the recovery is still out of range after re-injection of the CCC standard, the analysis is stopped and maintenance shall be performed on the system to return it to optimal operating conditions. All samples injected before the last successful CCC standard may be reported, but all samples after the failing CCC standard shall be re-analysed with a new calibration.
b) The surrogate recovery shall be monitored for each sample. Percent (%) surrogate recovery shall be calculated by the following formula:

$$SR = \frac{ms}{ss} \times 100 \quad (3)$$

where

SR is the surrogate recovery, as a percentage (%);

ms is the total mass (µg) of surrogate measured in the final sample solution;

ss is the total mass (µg) of spiked surrogate in the sample.

Acceptable surrogate recovery shall be between 70 % and 130 %. If the surrogate recovery for any sample is outside of these limits, the sample shall be re-analysed. If, after re-analysis, the surrogate recovery is not within these limits, the sample shall be re-extracted and re-analysed.

From the results of the calibrants (according to Table 3 and Table 4), calculate the average response (peak area) for the internal standard. The internal standard (IS) response for each sample shall be monitored throughout the analysis and compared with the average. If, at any point in the analysis, the IS response fluctuates below 50 % or above 150 % of the average, the sample is deemed out of control and shall be re-analysed. If the IS response is still out of range, check the results of the duplicate extract. If both are out of range and biased in the same direction, report data as suspect due to matrix effects.

A solvent blank run between each injection is recommended in order to be certain that there is no analyte carry-over from sample to sample. This is particularly important when samples containing high levels of PAHs and/or potentially interfering PAHs are analysed.

11.2 Limit of detection (LOD) or method detection limit (MDL) and limit of quantification (LOQ)

A limit of detection (LOD) or method detection limit (MDL) study shall be completed before conducting testing and each time there is a significant change in the method or instrument type. The LOD or MDL is most appropriately determined experimentally by performing replicate, independent measurements on low-level or fortified sample matrices (e.g. plastic) carried out

through the entire test procedure, including extraction. A minimum of six replicates and analyte concentrations of three to five times the estimated LOD or MDL shall be performed for this analysis. The complete LOD or MDL for an entire test procedure is determined by multiplying the standard deviation of the replicates by an appropriate factor. IUPAC recommends a factor of three for a minimum of six replicates, whilst US EPA utilizes a one-sided confidence interval with the multiplier equal to Student's t value chosen for the number of replicates and the level of confidence (e.g. t = 3,36 for six replicates for 99 % confidence).

a) Mill approximately 0,5 g of suitable polymer from a pure source known not to contain PAHs or other compounds that may interfere with the analysis.

b) Weigh out 100 mg of the milled polymer and place it in a new extraction tool. Repeat this step six more times.

c) Place the extraction thimble in the Soxhlet extraction or ultrasonic apparatus.

d) Spike the thimble with 0,1 ml of each PAH (1 g/ml) (8.4.3 k)) and 10 µl surrogate standard (50 g/ml) (8.4.5 d)) stock solution approximating the concentration of the lowest concentration calibrant.

e) Use the procedure (extraction according to 8.2.1 or 8.2.2) to extract each of the samples. Analyse accordingly.

The percent recovery of each congener shall be between 70 % and 130 %. If the recovery is above or below these limits, the analysis shall be repeated. If the recovery is outside of these limits a second time, the entire extraction and analysis procedure shall be repeated.

Each congener shall have a calculated LOQ of less than 0,2 mg/kg. If the calculated LOQ for any of the congeners is above these limits, the procedure, extraction and analysis shall be repeated for that/those congener(s).

The limits of quantification (LOQ) for each congener shall be, at a minimum, three times the respective LOD or MDL. Unlike the LOD or MDL, which relates to detection only, the limit of quantification (LOQ) is a concentration that can be accurately quantified for a given compound.

If the required LOD or MDL cannot be met, a concentration step can be added to the extraction procedure. Since the concentration step will also increase the resin concentration in the extract, a clean-up step is also recommended for each sample. This will extend the life of the column and reduce the frequency of instrument maintenance. If the concentration and clean-up steps are used in the analysis, they should also be used for the LOD or MDL samples.

12 Test report

For the purposes of this document, IEC 62321-1:2013, 4.8 (Test report) shall apply.

Annex A
(informative)

Additional GC-MS conditions

A.1 Instrumental parameters for GC-MS

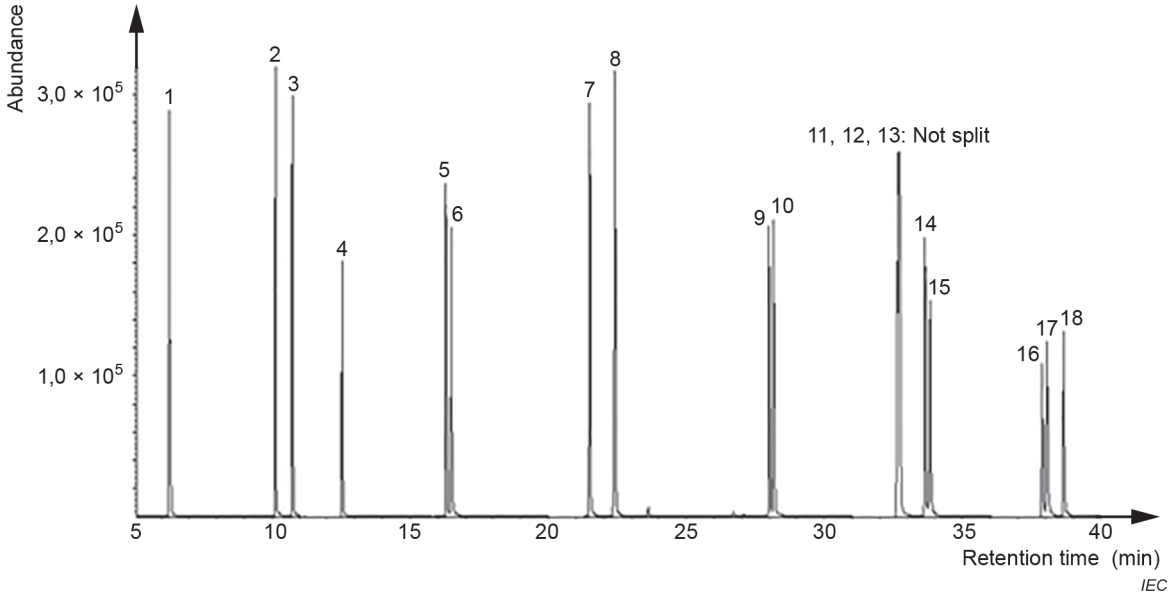
Table A.1 – Instrument parameters for GC-MS

GC parameters	
Injection volume	1,0 µl
Injection temperature	280 °C
Injection mode	Splitless
Injector liner	Split/Splitless liner (ID: 4 mm, single tap, with glass wool)
Column	DB-EUPAH, (20 m × 0,18 mm × 0,14 µm), capillary column
Carrier gas	Helium: 1,0 ml/min (constant flow)
Oven temperature	Initial (50 °C for 1 min) Ramp 1: 10 °C/min up to 200 °C for 0 min Ramp 2: 7 °C/min up to 250 °C for 2 min Ramp 3: 3 °C/min up to 300 °C for 5 min
Transfer line temperature	280 °C, direct
MS parameters	
Solvent holding	5 min
EM offset (relative voltage)	1 500 V
MS quadrupole temperature	150 °C (maximum: 200 °C)
MS source temperature	230 °C (maximum: 250 °C)
Scan range	50 amu to 550 amu
Sampling rate	2
Acquisition mode	Scan/SIM mode
Threshold	150

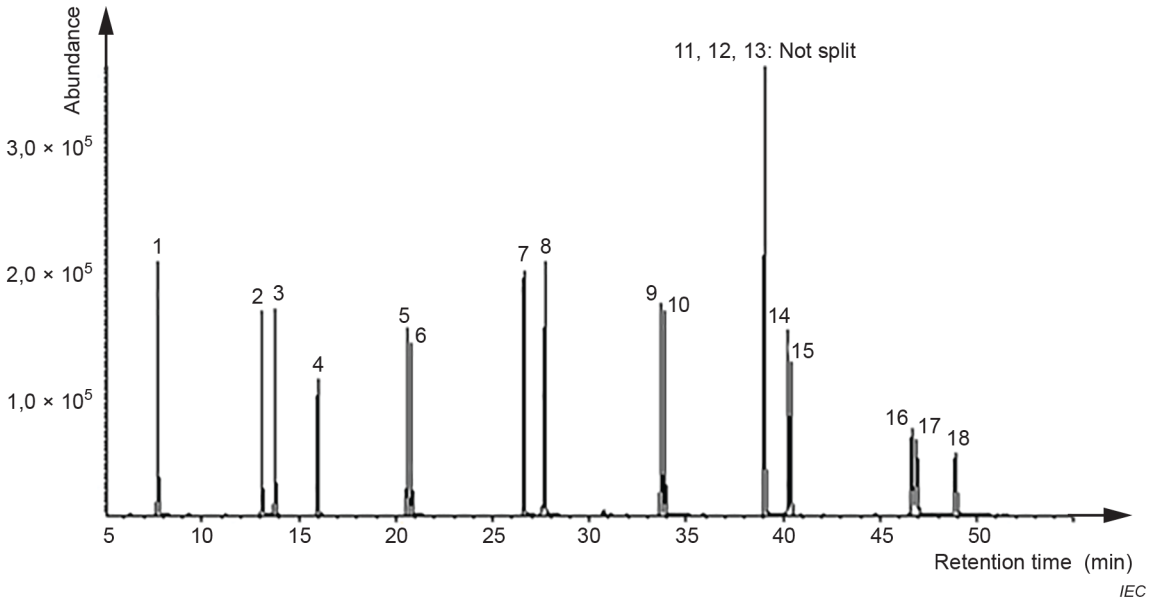
A.2 Examples of suitable column and its separation results for PAHs

Table A.2 – Examples of suitable column and its separation results for PAHs

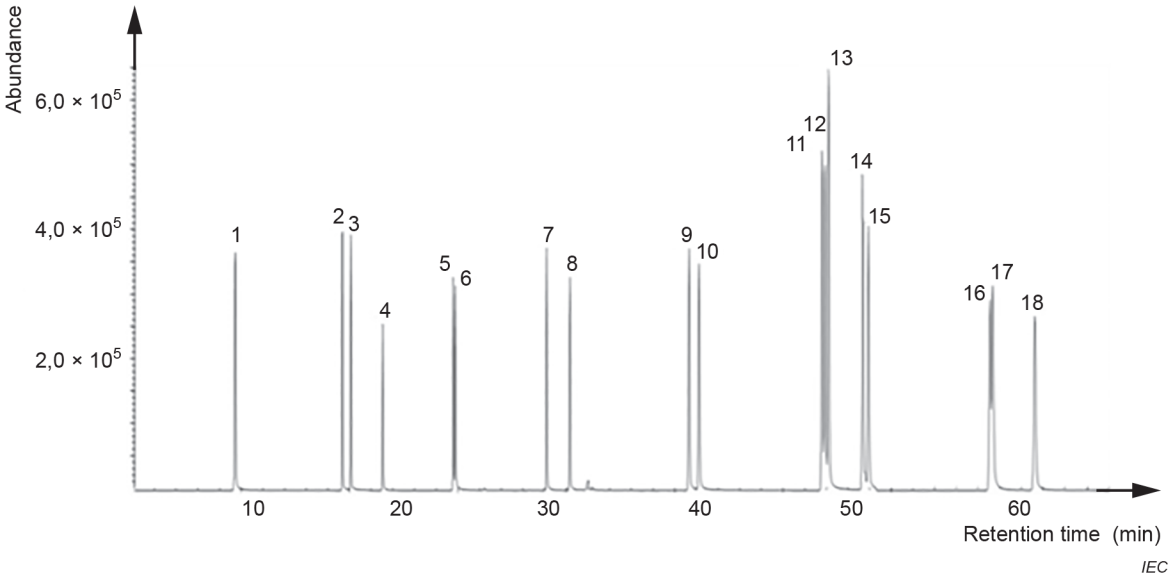
GC-MS PAHs column	DB-5MS	HT8	DB-EUPAH	ZB-PAH
Specification	Length 30 m: inner diameter 0,25 mm: film thickness 0,25 µm	Length 25 m: inner diameter 0,22 mm: film thickness 0,25 µm	Length 20 m: inner diameter 0,18 mm: film thickness 0,14 µm	Length 20 m: inner diameter 0,18 mm: film thickness 0,14 µm
Injection volume	1,0 µl	1,0 µl	1,0 µl	1,0 µl
Injection temperature	280 °C	280 °C	280 °C	290 °C
Injection mode	Splitless	Splitless	Splitless	Splitless
Injection liner	Split/Splitless liner	Split/Splitless liner	Split/Splitless liner	Split/Splitless liner
Carrier gas	Helium	Helium	Helium	Helium
Gas flow	1,0 ml/min (Constant flow)	1,0 ml/min (Constant flow)	1,0 ml/min (Constant flow)	1,0 ml/min (Constant flow)
Oven temperature	Initial (60 °C for 2 min) Ramp 1: 10 °C/min up to 200 °C for 0 min Ramp 2: 7 °C/min up to 250 °C for 2 min Ramp 3: 3 °C/min up to 300 °C for 15 min	Initial (60 °C for 2 min) Ramp 1: 10 °C/min up to 200 °C for 0 min Ramp 2: 7 °C/min up to 250 °C for 2 min Ramp 3: 3 °C/min up to 300 °C for 15 min	Initial (50 °C for 1 min) Ramp 1: 10 °C/min up to 200 °C for 0 min Ramp 2: 7 °C/min up to 250 °C for 2 min Ramp 3: 5 °C/min up to 300 °C for 30 min	Initial (120 °C for 1 min) Ramp 1: 10 °C/min up to 200 °C for 8 min Ramp 2: 11 °C/min up to 270 °C for 0,5 min Ramp 3: 2 °C/min up to 300 °C for 30 min
MS transfer temperature	280 °C	280 °C	280 °C	280 °C
Acquisition mode	Scan mode (50 amu to 550 amu)	Scan mode (50 amu to 550 amu)	Scan mode (50 amu to 550 amu)	Scan mode (50 amu to 550 amu)



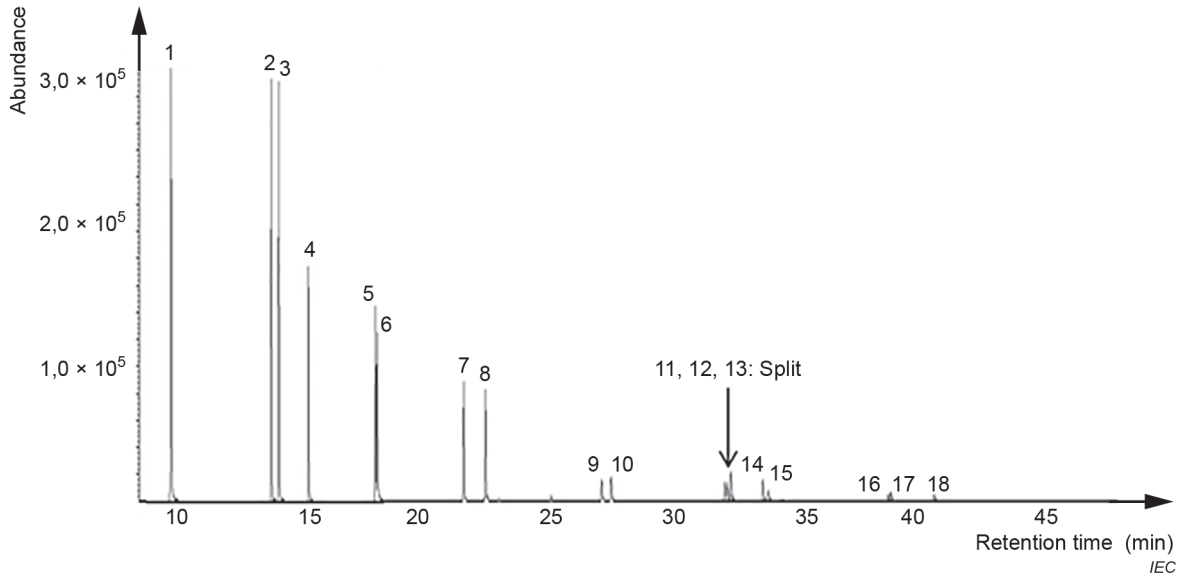
a) Separation result of the DB-5MS (30 m) for 18 PAHs



b) Separation result of the HT8 (25 m) for 18 PAHs



c) Separation result of the DB-EUPAH (20 m) for 18 PAHs



d) Separation result of the ZB-PAH (20 m) for 18 PAHs

Figure A.1 – Examples of total ion chromatograms of PAHs for each suitable PAH column, naphthalene to benzo[ghi]perylene

Table A.3 – Information of each PAH substance and numbers of aromatic rings

1	Naphthalene (2)[a]	7	Fluoranthene (3,5)	13	Benzo[k]fluoranthene (4,5)
2	Acenaphthylene (2,5)	8	Pyrene (4)	14	Benzo[a]pyrene (5)
3	Acenaphthene (2,5)	9	Benzo[a]anthracene (4)	15	Benzo[e]pyrene (5)
4	Fluorene (2,5)	10	Chrysene (4)	16	Indeno[1,2,3-cd]pyrene (5,5)
5	Phenanthrene (3)	11	Benzo[b]fluoranthene (4,5)	17	Dibenzo[a,h]anthracene (5)
6	Anthracene (3)	12	Benzo[j]fluoranthene (4.5)	18	Benzo[ghi]perylene (6)
[a]( ): number of aromatic rings.					

Annex B
(informative)

Results of international interlaboratory study of PAHs (IIS10-PAHs)

Table B.1 – Statistical data for GC-MS

Technique	Sample	Parameter	m	v	N	s(r)	r	s(R)	R	p	Outlier labs
			mg/kg	mg/kg		mg/kg	mg/kg	mg/kg	mg/kg		
GC-MS	IIS10-A01	Naphthalene	0	0	27	0,04	0,11	0,05	0,14	10	0
	IIS10-B02	Naphthalene	0	0	27	0,04	0,11	0,07	0,21	10	0
	IIS10-C03	Naphthalene	1,1	0	27	0,05	0,15	2,22	6,2	10	0
	IIS10-D04	Naphthalene	0,8	0	27	0,06	0,16	2,14	5,98	10	0
	IIS10-A01	Acenaphthylene	0	0	19	0	0	0	0	7	3
	IIS10-B02	Acenaphthylene	0	0	19	0	0	0	0	7	3
	IIS10-C03	Acenaphthylene	8,5	11,4	24	0,55	1,54	2,48	6,96	9	1
	IIS10-D04	Acenaphthylene	2,5	0	24	0,13	0,36	2,93	8,22	9	1
	IIS10-A01	Acenaphthene	72	96	24	3,5	9,79	15,92	44,58	9	1
	IIS10-B02	Acenaphthene	29,4	37,2	24	1,51	4,22	5,81	16,26	9	1
	IIS10-C03	Acenaphthene	8,2	16	23	0,47	1,32	2,27	6,36	8	2
	IIS10-D04	Acenaphthene	1,8	0	27	0,27	0,77	1,14	3,19	10	0
	IIS10-A01	Fluorene	65,3	97	24	2,79	7,81	13,22	37,03	9	0
	IIS10-B02	Fluorene	29,6	38,2	24	1,52	4,26	5,38	15,05	9	0
	IIS10-C03	Fluorene	30,6	47,2	24	2,96	8,3	4,37	12,25	9	0
	IIS10-D04	Fluorene	6,1	0	24	1,03	2,89	4,69	13,13	9	0
	IIS10-A01	Phenanthrene	72,1	113	24	3,1	8,67	16,28	45,58	9	1
	IIS10-B02	Phenanthrene	31,7	41,7	27	1,09	3,06	7,29	20,41	10	0
	IIS10-C03	Phenanthrene	196,1	221,2	21	5,34	14,95	30,12	84,32	8	2
	IIS10-D04	Phenanthrene	16	0	27	5,35	14,98	11,22	31,43	10	0
	IIS10-A01	Anthracene	71,7	109	24	2,84	7,96	17,91	50,14	9	1
	IIS10-B02	Anthracene	33	39,5	24	1,2	3,37	7,21	20,18	9	1
	IIS10-C03	Anthracene	57,5	57	27	2,47	6,91	10,94	30,62	10	0
	IIS10-D04	Anthracene	5,2	0	27	1,18	3,31	4,28	11,98	10	0
	IIS10-A01	Fluoranthene	76,5	119	24	3,22	9,02	19,08	53,44	9	1
	IIS10-B02	Fluoranthene	33,8	41,5	24	1,54	4,31	8,44	23,64	9	1
	IIS10-C03	Fluoranthene	185,1	208	21	4,85	13,57	34,11	95,51	8	2
	IIS10-D04	Fluoranthene	14,9	0	24	1,34	3,74	4,72	13,22	9	1
	IIS10-A01	Pyrene	73,2	111	24	3,06	8,56	18,09	50,65	9	1
	IIS10-B02	Pyrene	33,5	40,9	24	1,27	3,54	9	25,2	9	1
	IIS10-C03	Pyrene	139,8	168,7	24	4,49	12,57	27,58	77,23	9	1
	IIS10-D04	Pyrene	31,4	0	24	1,8	5,05	7,2	20,16	9	1
	IIS10-A01	Benzo[a]anthracene	78	116	18	4,05	11,34	12,19	34,13	7	2
	IIS10-B02	Benzo[a]anthracene	28,5	42,6	21	1,91	5,35	8,11	22,72	8	1
	IIS10-C03	Benzo[a]anthracene	71,9	102,1	24	3,16	8,86	5,53	15,5	9	0
	IIS10-D04	Benzo[a]anthracene	1,6	1	21	0,14	0,39	0,31	0,86	8	1
	IIS10-A01	Chrysene	2,3	0	25	1,02	2,86	6,73	18,86	9	1
	IIS10-B02	Chrysene	1,1	0	25	0,37	1,04	3,08	8,62	9	1
	IIS10-C03	Chrysene	74,6	105,2	24	3,57	10,01	8,7	24,37	9	1
	IIS10-D04	Chrysene	2,5	2,7	24	0,2	0,55	1,13	3,18	9	1
	IIS10-A01	Benzo[b]fluoranthene	0	0	20	0	0	0,06	0,18	7	2
	IIS10-B02	Benzo[b]fluoranthene	0	0	20	0	0	0,06	0,18	7	2

Technique	Sample	Parameter	*m* mg/kg	*v* mg/kg	*N*	s(*r*) mg/kg	*r* mg/kg	s(*R*) mg/kg	*R* mg/kg	*p*	Outlier labs
	IIS10-C03	Benzo[b]fluoranthene	58,3	0	20	3,47	9,72	4,19	11,73	7	2
	IIS10-D04	Benzo[b]fluoranthene	2,9	0	20	0,17	0,48	2,91	8,15	7	2
	IIS10-A01	Benzo[j]fluoranthene	0,1	0	20	0	0	0,29	0,82	7	2
	IIS10-B02	Benzo[j]fluoranthene	0,1	0	20	0	0	0,29	0,82	7	2
	IIS10-C03	Benzo[j]fluoranthene	22,8	0	20	2,32	6,49	4,57	12,81	7	2
	IIS10-D04	Benzo[j]fluoranthene	0,5	0	20	0,05	0,15	0,4	1,13	7	2
	IIS10-A01	Benzo[k]fluoranthene	0,1	0	23	0	0	0,39	1,08	8	2
	IIS10-B02	Benzo[k]fluoranthene	0,1	0	23	0	0	0,38	1,06	8	2
	IIS10-C03	Benzo[k]fluoranthene	25,3	32,5	23	1,47	4,11	2,23	6,25	8	2
	IIS10-D04	Benzo[k]fluoranthene	0,6	0	23	0,11	0,32	0,5	1,39	8	2
	IIS10-A01	Benzo[e]pyrene	0	0	24	0	0	0	0	9	0
	IIS10-B02	Benzo[e]pyrene	0	0	24	0	0	0	0	9	0
	IIS10-C03	Benzo[e]pyrene	48,3	63	22	2,23	6,26	7,63	21,37	8	1
	IIS10-D04	Benzo[e]pyrene	3,1	1,6	19	0,28	0,8	0,97	2,72	7	2
	IIS10-A01	Benzo[a]pyrene	66,5	115	27	4,44	12,43	14,13	39,57	10	0
	IIS10-B02	Benzo[a]pyrene	30,4	41,1	24	1,77	4,97	6,87	19,24	9	1
	IIS10-C03	Benzo[a]pyrene	51,7	80,8	24	2,66	7,44	5,57	15,6	9	1
	IIS10-D04	Benzo[a]pyrene	2,3	1,6	24	0,24	0,69	0,66	1,85	9	1
	IIS10-A01	Indeno[1,2,3cd]pyrene	0,1	0	27	0	0	0,53	1,47	10	0
	IIS10-B02	Indeno[1,2,3cd]pyrene	0,1	0	27	0	0,01	0,52	1,45	10	0
	IIS10-C03	Indeno[1,2,3cd]pyrene	35,6	58,4	23	2,43	6,8	7,62	21,34	8	2
	IIS10-D04	Indeno[1,2,3cd]pyrene	2,6	0	23	0,16	0,44	2,8	7,83	8	2
	IIS10-A01	Dibenzo[a,h]anthracene	0,2	0	24	0,03	0,09	0,78	2,19	9	0
	IIS10-B02	Dibenzo[a,h]anthracene	0,3	0	24	0,04	0,12	0,93	2,59	9	0
	IIS10-C03	Dibenzo[a,h]anthracene	9,9	13	23	0,74	2,07	2,09	5,85	8	1
	IIS10-D04	Dibenzo[a,h]anthracene	0,3	0	24	0,09	0,24	0,65	1,83	9	0
	IIS10-A01	Benzo[ghi]perylene	0,1	0	27	0	0	0,43	1,2	10	0
	IIS10-B02	Benzo[ghi]perylene	0,1	0	27	0	0	0,42	1,17	10	0
	IIS10-C03	Benzo[ghi]perylene	39,7	53	24	3,3	9,24	6,61	18,51	9	1
	IIS10-D04	Benzo[ghi]perylene	7,3	0	27	0,67	1,88	2,73	7,66	10	0
	IIS10-A01	sum of 3 PAHs	0,2	0	24	0	0	0,71	1,98	9	0
	IIS10-B02	sum of 3 PAHs	0,2	0	24	0,02	0,05	0,69	1,94	9	0
	IIS10-C03	sum of 3 PAHs	107,5	141,1	23	5,93	16,6	7,86	21,99	8	1
	IIS10-D04	sum of 3 PAHs	3	1,2	21	0,24	0,67	1,23	3,44	8	1
	IIS10-A01	sum of 18 PAHs	656	876	21	27,6	77,2	98,66	276,25	8	2
	IIS10-B02	sum of 18 PAHs	270	322,7	27	8,3	23,4	64,48	180,54	10	0
	IIS10-C03	sum of 18 PAHs	1 041	1 289,40	24	36,8	102,9	128,31	359,26	9	1
	IIS10-D04	sum of 18 PAHs	89,07	8,1	20	7,13	19,96	19,57	54,8	7	2

Key

m: general mean of the test property in mg/kg

v: expected value in mg/kg

N: number of test results taken into calculation

s(*r*): repeatability standard deviation

r: repeatability

s(*R*): reproduciblity standard deviation

R: reproducibility

p: number of laboratories taken into calculation

Annex C
(informative)

Labware cleaning procedure for PAH testing

C.1 With the use of furnace (non-volumetric glassware only)

a) Obvious loose contamination shall be removed mechanically from the glassware before starting the cleaning procedure, for example by brushing or shaking with water (if necessary, containing pieces of filter paper). If the solvent leaving the glassware gives off a pungent or bad smell, put the glassware in the fume hood until all the smell has gone.

b) Completely immerse the glassware in an aqueous solution of a soap-less detergent (the inner areas of the glassware shall be nearly filled with an aqueous solution of a soap-less detergent) for at least 4 h to loosen any particulates.

c) Scrub the glassware gently with the aid of a brush and shake it vigorously with the solution.

d) Rinse the glassware with plenty of tap water to remove all traces of detergent and then with acetone.

e) Arrange the non-volumetric glassware (e.g. beaker, round/flat bottom flask, vials) orderly into a furnace and then switch on the furnace and burn the glassware under 400 °C to 500 °C, for 4 h or overnight. (Never put volumetric glassware into the furnace).

f) When time is up, switch off the furnace and allow it to cool to room temperature.

   WARNING Do not open the furnace immediately, or you could burn yourself.

g) Take out the glassware from the furnace and store the glassware in a clean, solid and well labelled cabinet to minimize unnecessary exposure.

h) When using the laboratory glassware washer, load the non-volumetric glassware into the proper insert and then place the glassware in the basket. Put the basket into the washer. Use the appropriate programme stored for removing organic residues in the washer to clean the glassware. If there is still residue or something sticking on the surface of the glassware, perform steps C.1 e) to C.1 g) again.

C.2 Without the use of furnace (glassware and plastic-ware)

a) Obvious loose contamination shall be removed mechanically from the glassware and plastic-ware before starting the cleaning procedure, for example by brushing or shaking with water (if necessary containing pieces of filter paper). If the solvent leaving the labware gives off a pungent or bad smell, put the glassware in the fume hood until all the smell has gone.

b) Completely immerse the labware in an aqueous solution of a soap-less detergent (the inner areas of the glassware shall be nearly filled with an aqueous solution of a soap-less detergent) for at least 4 h to loosen any particulates.

c) Scrub the labware gently with the aid of a brush and shake it vigorously with the solution.

d) Rinse the labware with plenty of tap water to remove all traces of detergent and then with acetone.

e) Immerse the labware in an acid bath (5 % nitric acid) completely for at least 8 h or overnight.

f) Scrub the labware again as in step c) and rinse it with water (5 h) and acetone.

g) Place the glassware – except volumetric glassware (e.g. volumetric flask, pipette, burette) into a drying oven until all dry. (For volumetric glassware, air-drying is more appropriate).

h) Store the labware in a clean, solid and well labelled cabinet or stand or rack to minimize unnecessary exposure.

i) When using the laboratory glassware washer, load the glassware into the proper insert and then place the glassware in the basket. Place the basket into the washer. Use the appropriate cleaning programme for removing organic residues in the washer to clean the glassware. If there is still residue or something sticking on the surface of the glassware, Then perform steps C.2 b) to C.2 e) again.

C.3 Estimation of cleanness of the inner areas of volumetric glassware

To confirm that a glass apparatus has been satisfactorily cleaned, observe its behaviour while adding or removing liquid. For graduated vessels intended to deliver specific volume(s), begin slowly by filling with liquid below the highest volume marking and stop above the marking. The rising liquid meniscus shall not change shape (e.g. it shall be uniform at its edges). Likewise, after overfilling, withdraw a little liquid. The surface of the glass above shall remain uniformly wetted and the meniscus shall not deform at its edges but rather merge gradually onto the wall of the vessel. With experience, an observer is able to recognize the shape of a contaminated meniscus in relation to its diameter.

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