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Indoor air —

Part 31: Measurement of flame retardants and plasticizers based on organophosphorus compounds — Phosphoric acid ester

Air intérieur —

Partie 31: Mesurage des ignifugeants basés sur des composés organophosphorés — Ester d'acide phosphorique

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 146, *Air quality*, Subcommittee SC 6, *Indoor air*.

ISO 16000 consists of the following parts, under the general title *Indoor air*:

- *Part 1: General aspects of sampling strategy*
- *Part 2: Sampling strategy for formaldehyde*
- *Part 3: Determination of formaldehyde and other carbonyl compounds in indoor air and test chamber air — Active sampling method*
- *Part 4: Determination of formaldehyde — Diffusive sampling method*
- *Part 5: Sampling strategy for volatile organic compounds (VOCs)*
- *Part 6: Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA® sorbent, thermal desorption and gas chromatography using MS or MS-FID*
- *Part 7: Sampling strategy for determination of airborne asbestos fibre concentrations*
- *Part 8: Determination of local mean ages of air in buildings for characterizing ventilation conditions*
- *Part 9: Determination of the emission of volatile organic compounds from building products and furnishing — Emission test chamber method*
- *Part 10: Determination of the emission of volatile organic compounds from building products and furnishing — Emission test cell method*
- *Part 11: Determination of the emission of volatile organic compounds from building products and furnishing — Sampling, storage of samples and preparation of test specimens*
- *Part 12: Sampling strategy for polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polycyclic aromatic hydrocarbons (PAHs)*

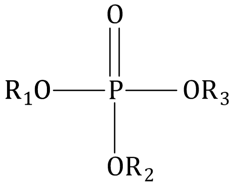
- *Part 13: Determination of total (gas and particle-phase) polychlorinated dioxin-like biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDDs/PCDFs) — Collection on sorbent-backed filters*
- *Part 14: Determination of total (gas and particle-phase) polychlorinated dioxin-like biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDDs/PCDFs) — Extraction, clean-up and analysis by high-resolution gas chromatography and mass spectrometry*
- *Part 15: Sampling strategy for nitrogen dioxide* (NO_2)
- *Part 16: Detection and enumeration of moulds — Sampling by filtration*
- *Part 17: Detection and enumeration of moulds — Culture-based method*
- *Part 18: Detection and enumeration of moulds — Sampling by impaction*
- *Part 19: Sampling strategy for moulds*
- *Part 21: Detection and enumeration of moulds — Sampling from materials*
- *Part 23: Performance test for evaluating the reduction of formaldehyde concentrations by sorptive building materials*
- *Part 24: Performance test for evaluating the reduction of volatile organic compound (except formaldehyde) concentrations by sorptive building materials*
- *Part 25: Determination of the emission of semi-volatile organic compounds by building products — Micro-chamber method*
- *Part 26: Sampling strategy for carbon dioxide* (CO_2)
- *Part 28*: *Determination of odour emissions from building products using test chambers*
- *Part 29: Test methods for VOC detectors*
- *Part 30: Sensory testing of indoor air*
- *Part 31: Measurement of flame retardants and plasticizers based on organophosphorus compounds — Phosphoric acid ester*
- *Part 32: Investigation of buildings for pollutants and other injurious factors — Inspections*

The following parts are under preparation:

- *Part 33: Determination of phthalates with gas chromatography/mass spectrometry (GC/MS)*
- *Part 34: Strategies for the measurement of airborne particles (PM 2,5 fraction)*
- *Part 35: Measurement of polybrominated diphenylether, hexabromocyclododecane and hexabromobenzene*
- *Part 36: Test method for the reduction rate of airborne bacteria by air purifiers using a test chamber*

Introduction

In general terms, phosphoric acid esters are formed by the reaction of alcohols or phenols with phosphoryl chloride ($POCl_3$). A distinction is made between mono-, di-, and triesters (see Figure 1). The triesters with aryl and alkyl groups, as well as with mixed halogenated and halogen-free ester groups serve as plasticizers and flame retardants in plastics and varnishes. Parallel therewith, phosphoric acid esters are incorporated in hardeners and accelerants, in mordant and adhesion boosting agents, and serve as cleaning, corrosion inhibition, and adhesion-facilitating substances by the treatment of metal surfaces. They are used as auxiliary means in paper and textiles, as wetting and defoaming agents, emulsifiers, and stabilizers, as additives to cleaning agents and detergents, as not readily flammable hydraulic liquids, and as oil and fuel additives (see Table 1). Not considered in this regard are the groups of the thio- and dithiophosphoric acid esters (pesticides), as well as the phosphoric acid esters with cyanide and halogen groups, with a special impact as acetylcholinesterase inhibitors (nerve gases).[3]



Key

R aryl, alkyl, halogenated, and halogen-free ester groups

Figure 1 — Structural formula of the phosphoric acid esters

Such multiplex applicability of the organophosporus compounds (OPCs) leads to the effect that large indoor areas with OPC-containing building materials, varnishes, paints, floor care products, or fire protection coatings can be encountered. Due to their varying physical and physical-chemical properties, OPC can also be detected in the indoor transfer media (dust and air). As a rule, OPCs boiling at high temperatures such as tris(2-butoxyethyl) phosphate (TBEP, see Annex A) can be found in relevant concentrations in indoor air only if the emission source reaches elevated temperatures. In the case of such sources (e.g. screens or roller blinds for sun protection), the importance of higher temperatures must be taken into consideration when emission chamber tests are carried out.

There is an increasing public interest in the possible health effects of OPCs indoors. For indoor air, a Guideline Value II of 0,05 mg/m^3 was published for TCEP and, in simplified terms, for the sum of TCEP, TCPP, TBP, TBEP, TEHP, and TPP as well. The Guideline Value I derived there amounts to 0,005 mg/m^3.[4] A review article on the occurrence and evaluation of OPC in an indoor environment is available.[5]

This part of ISO 16000 is based on VDI 4301 Part 5.

Indoor air —

Part 31:
Measurement of flame retardants and plasticizers based on organophosphorus compounds — Phosphoric acid ester

1 Scope

This part of ISO 16000 specifies a test method for the sampling and analysis of the phosphoric acid esters in indoor air and in test chamber air through gas chromatography/mass spectrometry. Both principle methods of the low-resolution mass spectrometry and the high-resolution mass spectrometry are described.

The methods described in this part of ISO 16000 are not suitable for the determination of the phosphoric acid esters in materials.

NOTE ISO 16000-6 can be applied for the determination of the more volatile compounds covered by this standard.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 16000-1, *Indoor air — Part 1: General aspects of sampling strategy*

ISO 16000-9, *Indoor air — Part 9: Determination of the emission of volatile organic compounds from building products and furnishing — Emission test chamber method*

ISO 16000-13, *Indoor air — Part 13: Determination of total (gas and particle-phase) polychlorinated dioxin-like biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDDs/PCDFs) — Collection on sorbent-backed filters*

3 Occurrence

The following compounds belonging to the halogen-free organophosphates are frequently detected in indoor air:

- triphenyl phosphate (TPP);
- tris(2-butoxyethyl) phosphate (TBEP);
- tri-n-butyl phosphate (TBP);
- tris(2-ethylhexyl) phosphate (TEHP);
- cresyl diphenyl phosphate (CDP);
- triethyl phosphate (TEP);
- tricresyl phosphate (TCP).

The following halogenated phosphoric acid esters are detected predominantly in house dust and indoor air:

- tris(2-chloroethyl) phosphate (TCEP);
- tris(chloropropyl) phosphate (TCPP);
- tris(1,3-dichloro-2-propyl) phosphate (TDCPP).

Bridged diphosphates based on resorcinol- and bisphenol-A are also increasingly implemented as flame retardants, e. g.

- tetraphenyl resorcinol diphosphate (RDP) or
- tetraphenyl bisphenol-A diphosphate (BDP).

So far, there is little information about the release of these compounds from primary sources.

Table 1 provides an overview of the organophosphates frequently detected in indoor air. The nomenclature and the chemical and physical data on the organophosphates are listed in Annex A.

Table 1 — Organophosphates and their intended use (see References[5] and[6])

OPC Abbreviation	Organophosphates	Intended use as flame retardant and plasticizer
CDP	Cresyl diphenyl phosphate	Flame retardant coatings
RDP	Tetraphenyl resorcinol diphosphate	Casing materials, special cables
TBEP	Tris(2-butoxyethyl) phosphate	Floor care products, floor wax, additives in elastomers, solvents for resins, antifoaming agents, additives for plastic, synthetic rubber, and varnishes
TBP	Tri-n-butyl phosphate	Defoaming agents for concrete additives, wall paper, dispersion paints, varnishes, rubber, plastic, and vinyl resins, antifoaming agents
TCEP	Tris(2-chloroethyl) phosphate	Paints, coatings, soundproofing ceilings, fibre glass wall paper, expanding foam, casing materials
TCPP	Tris(1-chloro-2-propyl)-phosphate[a]	Sound-absorbing polyurethane foam, expansion foam, soft foam (seats, mattresses), rear lining of textile, casing materials
TDBPP	Tris(2,3-dibromo-propyl) phosphate	Foamed rubber, varnishes, paper, paints, cellulose-, triacetate-, and polyester fabrics, carpets, resins, furniture, car interior details
TDCPP	Tris(1,3-dichloro-2-propyl) phosphate	PU foam, casing materials, rear lining of textile
TEHP	Tris(2-ethylhexyl) phosphate	Stabilizers, fat additives, additives for synthetic rubber
TCP	Tricresyl phosphate	Lubricants, car interiors, additives to floor covering and wall cladding
TPP	Triphenyl phosphate	Expanding foam, paints and varnishes, brighteners, casing materials, photographic films, phenol resins, additives for lubricants, car interior details

[a] Technical TCPP does not exist as a pure isomer. Hence it usually leads to up to three GC signals.

The published concentrations of indoor air measurements are compiled in Table 2. Citing of occasion-relevant measurement values cannot be excluded.

Table 2 — Published results on OPC in indoor air

Substance	**Concentration in indoor air** µg/m^3		
	Range	**Median**	**Reference**
TCEP	< 0,005 to 6	0,10 to 0,38	[8][9][10]
TCPP	0,019 to 0,058	–	[10]
TBP	0,01 to 0,064	–	[10]
TBEP	0,001 to 0,03	–	[9] and[10]
TEHP	< 0,001 to 0,01	–	[10]
TPP	< 0,01	–	[9] and[10]
TCP	< 0,01	–	[9]

4 Indoor air

4.1 Measurement planning

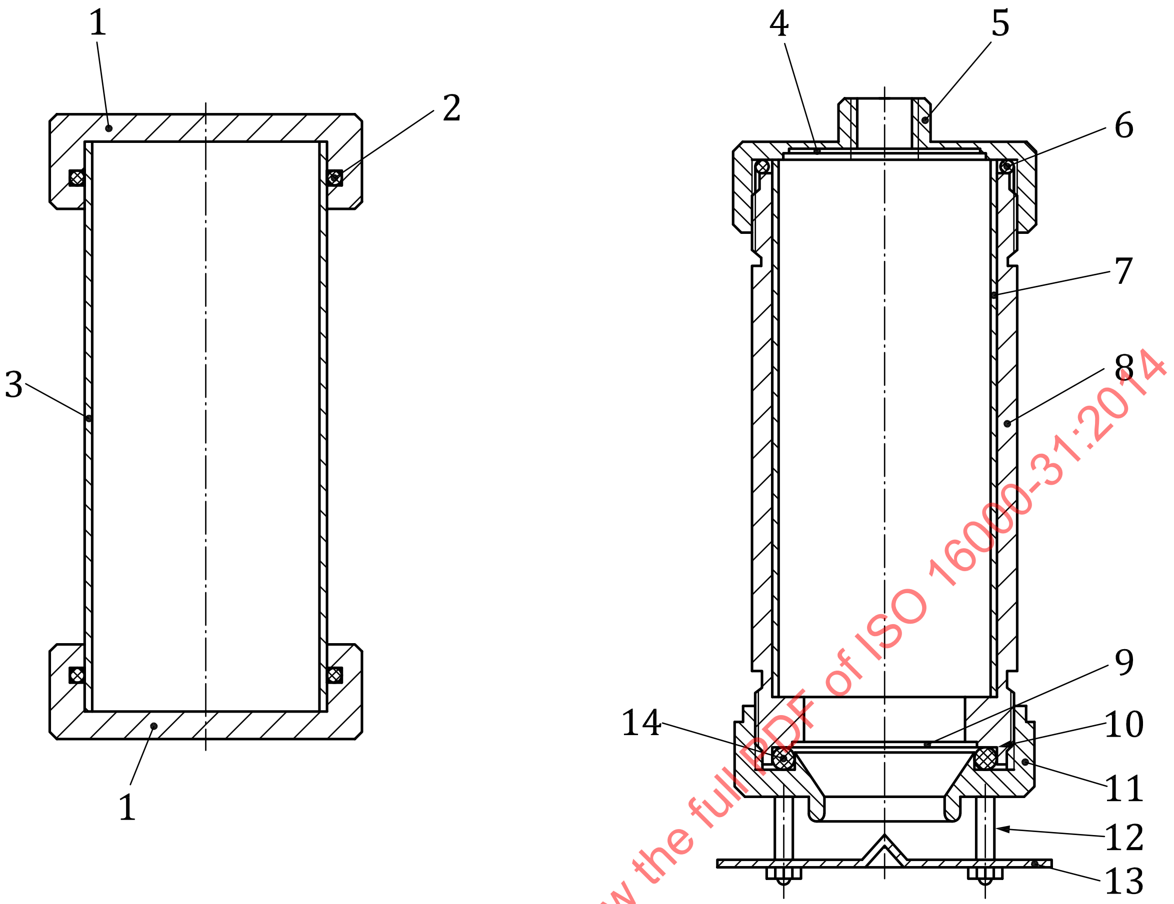
The measurement planning for the determination of the indoor air for phosphoric acid esters is performed according to the requirements of ISO 16000-1.

4.2 Apparatus and materials for sampling and sample preparation

4.2.1 Sampling apparatus

The sampling system is described in detail in ISO 16000-13.

4.2.1.1 Sampling head, with a sleeve for holding the PU foams (Figures 2a and 2b) (see also ISO 16000-13).



a) PU foam sleeve with cover (aluminium)

b) Sampling head

Key

1	cover
2	O-ring
3	PU foam sleeve (external diameter: 49,5 mm, length: approx. 120 mm)
4	stainless steel mesh
5	cap
6	O-ring
7	PU foam sleeve
8	cylinder (internal diameter: 49,8 mm)
9	stainless steel mesh to carry the glass fibre filter
10	PTFE-ring/filter disc/PTFE-ring
11	cap with inlet bore (internal diameter of the inlet bore: 27 mm)
12	spacer
13	baffle plate
14	O-ring

Figure 2 — Sampling apparatus consisting of a sampling head with a sleeve for holding PU foams

4.2.1.2 Pump, with volumetric flow of 2,7 m^3/h to 2,8 m^3/h (45 l/min to 46,7 l/min) under sampling conditions.

4.2.1.3 Gas volume meter.

4.2.1.4 Hygrometer.

4.2.1.5 Thermometer.

4.2.1.6 Barometer.

NOTE OPC sampling by means of “low-volume sampling systems” (PU foams, e.g. ORBO 1000[1]) with a sampling rate of 1 l/min to 5 l/min is possible within specified limits only. The sampling efficiency of such adsorbents for airborne particles is not known (see Reference [11]). This procedure does not correspond to the particle sampling requirements. Hence, its application comparability with the method described herein has to be proven.

4.2.2 Sample preparation apparatus

4.2.2.1 Glass apparatus, conventional laboratory equipment.

4.2.2.2 Extractor, Soxhlet.

4.2.2.3 Microlitre syringes, 10 µl, 50 µl, and 100 µl.

4.2.3 Materials for the sampling and sample preparation

4.2.3.1 Dichloromethane and toluene, all listed solvents shall be of sufficient purity for trace analysis.

4.2.3.2 Internal standards, ^{13}C-γ-HCH and ^{13}C-DDE (see 6.1).

4.2.3.3 Glass fibre filter, ∅ 5 cm, blank free.

4.2.3.4 PU foam, ∅ 5 cm, length of 2,5 cm, with low contaminations.

Step-by-step cleaning instructions for a “factory new” PU foam:

1) 24 h extraction with methanol in Soxhlet extractor;
2) 24 h extraction with dichloromethane in Soxhlet extractor;
3) 24 h extraction with toluene in Soxhlet extractor;
4) 24 h extraction with acetone in Soxhlet extractor.

Cleaning instructions for a sampled and extracted PU foam:

1) 24 h extraction with toluene in Soxhlet extractor;
2) 24 h extraction with acetone in Soxhlet extractor.

Dry the PU foam in a desiccator under adjacent vacuum conditions and with a gentle ultrapure nitrogen flow (from the evaporation of liquid nitrogen) or in a vacuum drying cabinet at 40 °C.

PU foams can shrink during extraction or respectively cleaning. Care shall be taken that these remain precisely fitting after cleaning.

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[1] ORBO 1000 is the trade name of a commercially available product. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

4.3 Sampling

Enrichment of the substances to be analysed from the indoor air takes place on a glass fibre filter and PU foam under the application of the sampling head as described in ISO 16000-13. Particle-bound as well as gaseous OPC are sampled in this way.

The internal standard is applied to the PU foam, whereas a total of 100 µl (for LRMS) or 50 µl (for HRMS) of the internal standard solution (see 6.1 and 6.2.1) are injected at different locations into the foam (e.g. with a microlitre syringe).

The internal standard should preferably be applied before sampling. If this proves impossible under justified occasions, the internal standard can also be spiked prior to the extraction, and a note thereof shall be entered in the test report.

At the measurement location, the PU foam is inserted in the sampling head. The glass fibre filter is placed in the filter holder by the aid of a pair of tweezers and fixed. The sampling head is positioned on the stand in such manner that the sampled air will flow through the sampling head in a vertical direction from the bottom to the top. The suction orifice is located at 1,2 m to 1,5 m above the floor. The sampling duration is normally 1 h. The volumetric flow shall be 2,7 m^3/h to 2,8 m^3/h. The sampling volume taken in 1 h should not exceed 10 % of the air exchange rate. If the latter is unknown, then the hourly drawn sampling volume shall not exceed 10 % of the room volume. The room temperature, the relative air humidity, and the air pressure shall be measured and recorded immediately prior to and after the sampling. Upon the sampling completion, the PU foam and the glass fibre filter are removed from the sampling head and transferred to suitable transportation containers.

4.4 Sample preparation

All deployed glass apparatus are rinsed with dichloromethane (DCM). If no blank-free glass apparatus can be obtained despite cleaning it with DCM, these shall then be additionally heated up for 24 h at 150 °C in a drying cabinet.

The PU foams and the filter are extracted jointly in a Soxhlet extractor. A minimum of 50 extraction cycles shall be achieved thereby.

The obtained extract is reduced to a volume of approximately 1 ml to 5 ml in a rotary evaporator under a controlled vacuum or in a Turbovap®[2]. A further volume reduction to approximately 0,1 ml to 1 ml is performed by using a flow of pure nitrogen. The solvent shall not be allowed to evaporate completely because losses of more volatile OPC are very likely. Losses can be prevented by the addition of toluene as a keeper.

NOTE Gas chromatography retention times can be altered when toluene is applied as a keeper.

Calibration is performed in accordance with Clause 6, and quantification is according to Clause 7.

5 Test chamber air

5.1 General

Emission measurements with building products and consumer goods under controlled climatic conditions are undertaken in order to establish substance-specific release rates [specific emission rates (SERs)].[12][13][14] The chamber air measurement takes place in a dust-free atmosphere so as to enable a simplified sampling procedure without particle separation as hereafter described. Care shall be taken with regard to the chamber volume, air exchange rate, and sampling volume so that the sampling volume is smaller than the amount of supplied air. The sample preparation, and in particular the sample storage, shall be coordinated with the test chamber measurement.

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2) Turbovap is the trade name of a commercially available product. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

Due to the physical properties of the compound class, the measurement of the OPC emissions from building products and from devices for indoor use is a complex process. Principally, such emissions can be determined by the chamber analyses according to ISO 16000-9. If ISO 16000-9 developed for volatile organic compounds (VOCs) is applied to semi-volatile OPC (SVOC), the specific chamber properties (e.g. sink effects) shall be taken into consideration.[14][15] A precondition for performing the test chamber analyses is the knowledge of ISO 16000-9.

5.2 Apparatus and materials for sampling

5.2.1 Emission test chamber, according to ISO 16000-9.

5.2.2 Sampling pump.

5.2.3 Gas volume meter.

5.2.4 Glass apparatus, conventional laboratory equipment.

5.2.5 Extractor, Soxhlet.

5.2.6 Microlitre syringes, 10 µl, 50 µl, and 100 µl.

5.2.7 Internal standards, ^{13}C-γ-HCH or ^{13}C-DDE (see 6.1).

5.2.8 Adsorbents, XAD-2®[3] or PU foam.

5.2.9 Quartz wool, silanized quartz wool.

The pre-cleaning is performed by Soxhlet extraction with methanol for at least 14 h.

5.3 Sampling

5.3.1 Chamber preparation

The chamber is cleaned prior to the start of the emission measurement (see ISO 16000-9). The chamber cleanness is subsequently documented by a blank measurement.

5.3.2 Preparation of the sampling tubes

The PU sampling media are cleaned and introduced in accordance with ISO 16000-13.

Commercially available XAD-2 adsorbent is only introduced following an appropriate pre-treatment. In the course of which, any distinct contamination of the XAD-2 adsorbent shall be removed as follows:

a) The chromatography column is filled with approximately 150 g XAD-2.

b) XAD-2 is rinsed with the double-distilled H_2O (approximately 1 l).

c) XAD-2 is rinsed four times, each time with approximately 100 ml acetone.

d) XAD-2 is dried in a N_2 flow.

e) XAD-2 is transferred to 100 ml Soxhlet and extracted for 24 h with methanol.

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[3] XAD-2 is the trade name of a product supplied by Buchem. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

f) Methanol is replaced by 100 ml DCM and XAD-2 is extracted for 24 h.

g) The cleaned XAD-2 is transferred to the chromatography column and dried in a N_2 flow.

The cleaned XAD-2 is transferred to a suitable glass vessel with ground neck.

Approximately 500 mg (±10 mg) are weighed out in a Pasteur pipette. The tip is then neatly broken and some amount of the silanized quartz wool is placed on the taper, and the XAD-2 is spiked with the internal standard. Closure of the XAD-2 package is also carried out by some silanized quartz wool.

5.4 Sampling procedure

The sampling on the XAD-2 or PU foam is carried out in accordance with the requirements of ISO 16000-9 at prescribed times within the exhaust air flow of the chamber. The maximum volume flow during the sampling is, on one hand, limited by the predetermined air exchange in the test chamber according to ISO 16000-9 while on the other hand, it shall not exceed 2 l/min.

5.5 Sample preparation

The XAD-2 sampling tubes are eluted with 10 ml DCM. The concentration is then increased in the rotary evaporator, and if required under N_2 flow, to approximately 100 µl. The solvent shall not be allowed to evaporate completely because losses of more volatile OPC are very likely. Losses can be prevented by the addition of toluene as a keeper.

NOTE Gas chromatography retention times can be altered when toluene is applied as a keeper.

Calibration is performed in accordance with Clause 6, and quantification is according to Clause 7.

6 Calibration

6.1 Internal standard solutions and calibration solutions

The verification of the standard solutions (solution for the internal standards and calibration solutions) is performed in accordance with the requirements for the quality assurance concerning weight control.

6.2 Internal standard solutions

6.2.1 General aspects

^{13}C-labelled organophosphates are currently not available. Hence, ^{13}C-γ-HCH or ^{13}C-DDE shall be used as an internal standard.

NOTE It is advisable to abstain from the use of deuterated TBP (D24-TBP) as an internal standard because an unidentified compound occurs by the analysis of a series of house dust samples on specific columns (e.g. HP Ultra), which appears at the same retention time as D24-TBP.

Solutions of the required concentration are either used as they have been obtained from the supplier or prepared as follows: 5 mg ^{13}C-γ-HCH and ^{13}C-DDE are dissolved in 50 ml isooctane (0,1 mg/ml).

6.2.2 Internal standard solution for low resolution

The solution of the internal standard is diluted with DCM at a ratio of 1:10 (1 + 9). The result is a solution with a concentration of 10 ng/µl.

6.2.3 Internal standard solution for high resolution

The solution of the internal standard is diluted with DCM at a ratio of 1:100 (1 + 99). The result is a solution with a concentration of 1 ng/µl.

6.3 Calibration solutions for low resolution

6.3.1 Example of a calibration scheme

The calibration scheme in Table 3 is referred to a practical example with ^{13}C-DDE implemented as an internal standard.

Table 3 — Scheme for the preparation of the calibration solutions for low-resolution measurements (example for ^{13}C-DDE)

Calibration solution (Concentration of OPC to be measured) µg/ ml	^{13}C-DDE-solution µl	Solution 1 µl	Solution 2 µl
0,2	100		20
0,5	100		50
1,0	100		100
2,0	100		200
5,0	100	50	
10	100	100	

6.3.2 Stock solutions

Original substances are prepared for the stock solutions TCEP, TCPP, TDCPP, TBP, TBEP, TEHP, TPP, and TCP.

The solutions are prepared as follows:

a) Each 250 mg of the respective phosphoric acid compound are dissolved in 25 ml methanol (10 mg/ml).

b) These stock solutions are diluted with DCM at a ratio of 1:100 (solution 1) and 1:1000 (solution 2).

c) Two solutions are obtained, with concentrations of 100 ng/µl and 10 ng/µl respectively.

6.3.3 Calibration solutions

The calibration solutions shall be prepared according to the scheme shown in Table 3 from the internal standard solutions and the two stock solutions. The six calibration solutions are prepared as follows:

a) 100 µl of the internal standard solution are filled to a vial with a volume of 2 ml using a microliter syringe.

b) The relevant stock solution is then added by a suitable microliter syringe and filled up to a final volume of 1 ml.

c) The vial is promptly closed by means of a septum flanged cap.

NOTE The required use of an internal standard ensures the compensation of the possible losses during the sampling preparation, e.g. errors and inaccuracies by topping up to the end volume are compensated by the internal standard.

The same solution of the internal standard as later utilized for spiking the PU foams shall be used for preparing the calibration solutions.

6.4 Calibration solutions for high resolution

6.4.1 Example of a calibration scheme

The calibration scheme in Table 4 is referred to a practical example with ^{13}C-γ-HCH implemented as an internal standard.

Table 4 — Scheme for the preparation of the calibration solutions for high-resolution measurements (example for ^{13}C-γ-HCH, see 6.2.1)

Calibration solution (Concentration of OPC to be measured) ng/ml	13C-γ-HCH µl	Solution A µl	Solution B µl
5	50	–	50
50	50	50	–
500	50	500	–

6.4.2 Stock solutions

Original substances are prepared for the stock solutions TCEP, TEHP, TBEP, and TPP (97 % purity).

For TCP, use the isomer mixture (90 % purity).

The solutions are prepared as follows:

a) Each 10 mg of the respective phosphoric acid compound are dissolved in 10 ml DCM (1 mg/ml).

b) These stock solutions are diluted with DCM at a ratio of 1:1000 (solution A).

c) The resulting solutions have concentrations of 1 µg/ml.

Solution A is diluted again with DCM at a ratio of 1:10. The result is solution B with a concentration of 0,1 µg/ml.

6.4.3 Calibration solutions

The calibration solutions shall be prepared according to the scheme shown in Table 4 from the internal standard solutions and the two stock solutions.

The three calibration solutions are prepared as follows:

a) 50 µl of the internal standard solution (= 50 ng) and the volumes of the relevant stock solutions as shown in Table 4 are filled up to a final volume of 1 ml.

b) The concentration of the internal standards amounts to 50 ng/ml in all calibration solutions.

c) The same solution of the internal standard as later utilized for spiking the PU foams shall be used for preparing the calibration solutions.

NOTE 1 The required use of an internal standard ensures the compensation of the possible losses during the sampling preparation, e.g. errors and inaccuracies by topping up to the end volume are compensated by the internal standard.

NOTE 2 DCM is selected as the solvent for the calibration solutions because of the limited solubility of OPC in non-polar solvents.

7 Identification and quantification

7.1 General

The analysis of the phosphoric acid esters is performed by the aid of a high- or low-resolution gas chromatography-mass spectrometry (GC/HR-MS or GC/LR-MS). The quantification is carried out after the internal standard method. The operating range extends from 0,2 µg/ml to 10 µg/ml for GC/LR-MS and 0,005 µg/ml to 0,5 µg/ml for GC/HR-MS.

The following apparatus are specified as practical examples. If other equipment is used, the parameters shall be transferred accordingly.

7.2 Analysis apparatus

7.2.1 Capillary gas chromatograph, with a mass spectrometric detector (practical examples given below).

7.2.2 Split/splitless injector.

7.2.3 Capillary column, of low polarity.

7.3 Analysis with GC/LR-MS

7.3.1 Analysis apparatus (practical example)

7.3.1.1 Gas chromatograph.

7.3.1.2 Mass spectrometer.

7.3.2 GC conditions

7.3.2.1 Capillary column, DB 1701, length of 30 m, internal diameter of 0,25 mm, film thickness of 0,25 µm.

7.3.2.2 Injector, splitless, 2 µl.

7.3.2.3 Column initial pressure, 90 kPa.

7.3.2.4 Temperature program, 40 °C (2 min) ⇒ (15 K/min) ⇒ 180 °C ⇒ (5 K/min) ⇒ 280 °C (8,67 min), total run time of 40 min, injector and transfer tube are kept at 270 °C.

7.3.3 MS conditions

7.3.3.1 SIM modus.

7.3.3.2 SIM mass, see Table 5.

7.4 Analysis with GC/HR-MS

7.4.1 Analysis apparatus (practical example)

7.4.1.1 Gas chromatograph.

7.4.1.2 Mass spectrometer.

7.4.2 GC conditions

7.4.2.1 Capillary columns, HP Ultra, length of 50 m, internal diameter of 0,2 mm, film thickness of 0,33 µm.

7.4.2.2 Injector, splitless, 1 µl.

7.4.2.3 Column pressure, 186 kPa.

7.4.2.4 Injector and transfer line, 270 °C.

7.4.2.5 Temperature program (column), 60 °C (2 min) ⇒ (20 K/min) ⇒ 200 °C ⇒ (4 K/min) ⇒ 220 °C ⇒ (20 K/min) ⇒ 250 °C (2 min).

7.4.3 MS conditions

7.4.3.1 Resolution, 7 000.

7.4.3.2 MID Program, for TCEP, TBEP, TPP, TEHP and p,p,p-TCP (see Table 6).

Table 5 — Mass traces — low-resolution mass spectrometry (SIM masses)

Substance	Retention time[b] min	Quant.-ion m/z	Qual.-ion m/z
TBP	14,16	211	155 (150 %)
TCEP	17,58	249	251 (65 %)
TCPP	17,46[a]	277	279 (65 %)
TDCPP	27,21	191	193 (65 %)
TBEP	26,36	199	299 (56 %)
TEHP	26,10	211	113 (500 %)
TPP	26,61	326	325 (82 %)
TCP	30,81[a]	367	368 (130 %)
$^{13}C_{12}$-DDE (internal standard)	21,77	330	328 (86 %)

[a] Several isomeric compounds.

[b] Example according to the column.

Table 6 — Mass traces — high-resolution mass spectrometry (MID program)

	Compound	Fragmentation m/z
1. window	TCEP	204,958 8
		206,955 9
		248,985 0
		250,982 1
	^{13}C-HCH	188,955 0
		226,928 6
2. window	TBEP	199,073 5
		227,104 8
		299,162 3
3. window	TPP	325,063 0
		326,070 8
		327,074 2
4. window	TEHP	98,984 7
		113,000 4
5. window	TCP	367,109 9
		368,117 7
		369,121 1

7.5 Calculation result interpretation and presentation

7.5.1 General aspects

Calibration solutions (a minimum of three) are injected for calibration and analysed. The calibration shall be checked for each analysis or a series of analyses in accordance with the quality assurance guidelines.

After the analysis, the quotient of the peak areas of the fragment ion trace of the substance to be analysed versus the peak areas of the fragment ion trace of the internal standard (peak area ratio) is calculated for each calibration solution (e.g. m/z = 330 for ^{13}C-DDE and m/z = 189 and m/z = 227 for ^{13}C-γ-HCH).

For the visualization of the calibration function, the peak area ratio is plotted against the concentrations. The calibration function is determined by a linear regression $v_{\mathrm{PF}} = b\rho + a$.

The determined coefficients are used for calculating the concentrations in the measurement solutions:

$$\rho = \frac{v_{\mathrm{PF}} - a}{b} \tag{1}$$

where

ρ is the concentration;

v_{PF} is the peak area ratio;

b is the slope;

a is the intercept.

7.5.2 Indoor air samples

The measurement result shall be expressed in µg/m^3 and is to be rounded to two significant digits.

7.5.3 Test chamber air samples

The measurement result shall be expressed in µg/m^3. The specific emission rates (SERs) can be calculated therefrom (e.g. according to ISO 16000-9). The result is to be rounded to two significant digits, respectively.

8 Performance characteristics

8.1 Performance characteristics of the air analyses

Analytical characteristics for TBEP, TBP, TCEP, TCPP, TEHP, TCP, and TPP in indoor air and test chamber air:

- sampling volume of 1 m^3;
- limit of quantification (relative to blank) of 10 ng/sample, corresponding to 0,01 µg/m^3;
- standard deviation (day-to-day precision) of 15 % to 20 %;
- recovery rate of the analytical method > 90 %.

For the breakthrough behaviour, no breakthrough of the utilized sorbents can be anticipated under the standard concentrations of the indoor air or test chamber air for a sampling volume of up to 2 m^3.

9 Quality assurance

Carrying out of multiple sampling is recommended. The measurement plan shall specify which measures are being taken to meet the quality requirements specified by the client. In the selection and specification of the quality assurance measures, the following questions shall be answered in advance:

- Does the measuring institute have a documented quality assurance system?
- Are duplicate measurements or comparative measurements (e.g. with other laboratories) to be carried out?
- How will the measurement uncertainties be determined (e.g. according to DIN 1319-3)?
- In which interlaboratory test has the measuring institute participated?

10 Interferences

The described physical and physical-chemical properties of OPC, as well as their wide distribution, lead to substantial difficulties in the quantification of OPC. It is recommended to regularly check each step of the procedure to be free of blanks or carry-over effects. In case of doubt, the blanks shall be checked prior to each determination.

The following interferences that should be avoided by the proper application of the guideline have been found in the course of the development of the method and during the drafting of this guideline:

Relevant blanks and, consequently, carry-over effects are caused both by OPC-containing materials (e.g. paper filters) and by the losses from adsorptions on the apparatus walls. For example, cyclohexane is not in the position to keep strong polar OPC in the solution. When acetone/cyclohexane is used for extraction, it can be found that up to 100 % of the available TCEP is irreversibly adsorbed on the glass walls of the extraction or concentration apparatus if acetone is removed from the solvent mixture by distillation.[4] Automatic extraction apparatus featuring plastic seals are generally not suitable due to the OPC absorption in plastics.[4] Special care shall be given to the cleaning of the glass apparatus for the sample preparation.

When deuterated TBP (D24-TBP) is used as an internal standard, an unidentified compound occurs in specific columns (e.g. HP Ultra) by a series of house dust samples which appears at the same retention time as D24-TBP.

Annex A
(informative)

Nomenclature and physical characteristics

Table A.1 — Physical properties of the selected organophosphorus compounds

Group/Name	Abbreviated term	CAS No.	Summary formula	Mol. mass g/mol	Boiling point °C	Vapor pressure hPa	Note
Alkylated OPC							
Triethyl phosphate	TEP	78–40–0	$C_6H_{15}O_4P$	182,2	215 to 216 (1 013 hPa)[d]	< 1,3 (25 °C)[c] 1,4 (40 °C)[d]	
Tri-n-butyl phosphate	TBP	126–73–8	$C_{12}H_{27}O_4P$	266,3	289 (1 013 hPa)[g] 130 (5 hPa)[d]	< 6,6 (25 °C)[g] 0,08 (50 °C)[d]	
Tris(2-butoxyethyl) phosphate	TBEP	78–51–3	$C_{18}H_{39}O_7P$	398,5	200 to 230 (5 hPa to 5,3 hPa)[j] 215 to 228 (5 hPa)[c]	$2,8 \times 10^{-7}$ (25 °C)[j] < 1,3 (25 °C)[c] 0,04 (150 °C)[c]	
Tris(2-ethylhexyl) phosphate	TEHP	78–42–2	$C_{24}H_{51}O_4P$	434,6	220 (7 hPa)[j] 210 (5 hPa)[d]	< 0,1 (20 °C)[j] < 6,6 (20 °C)[c] 2,5 (200 °C)[d]	
Arylated OPC							
Triphenyl phosphate	TPP	115–86–8	$C_{18}H_{15}O_4P$	326,3	370 (1 013 hPa)[f] 247 (15 hPa)[d]	0,2 (150 °C)[f] 1,3 (193 °C)[d]	
Cresyl diphenyl phosphate	CDP	26444–49–5	$C_{19}H_{17}O_4P$	340,3	235 to 255 (no data)[c]	no data	GC: 2 isomers
Tricresyl phosphate (isomer mixture)	TCP	1330–78–5	$C_{21}H_{21}O_4P$	368,4	262 to 264 (11 hPa)[a] 241 to 255 (5 hPa)[e]	$1,3 \times 10^{-4}$ (20 °C)[e]	
o,o,o-Tricresyl phosphate	o,o,o-TCP	78–30–8	$C_{21}H_{21}O_4P$	368,4	410 (1 013 hPa)[e]	13,3 (265 °C)[e] $2,3 \times 10^{-6}$ (25 °C)[c]	

Table A.1 *(continued)*

Group/Name	Abbreviated term	CAS No.	Summary formula	Mol. mass g/mol	Boiling point °C	Vapor pressure hPa	Note
m,m,m-Tricresyl phosphate	m,m,m-TCP	563–04–2	$C_{21}H_{21}O_4P$	368,4	260 (20 hPa)[e]	no data	
p,p,p-Tricresyl phosphate	p,p,p-TCP	78–32–0	$C_{21}H_{21}O_4P$	368,4	244 (5 hPa)[e]	no data	
Halogenated OPC							
Tris(2-chloroethyl) phosphate	TCEP	115–96–8	$C_6H_{12}O_4Cl_3P$	285,5	351 (1 013 hPa)[i]	< 13,3 (25 °C)[i]	
Tris(1-chloro-2-propyl) phosphate	TCPP	13674–84–5	$C_9H_{18}O_4Cl_3P$	327,6	236 to 248 (1 013 hPa)[i]	< 2,7 (25 °C)[i]	GC: 3 isomers
Tris(3-chloropropyl) phosphate	TCPP	no data	$C_9H_{18}O_4Cl_3P$	327,6			
Tris(1,3-dichloro-2-propyl) phosphate	TDCPP	13674–87–8	$C_9H_{15}O_4Cl_6P$	430,9	236 to 237 (7 hPa)[i]	0,01 (30 °C)[i]	
Tris(2,3-dichloro propyl) phosphate	TDCPP	no data	$C_9H_{15}O_4Cl_6P$	430,9			not significant as flame retardant
Tris(2,3-dibromo propyl) phosphate	TDBPP	126–72–7	$C_9H_{15}O_4Br_6P$	697,7	390 (no data)[h]	$2,5 \times 10^{-4}$ (25 °C)[h] $1,6 \times 10^{-3}$ (45 °C)[h] $6,4 \times 10^{-3}$ (65 °C)[h]	“Tris”
Bridged OPC							
Tetraphenyl Resorcinol diphosphat	RDP	57583–54–7	$C_{30}H_{24}O_8P_2$	574,5	> 300 (no data)[b]	< 1,3 (38 °C)[b]	data on the idealized structure

Table A.1 *(continued)*

Group/Name	Abbreviated term	CAS No.	Summary formula	Mol. mass g/mol	Boiling point °C	Vapor pressure hPa	Note
Tetraphenyl Bisphenol-A diphosphate	BDP	no data	$C_{39}H_{34}O_8P_2$	692,6	no data	no data	data on the idealized structure

[a] ABCR Safety data sheet.

[b] Akzo Nobel 98, Flyoflex product information.

[c] Chem Finder.

[d] Merck Safety data sheet 96, 99.

[e] WHO 1991, Environmental Health Criteria, 110.

[f] WHO 1991, Environmental Health Criteria, Heft 111.

[g] WHO 1991, Environmental Health Criteria, 112.

[h] WHO 1995, Environmental Health Criteria, 173.

[i] WHO 1998, Environmental Health Criteria, 209.

[j] WHO 2000, Environmental Health Criteria, 218.