
Indoor air —

Part 31:

**Measurement of flame retardants
and plasticizers based on
organophosphorus compounds —
Phosphoric acid ester**

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Air intérieur —

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

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Foreword

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

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).

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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)*

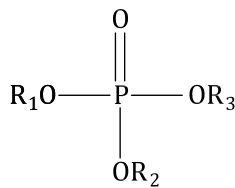
- Part 13: Determination of total (gas and particle-phase) polychlorinated dioxin-like biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDDs/PCDFs) — Collection on sorbent-backed filters
- Part 14: Determination of total (gas and particle-phase) polychlorinated dioxin-like biphenyls (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 (NO₂)
- 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 (CO₂)
- 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 (POCl₃). 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 organophosphorus 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/m³ 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/m³.^[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.

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2 Normative references

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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-dibromopropyl) 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 $\mu\text{g}/\text{m}^3$		
	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

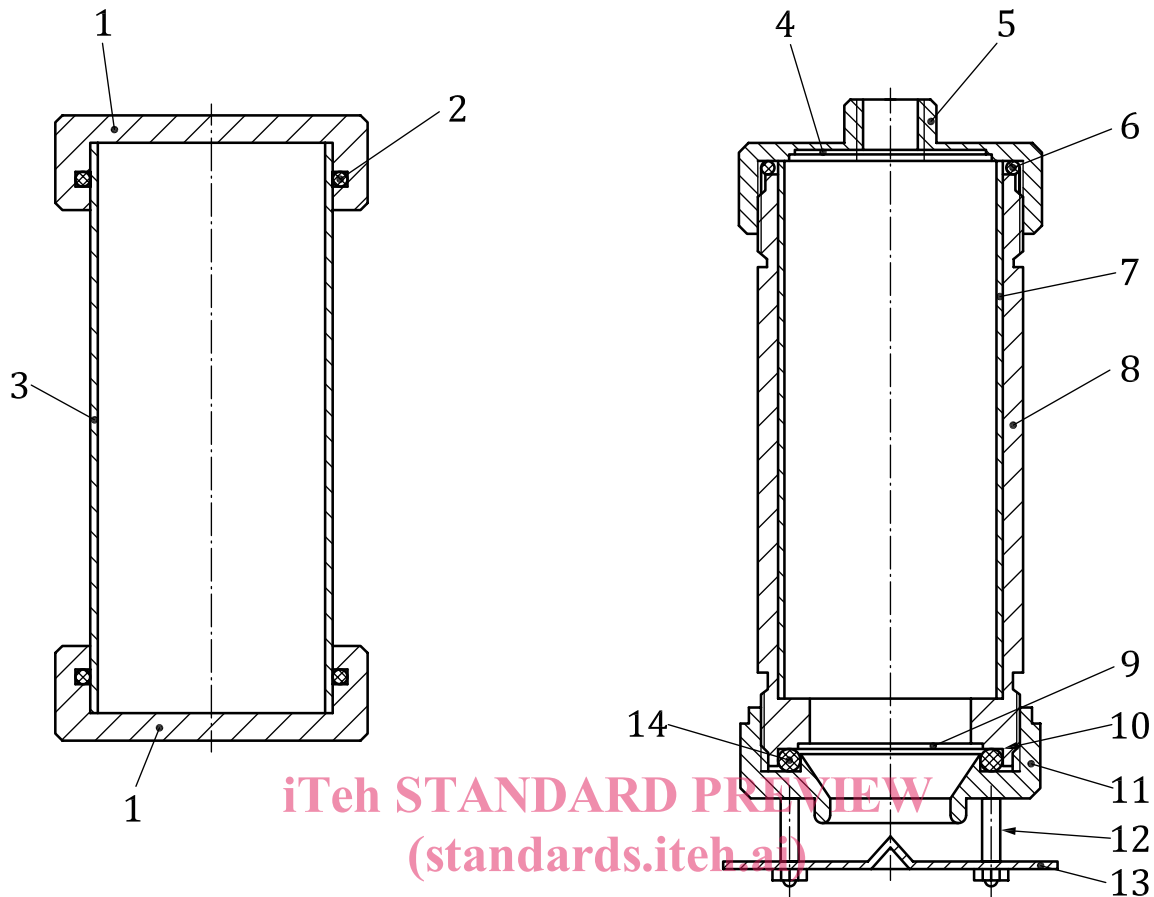
The measurement planning for the determination of the indoor air for phosphoric acid esters is performed according to the requirements of ISO 16000-1.

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 m³/h to 2,8 m³/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 1000¹) 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**, ¹³C-γ-HCH and ¹³C-DDE (see 6.1).

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4.2.3.3 Glass fibre filter, Ø 5 cm, blank free.**4.2.3.4 PU foam**, Ø 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.

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 m³/h to 2,8 m³/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

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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.

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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.

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.