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Indoor air —

Part 33: Determination of phthalates with gas chromatography/mass spectrometry (GC/MS)

Air intérieur —

Partie 33: Détermination des phthalates par chromatographie en phase gazeuse/spectrométrie de masse (CPG/SM)

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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 document 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).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 6, *Indoor air*.

This second edition cancels and replaces the first edition (ISO 16000-33:2017), which has been technically revised.

The main change is as follows: a description of an adsorbent which can alternatively be used has been added.

A list of all parts in the ISO 16000 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Different parts of the ISO 16000 series describe the general requirements relating to the measurement of indoor air pollutants and the important conditions to be observed before or during the sampling of individual pollutants or groups of pollutants, as well as the measurement procedures themselves.

The definition of indoor environment is given by ISO 16000-1. Dwellings [living rooms, bedrooms, do-it-yourself (DIY) rooms, sports rooms and cellars, kitchens and bathrooms], workrooms or workplaces in buildings which are not subject to health and safety inspections with respect to air pollutants (e.g. offices, salesrooms), public buildings (e.g. restaurants, theatres, cinemas and other meeting rooms) and passenger cabins of motor vehicles and public transport are among the most important types of indoor environment.

Phthalates, the diesters of the ortho-phthalic acid (1,2-benzene dicarboxylic acid), are emitted into the indoor air primarily from articles of daily use made of soft polyvinyl chloride (PVC). Typically, phthalates are used as plasticizers in soft PVC. Four most frequently used phthalates are diisodecylphthalate (DiDP), diisononylphthalate (DiNP), di-2-ethylhexyl terephthalate (DOTP) and di-isononyl cyclohexane dicarboxylate (DINCH) but other families of esters are available. Di(2-ethylhexyl)-phthalate (DEHP), di-n-butyl-phthalate (DBP) and benzyl-n-butyl-phthalate (BBP) were used in Europe until more recent regulatory developments placed restrictions on their use in the manufacture of new articles. However, these can still be present in articles currently in use and are subject to assessment. An overview of the most important phthalates, their acronyms and several relevant substance properties can be found in Table A.1. These phthalates can be determined in indoor environments by means of the analytical methods incorporating gas chromatography-mass spectrometry specified in this document.

Indoor air —

Part 33: Determination of phthalates with gas chromatography/mass spectrometry (GC/MS)

1 Scope

This document specifies the sampling and analysis of phthalates in indoor air and describes the sampling and analysis of phthalates in house dust and in solvent wipe samples of surfaces by means of gas chromatography-mass spectrometry (GC-MS).

Two alternative sampling, sample preparation and sample introduction methods, whose comparability has been proven in an interlaboratory test, are specified for indoor air[1]:

— sorbent tubes sampling with subsequent thermal desorption GC-MS, and

— sampling by adsorption and subsequent solvent extraction and injection to GC-MS.

Additional adsorbents that can be used are described in Annex B.

Depending on the sampling method, the compounds dimethyl phthalate to diisoundecylphthalate can be analysed in house dust as described in Annex D[2]. The investigation of house dust samples is only appropriate as a screening method. This investigation only results in indicative values and is not acceptable for a final assessment of a potential need for action.

Dimethyl phthalate to diisoundecylphthalate can be analysed in solvent wipe samples as described in Annex C. Solvent wipe samples are suitable for non-quantitative source identification.

NOTE In principle, the method is also suitable for the analysis of other phthalates, adipates and cyclohexane dicarboxylic acid esters, but this is confirmed by determination of the performance characteristics in each case.

General information on phthalates are given in Annex A.

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.

ISO 16000-6, *Indoor air — Part 6: Determination of organic compounds (VVOC, VOC, SVOC) in indoor and test chamber air by active sampling on sorbent tubes, thermal desorption and gas chromatography using MS or MS FID*

3 Terms and definitions

No terms and definitions are listed in this document.

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

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 Abbreviated terms

For the purpose of this document, the following abbreviated terms apply.

BBP	benzyl-*n*-butyl phthalate
DAIP	diallyl phthalate
DBP	di-*n*-butyl phthalate
DCHP	dicyclohexyl phthalate
DEHP	di(2-ethyl hexyl) phthalate
DEP	diethyl phthalate
DiBP	diisobutyl phthalate
DiDP	diisodecylphthalate
DiNP	diisononylphthalate
DiUP	diisoundecyl phthalate
DMP	dimethyl phthalate
DOP	di(*n*-octyl) phthalate
DPhP	diphenyl phthalate
DPP	di-*n*-propyl phthalate
D_4-BBP	D_4-benzyl-*n*-butyl phthalate
D_4-DBP	D_4-di-*n*-butyl phthalate
D_4-DEP	D_4-diethyl phthalate
D_4-DEHP	D_4-di(2-ethyl hexyl) phthalate
D_4-DMP	D_4-dimethyl phthalate
D_4-DOP	D_4-di(*n*-octyl) phthalate
GC	gas chromatographic
IS	internal standard
LOD	limit of detection
LOQ	limit of quantification
MS	mass spectrometry
ODS	octadecyl silica
PE	polyethylene
PP	polypropylene
PTFE	polytetrafluoroethylene

SDB	styrene-divinylbenzene
SIM	selected ion monitoring
SVOC	semi-volatile organic compounds
TBME	tertiary butyl methyl ether
TDS	thermal desorption system
4-NP	4-nonylphenol

5 Sampling methods and analytical apparatus

5.1 General

Sampling of indoor air takes place either by adsorption on a thermal desorption tube filled with quartz wool and Tenax® TA[1]or on adsorbents such as Florisil®[2] octadecyl silica (ODS) and styrene–divinylbenzene (SDB) copolymer with subsequent solvent extraction.[1],[3],[22] The quantity of solvent used for solvent extraction procedures should be minimized in order to minimize blank values. All apparatus and reagents used should be clean, i.e. without detectable quantities of the compounds of interest.

The experiences from the interlaboratory test have indicated that significant blank value differences can also be introduced by the solvent. Each new bottle of solvent shall therefore be tested for phthalate contamination before use[1].

NOTE The experiences from the interlaboratory test have indicated that rinsing with clean solvent (no detectable phthalates) is sufficient to remove contamination from the apparatus and that a sterilization by heating with subsequent deactivation of the heated glass apparatus is not mandatory.

The ubiquitous distribution of phthalates shall be considered during sampling of indoor air in order to avoid contamination of the sample. The measures to be considered for blank value minimization, as well as the advantages and disadvantages of the individual methods, are described in detail in 5.3.3, Clause B.2, Clause D.6 and Annex I. Further hints to quality assurance and problems related to blank values that shall be considered are listed in Clause 11.

5.2 Sampling by adsorption with subsequent thermal desorption

5.2.1 Apparatus, operating materials and chemicals

Use the apparatus, reagents and materials described in ISO 16000-6 with the following specific requirements.

5.2.1.1 Thermal desorption tube, stainless steel, inert-coated steel or glass tube filled with a 1 cm loosely packed plug of non-friable quartz wool backed up by a minimum of 50 mg of Tenax® TA (see ISO 16000-6).

5.2.1.2 Sampling system, in accordance with Figure 1.

5.2.1.3 Pump, suitable for a volume flow in the range 50 ml/min to 200 ml/min under sampling conditions; recommended sampling volume of approximately 20 l to approximately 70 l.

5.2.1.4 Gas volume meter, the maximal measurement inaccuracy shall not exceed 5 %.

1) Tenax® TA is the trade name of a product supplied by Buchem. This information is given for the convenience of the 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.

2) Florisil® is the trade name of product supplied by US Silica. This information is given for the convenience of the 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.

5.2.1.5 Laboratory sampling facilities, hygrometer, thermometer, barometer.

5.2.1.6 Internal standards, required as quality control measure of the whole analytical process including sampling. Suitable examples include the ring-deuterated compounds D_4-DMP, D_4-DEP, D_4-DBP, D_4-BBP, D_4-DEHP, D_4-DOP as well as the non-deuterated DAIP, see Clause 6 and Table 3. Standards shall be prepared in phthalate-free methanol, as described in ISO 16000-6, at a level such that a maximum 1 µl injection introduces approximately the same mass of analyte onto the sampling end of the tubes as is expected to be collected during sampling.

5.2.1.7 Thermal desorption system, coupled to GC-MS for two-stage thermal desorption of the sorbent tubes. Transfer of desorbed vapours via a carrier gas flow into a GC system, fitted with a MS detector.

NOTE Deactivated (silanised) glass wool or quartz wool can also be used as adsorbent after an appropriate method validation.

5.2.2 Preparation of the thermal desorption tube

The use of a tube packed with quartz wool and Tenax® TA assumes knowledge of ISO 16000-6. Prepacked and preconditioned sorbent tubes are available commercially or can be prepared in the laboratory as follows.

A plug of non-friable quartz wool, usually supported by a stainless steel mesh, is inserted at the sampling end of the tube. The required mass of sorbent is poured into the tube behind the quartz wool plug. The far end of the sorbent bed is typically supported by a second plug of quartz wool or a stainless steel mesh.

A minimum of 50 mg of Tenax® TA shall be used per tube in order to guarantee the sorption capacity.

NOTE Determination of the breakthrough volume is described in ISO 16017-1:2000, Annex B. The breakthrough volumes are proportional to the dimensions and masses of the sorbents. The rule of the thumb is that the guaranteed sample volume doubles itself when the sorbent bed length is doubled (while retaining the tube diameter).

After filling of the thermal desorption tubes (e.g. with Tenax® TA), the tubes are conditioned for approximately 8 h at 280 °C followed by approximately 30 min at 300 °C in an inert gas flow (100 ml/min). The purified sorption tubes are closed and stored at room temperature and in the dark in a container that prevents sample contamination.

Analyse a representative number of conditioned tubes for blank value, using routine analytical parameters, to ensure that thermal desorption blank is sufficiently small (see ISO 16000-6:2021, Clause 9).

Sampling should take place as soon as possible after conditioning. If sampling is not possible within approximately 14 d after conditioning, then the tube shall be reconditioned for 15 min at approximately 300 °C before sampling. Cotton gloves can be used to minimize the risk of contamination of the sorbent tubes. In addition, labelling shall be omitted.

The thermal desorption device should ensure that any contamination from external tube surfaces is excluded from the analytical sample flow path.

Tubes should be individually identifiable via etched barcodes. No adhesive labels or writing on the tube is allowed.

5.2.3 Sampling

Prior to sampling, the conditioned tubes are spiked with a maximum of 1 µl of internal standard solution in methanol (e.g. 20 ng/µl for a sampling volume of 50 l; the absolute mass of the additionally spiked standard depends on the sampling volume and the operating range of the method). The standard solution is usually applied on the sampling end of the sorbent tube.

The sampling equipment is assembled according to Figure 1. The sampling equipment shall be free of leaks. The pump is connected to the non-sampling end of the sorbent tube by means of polyethylene or PTFE connectors and is switched on. If the breakthrough volume of the analysed phthalates is unknown, then two sorption tubes shall be connected in series. The tubes shall be connected with a phthalate-free coupling.

The volume flow, as well as the temperature, the absolute air pressure and the relative air humidity, shall be recorded. The suitable sampling volume flows are within the range of 50 ml/min to 200 ml/min. This corresponds to a recommended sampling volume of approximately 20 l to 70 l for a sampling duration of approximately 2 h to 24 h. After sampling, the sorption tube is removed from the sampling equipment; both ends of the sorption tube shall be closed.

A duplicate sampling of the indoor air is recommended.

Sampled tubes shall be transported to the laboratory and analysed as soon as possible.

5.3 Sampling by adsorption and subsequent solvent extraction

5.3.1 Apparatus, operating materials and chemicals

5.3.1.1 Sampling system, in accordance with Figure 1.

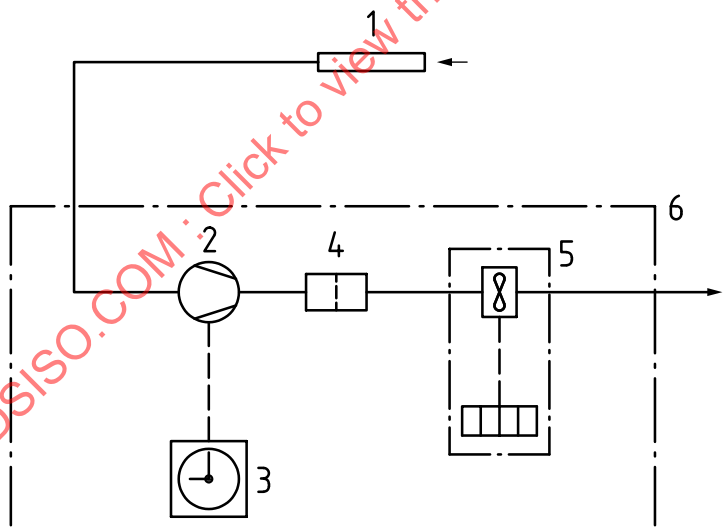
5.3.1.2 Pump, suitable for a volume of approximately 2 l/min under the conditions of the sampling, recommended sampling volume of approximately 1 m^3 to 3 m^3 in 8 h to 24 h.

5.3.1.3 Gas volume meter, the maximal measurement inaccuracy shall not exceed 5 %.

5.3.1.4 Muffle furnace.

5.3.1.5 Flat, heat resistant evaporating dish, for heating Florisil®.

5.3.1.6 Florisil®, 60 to 100 mesh.



Key

1 sampling tube
2 membrane vacuum pump
3 timer switch (optional)
4 anti-abrasion filter
5 volume measuring device or mass flow controller
6 protective housing

Figure 1 — Schematic diagram of the sampling equipment

5.3.1.7 Glass wool, silanized.

5.3.1.8 Glass flask, with screw-cap and PTFE sealing, 50 ml.

5.3.1.9 Adsorption tubes, glass tube, approximately 200 ml long, internal diameter approximately 10 mm to 12 mm.

5.3.1.10 Laboratory sampling facilities, hygrometer, thermometer, barometer.

5.3.1.11 Solvent, e.g. TBME or toluene, free of blank values (the solvent shall be tested for the absence of phthalate blank values).

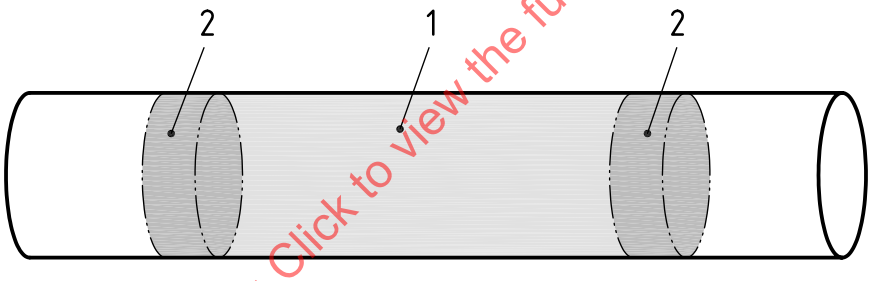
5.3.1.12 Internal standards. Suitable examples include the ring-deuterated compounds D_4-DMP, D_4-DEP, D_4-DBP, D_4-BBP, D_4-DEHP, D_4-DOP as well as the non-deuterated DAIP; see Clause 6 and Table 3.

5.3.1.13 GC-MS, gas chromatographic system fitted with a mass spectrometric detector.

5.3.2 Preparation of Florisil® and the adsorption tubes

Florisil® is brought out in a thin layer (approximately 3 cm to 4 cm) on an evaporation dish and heated at 800 °C for 6 h. After cooling down in the desiccator it is deactivated with bi-distilled water (3 % proportion by mass). To this end, 5 g of Florisil® and 150 µl of water are added to a 50 ml glass flask with a screw-cap and PTFE sealing. After closing the flask, Florisil® shall be mixed for approximately 45 min until a uniformly flowing powder has formed again. The deactivated Florisil® is then filled into an adsorption tube (see Figure 2). The filling height should be approximately 10 cm to 13 cm. The ends of the Florisil® filling are closed with silanised glass wool. The filled tubes are stored in the desiccator over silica gel until air sampling.

NOTE The geometry of the tube is based on the method described in Reference [4].



Key

1 Florisil®

2 glass wool

Figure 2 — Filling of the glass tube

5.3.3 Suggestions regarding the application of Florisil®

Each batch of Florisil® newly heated and deactivated in accordance with 5.3.2 shall be examined for blank values. Batches where high phthalate blank values are still measured after such treatment shall be heated and deactivated anew.

As long as the prepared tubes are stored in the desiccator, they are suitable for storage and use within six months. After expiration of this period, unused tubes shall be emptied and the Florisil® shall be treated again in accordance with 5.3.2.

Other adsorbents such as Chromosorb 106®[3] or comparable carrier materials can be utilized as adsorption agents. Absorbent preparation and sampling shall then be modified accordingly, and the suitability shall be proven by a determination of the performance characteristics.

3) Chromosorb 106® is the trade name of a product supplied by SKC Ltd. 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.

5.3.4 Sampling

A known volume (e.g. 10 µl) of the internal standard solution (e.g. 100 mg/l which corresponds to an absolute mass of the internal standard of 1 µg) shall be added prior to sampling. The preparation of the solutions of the internal standards is described in Annex E for thermal desorption method and in Annex F for solvent extraction method using Florisil®.

The internal standard is added, for example, by means of a microlitre syringe. The standard solution is usually placed on the adsorbent on the side oriented towards the flow. The amount to be added for the anticipated operating ranges from 0,05 µg/m^3 to 10 µg/m^3 is listed in Table 1. The compounds listed in Clause 6 are suitable as internal standards.

The sampling equipment is assembled according to Figure 1 and a leak test is performed. The volume flow, as well as the temperature, the absolute air pressure and the relative air humidity, shall be recorded. Sampling takes place by means of a pump, and the sampling volume amounts to 1 m^3 to 3 m^3. For a volume flow of 2 l/min to 3 l/min, the sampling duration shall be approximately 8 h to 24 h depending on the sampling strategy.

The loaded tubes shall be transported to the laboratory promptly, and processing of the tubes shall take place as soon as possible after sampling.

Table 1 — Operating range to determine the phthalates with contents from 0,05 µg/m^3 to 10 µg/m^3 in an air sample

Concentration of the reduced sampling solution mg/l	Corresponds to a concentration in the air µg/m^3
0,05	0,05
0,1	0,1
0,5	0,5
1,0	1,0
2,5	2,5
5,0	5,0
10,0	10,0
The data concerning the calculated concentrations in the air are tentative. The actual detection and quantification limits of the method shall be determined by the test laboratory based on the calibration under consideration of the blank value. NOTE The data given in Table 1 are valid for an air volume of 1 m^3 and sample processing as described in 5.3.5.	

5.3.5 Sample conditioning

The Florisil® and the glass wool from the adsorption tube are transferred completely to a 50 ml glass flask with screw and mixed with 25 ml solvent. The flask is closed by a screw-cap with a PTFE-coated seal, effectually shacked up for thorough wetting and placed for 15 min in the ultrasonic bath.

TBME and toluene have been proven successful as solvents. The use of another slightly polar solvent is possible. Non-polar solvents (e.g. hexane) are not suitable. However, it shall be guaranteed that the same solvent is used for calibration and gas chromatographic determination of the sampling solution.

Five millilitres of the supernatant are then extracted by a pipette and reduced to 0,2 ml by evaporation. Reduction to dryness leads to considerable substance loss, especially of the volatile phthalates. A 100 µl of this concentrated extract is transferred to the auto sampler vials and used for the GC-MS analysis (see Clause 7). Under application of the specifications described in 5.3.4, the concentration of the internal standard in the concentrated extract amounts to 1 mg/l.

6 Calibration

6.1 General

Phthalates present in indoor environments tend to undergo gas-particle-partitioning which is mainly characterized by the vapour pressure of the individual compound. Phthalates exhibiting high vapour pressures are most likely found in the gas phase whereas phthalates with low pressures tend to condense and are predominantly found in the particle phase. Therefore, some phthalates like DPhP, DiNP, DiDP and DiUP are not normally present at detectable concentrations in indoor air. Those compounds will be found in solvent wipe samples and house dust samples. Methods for screening phthalates in solvent wipe tests and house dust are described in Annex C and Annex D, respectively. Table 2 gives an overview for a range of phthalates and their occurrence in air samples or house dust as well as in wipe samples.

Table 2 — Ascertainable phthalates in various media

Compound	Air sample	House dust	Wipe sample
DMP	X	X	X
DEP	X	X	X
DPP	X	X	X
DiBP	X	X	X
DBP	X	X	X
BBP	X	X	X
DCHP	X	X	X
DEHP	X	X	X
DOP	X	X	X
DPhP		X	X
DiNP		X	X
DiDP		X	X
DiUP		X	X

A calibration shall be performed in order to specify the concentration and working range to be determined, respectively. A multiple calibration (at least a five-point calibration) is required for the establishment of the basic calibration. It shall be repeated regularly, at the latest after substantial changes of the measurement system. A multiple calibration (at least a three-point calibration) shall be performed for the validation of the calibration function. The ring-deuterated compounds listed in 5.2.2 as well as the non-deuterated DAIP are suitable as internal standards (see ISO 18856).

6.2 Calibration of the thermal desorption method

A minimum five-point thermal desorption GC-MS calibration shall be performed by desorbing a blank tube and preparing standard tubes at four or more different levels covering the work range. Methanol is used as solvent. A detailed example for a calibration procedure is given in Annex E.

6.3 Calibration of the solvent extraction method

A minimum five-point solvent extraction GC-MS calibration shall be performed by desorbing a blank tube and preparing standard tubes at four or more different levels covering the work range. More calibration points can be added if an extended calibration range is required. Either toluene or TBME is used as solvent. A detailed example for a calibration procedure is given in Annex F.

7 Identification and quantification

7.1 Mass spectrometric analysis

During phthalate breakup through electron ionization, the anhydride fragment with a mass to charge ratio (m/z) of 149 forms the base peak. The masses usually used in SIM mode are listed in Table 3.

Specific problems arise during quantification of the isomer mixtures, e.g. nonyl, decyl and undecyl phthalates. Since isomeric phthalates fragment stronger than their *n*-compounds, the determination of phthalates using the ion m/z = 149 and the response factor of the corresponding *n*-compound leads to a result that lies lower than the actual value. Thus, for example, DEHP and DiBP show an approximately 20 % lower detection sensitivity towards their *n*-compounds upon quantification by means of m/z = 149. The lower results for components with longer chains can amount to 50 %.

Table 3 — Mass traces (SIM masses)

Compound	Quantification mass	Qualification mass
DMP	163	194
DEP	149	177
DPP	149	191,209
DiBP	149	167,223
DBP	149	205,223
BBP	149	91,206
DCHP	149	167,249
DEHP	149	167,279
DOP	149	167,279
DPhP	225	77,226
DiNP	293	149,167
DiDP	307	149
DiUP	321	149
D_4-DMP[a]	167	198
D_4-DEP[a]	153	181
D_4-DBP[a]	153	209,227
D_4-BBP[a]	153	95,212 0
D_4-DEHP[a]	153	171,283
D_4-DOP[a]	153	171,283
DAIP[b]	149	104,189

[a] These compounds are ring-deuterated phthalate internal standards.

[b] This compound is an internal standard.

When DAIP is used as an internal standard, it is necessary to confirm that the retention times of DAIP and 4-NP are not identical.

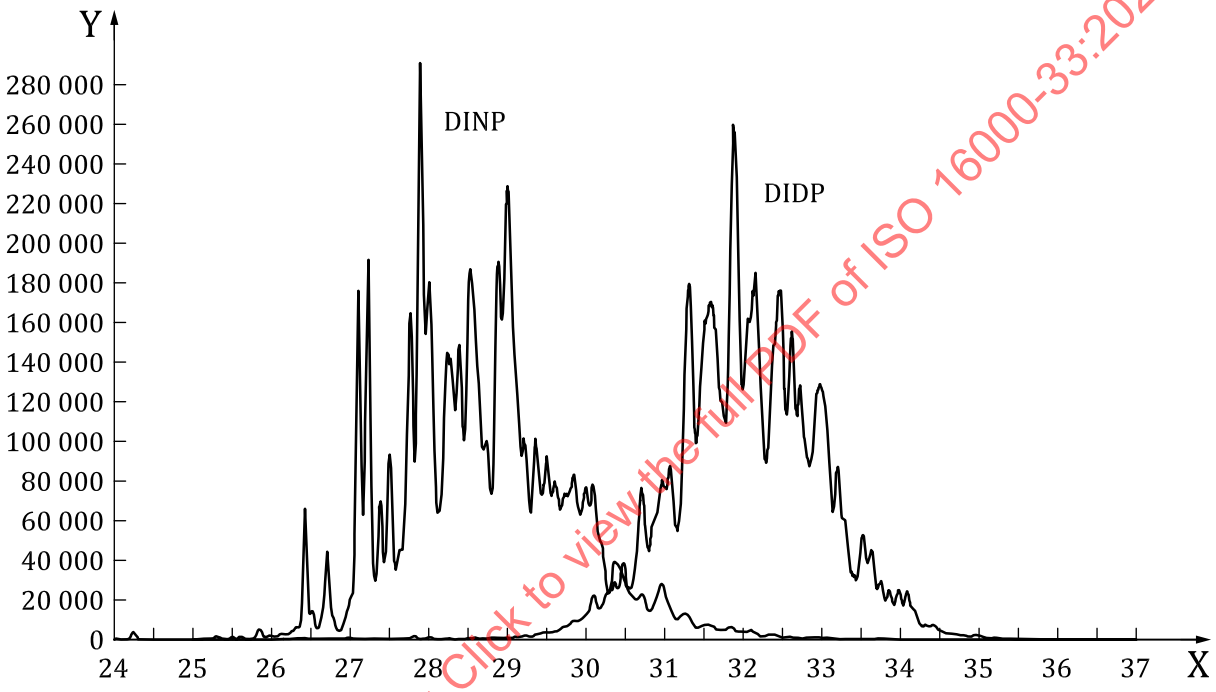
In addition, numerous peaks in the chromatogram are obtained in the case of the isomeric nonyl, decyl and undecyl phthalates (especially in house dust samples or solvent wipe samples)[5],[6],[7] (see Figure 3). Thus, for the same concentration, the height and the area of the individual peaks within a peak pattern of this type are smaller than for the phthalates consisting of only one isomer, e.g. DEHP. Smaller concentrations of the isomeric nonyl and decyl phthalates can present difficulties with conforming identities compared with the same concentrations of phthalates consisting of a single isomer. Hence, the achievable quantification limits for isomer mixtures are higher than for the common phthalates.

If several different isomer mixtures are present in a single sample (e.g. nonyl and decyl phthalates), then an exact quantification of the single isomer mixture is no longer possible[5]. Two different approaches can be attempted to identify the mixtures and to quantify them by approximation.

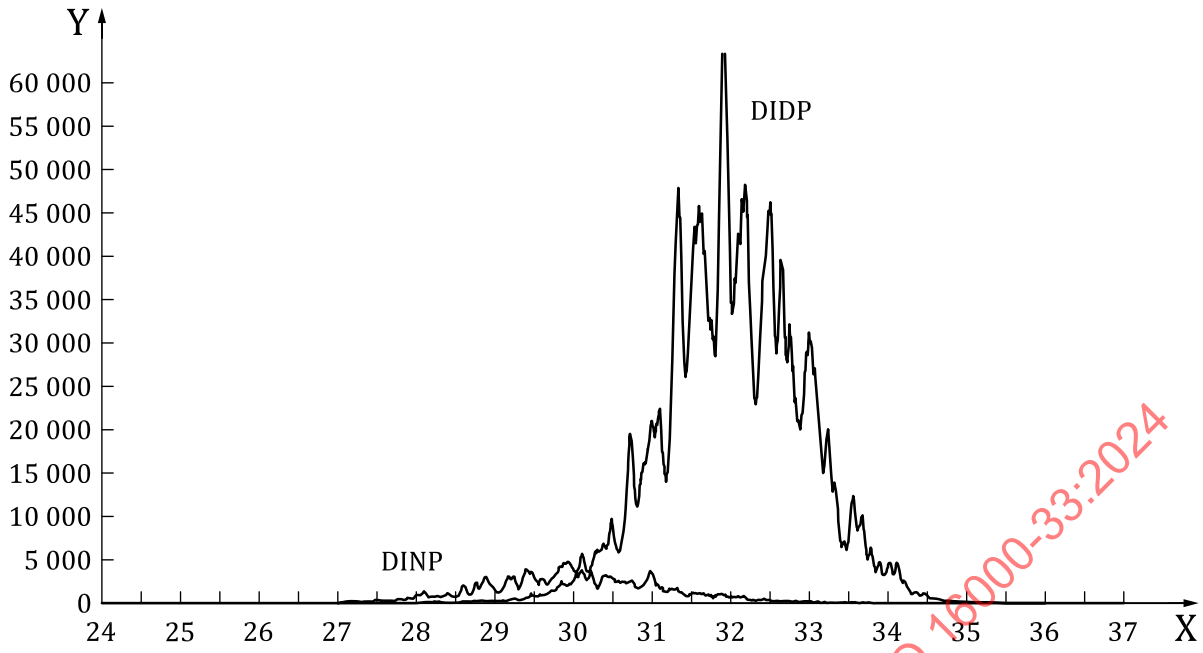
— The identification and quantification takes place using the specific masses m/z = 293; 307; 321 according to Table 3. This is, however, related to a sensitivity loss. Furthermore, the specific masses of the isomer mixtures cannot be clearly allocated (see Figure 3).

— The identification and determination of the integration times takes place using the specific masses m/z = 293; 307; 321 according to Table 3.

Quantification takes place using the mass m/z = 149. The integration limits are determined within the overlapping range of both peaks (see Figure 3). This inaccurate determination of the integration window can lead to substantial uncertainties.



a) Superimposed GC-MS chromatogram of a DiNP standard



b) Superimposed GC-MS chromatogram of a DiDP standard

Key

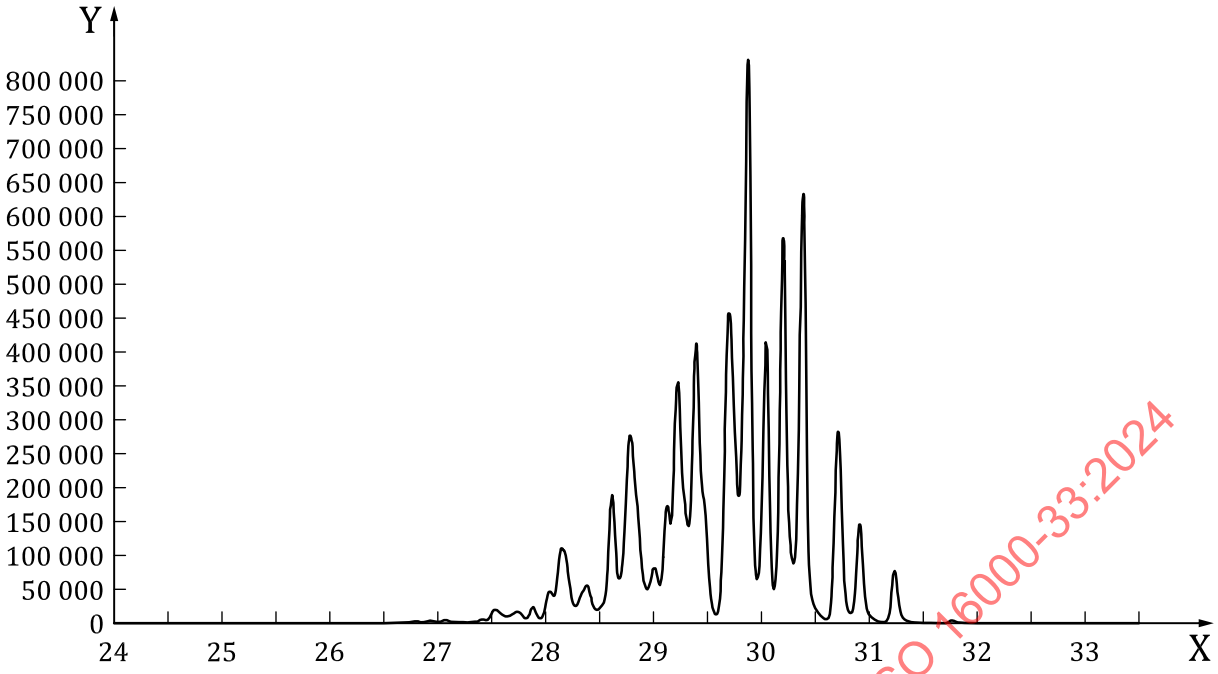
X retention time

Y strength of the signal

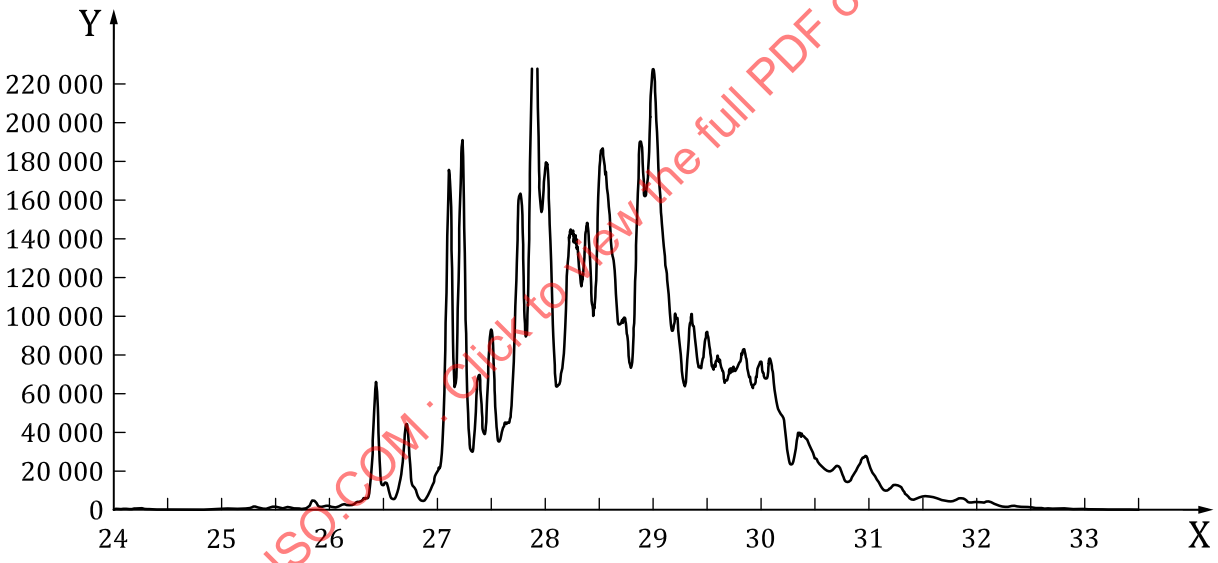
SOURCE: Reference [27]. Reproduced with the permission of the authors.

Figure 3 — Superimposed GC-MS chromatograms

The selected quantification method shall be recorded in the test report. A known problem is that commercially used semi-volatile phthalates are not widely available as analytical standards. Furthermore, the available analytical standards can have a substantially different composition as shown in Figure 4. It shows the substantial mass trace m/z = 149 of two different commercially available DiNP mixtures. Both DiNP mixtures show different peak patterns with a different retention range. Also, standards with the same CAS number can reveal different compositions.



a) GC-MS chromatogram (m/z = 149) for DiNP standard producer A



b) GC-MS chromatogram (m/z = 149) for DiNP standard producer B

Key

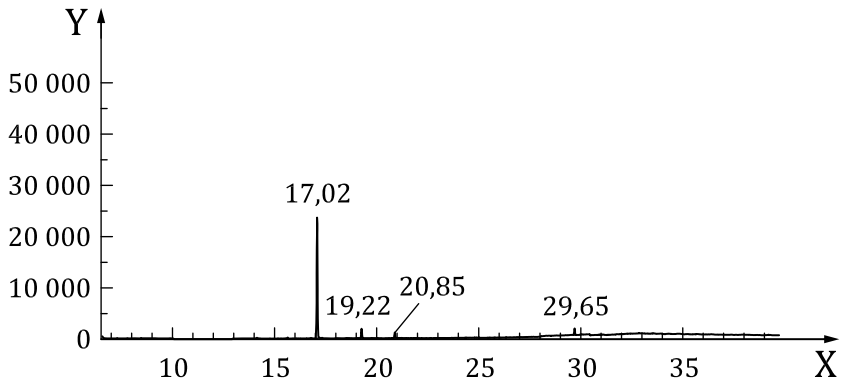
X retention time

Y strength of the signal

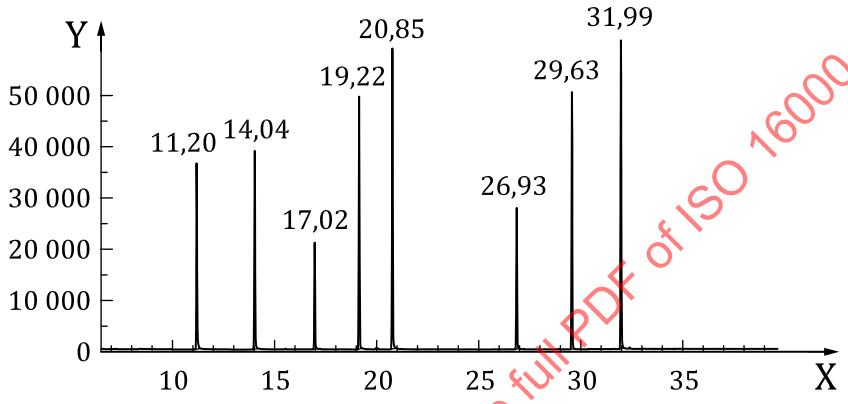
SOURCE: Reference [27]. Reproduced with the permission of the authors.

Figure 4 — GC-MS chromatograms (m/z = 149) of two different DiNP standards

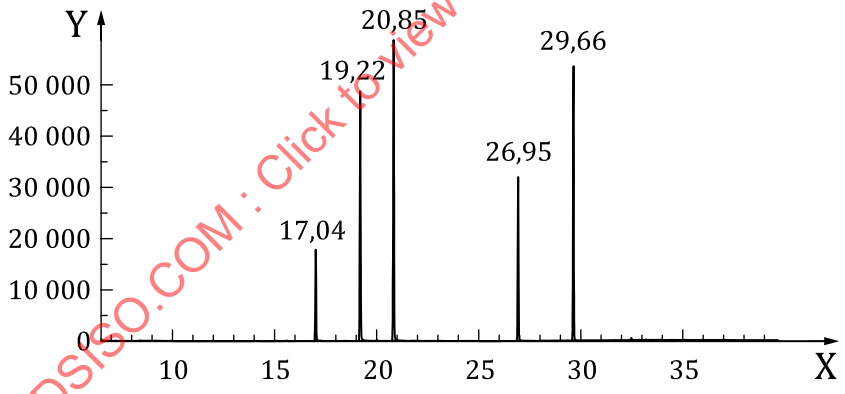
Figure 5 shows example chromatograms of an air sample, blank and calibration typical to Florisil® sampling and analysis.



a) Chromatogram of a laboratory blank value from a Florisil® tube spiked with the IS and the concentrate[a]



b) Chromatogram of a calibration standard of 1 mg/l[b]



c) Chromatogram of a processed air sample[c]

Key

X retention time

Y strength of the signal

[a] IS (DAlP): 17,02 min, DiBP: 19,22 min, DBP: 20,85 min, DEHP: 29,65 min.

[b] DMP: 11,20 min, DEP: 14,04 min, IS (DAlP): 17,02 min, DiBP: 19,22 min, DBP: 20,85 min, BBP: 26,93 min, DEHP: 29,63 min, DOP: 31,99 min.

[c] IS (DAlP): 17,04 min, DiBP: 19,22 min, DBP: 20,85 min, BBP: 26,95 min, DEHP: 29,66 min.

Figure 5 — Typical chromatograms of an air sample

8 Establishment of calibration curves and calculation of the analyte mass

8.1 Establishment of a calibration curve

A calibration curve is established by using calibration solutions. The calibration procedure is described in Annex E for the thermal desorption method and in Annex F for the solvent extraction method. To establish the calibration function, the ratio of the peak area of the fragment ion trace of the analyte to the peak area of the fragment ion trace of the internal standard is calculated. The calibration function is given by Formula (1):

$$v_{PA} = bm + a \quad (1)$$

where

v_{PA} is the peak area ratio (ratio of the peak area of the analyte to the peak area of the internal standard);

a is the intercept;

b is the slope in μg^{-1};

m is the analyte mass in µg.

A linear regression analysis using the known analyte masses, m, and the corresponding peak area ratios, v_{PA}, is performed. In addition to the intercept, a, and the slope, b, mentioned above, the regression analysis also gives the following parameters: the standard deviation of the intercept, s_a, the standard deviation of the slope, s_b, the linear correlation coefficient, r, and the standard deviation of the regression (standard deviation of the estimate), $s_{y,x}$, and the number of measurement points, n.

8.2 Calculation of the analyte mass

First of all, the ratio of the peak area of the analyte to the peak area of the internal standard is established, v_{PA}. The analyte mass, m, in µg is calculated using the peak area ratio and the regression coefficients (slope and intercept). Assuming $m = m_{sol}$, i.e. the analyte mass refers to the mass of analyte in the measurement solution, in µg, the rearrangement of Formula (2) gives:

$$m_{sol} = (v_{PA} - a) / b \quad (2)$$

Assuming $m = m_{tube}$, i.e. the analyte mass refers to the mass of analyte in the thermal desorption tube, in µg, the rearrangement of Formula (1) gives Formula (3):

$$m_{tube} = (v_{PA} - a) / b \quad (3)$$

If the value for intercept is not significantly different from zero, m_{sol} and m_{tube} can also be calculated by using Formula (4):

$$m_{sol} = v_{PA} / b \quad (4)$$

Or Formula (5):

$$m_{tube} = v_{PA} / b \quad (5)$$

A t-test with hypothesis zero, H_0: $a = -\alpha$ (with = 0), is used to prove if the intercept, a, deviates significantly from zero. The test parameter, $\hat{t}$, is calculated here according to the algorithm[20] in Formula (6):

$$\hat{t} = |a| / s_a \quad (6)$$

The calculated $\hat{t}$-value is then compared with the tabulated t-value: $t_{tab} = t_{95\,\%,n-2}$ (see Table 4).

If the calculated $\hat{t}$-value exceeds the tabulated t-value, the zero hypothesis (intercept is equal to zero) shall be rejected; that is, the intercept shall be considered by the concentration calculated based on the peak area ratio, v_{PA} [see Formulae (2) and (3)].

Table 4 — Values of the *t*-distribution

f	$P(90)$ %	$P(95)$ %	$P(99)$ %
1	6,31	12,71	63,66
2	2,92	4,30	9,92
3	2,35	3,18	5,84
4	2,13	2,78	4,60
5	2,01	2,57	4,03
6	1,94	2,45	3,71
7	1,89	2,36	3,50
8	1,86	2,31	3,36
9	1,83	2,26	3,25
10	1,81	2,23	3,17
∞	1,64	1,96	2,58

Key
f number of degrees of freedom
$P(x)$ probability

9 Calculation of indoor air concentrations

The indoor air concentrations are determined from measurement solutions according to Formula (7):

$$c_A = m_{sol} / V_A \quad (7)$$

where

c_A is the analyte concentration in the indoor air in µg/m^3;

m_{sol} is the analyte mass in the measurement solution in µg;

V_A is the sampling volume in m^3.

The indoor air concentrations are determined from thermal desorption tubes according to Formula (8):

$$c_A = m_{tube} / V_A \quad (8)$$

where

c_A is the analyte concentration in the indoor air in µg/m^3;

m_{tube} is the analyte mass in the thermal desorption tube in µg;

V_A is the sampling volume in m^3 under sampling conditions.

10 Performance characteristics

10.1 Detection limit

The analytical LOD is usually defined as a signal-to-noise ratio of 3:1, where the noise of the baseline of the native mass trace used for quantification is measured in a signal-free window corresponding to the 10-fold signal width at half signal height before the anticipated signal. Due to the potential significance of matrix interferences, samples, not standards, shall be used to determine detection limits.

10.2 Quantification limit and problems related to blank values

The analytical LOQ is calculated as a signal-to-noise ratio of 9:1 here. The user shall determine the quantification limit based on validation measurements.

LOD and LOQ generally depend on:

— sampled air volume,

— general level of air contamination in the laboratory,

— detection limit of the apparatus under the given analytical conditions (including detector sensitivity, selectivity and split ratio)

— final volume of the analysis solution (specific to the determination of detection limits for solvent extraction methods),

— injection volume (specific to the determination of detection limits for solvent extraction methods),

— system blank levels including sorbent and solvent background.

During the phthalate analysis, the quantification limit is dominated by the occurrence and the fluctuations of the field blank value (see Table 5). It is therefore inappropriate to determine the quantification limits based on calibration and declare them as quantification limits of the method. For blank values exceeding the ninefold of the noise, the quantification limit of the method is defined as the double of the field blank value of the sample series (see 11.1). Measured values below the respective quantification limit are indicated as "< LOQ". As a matter of principle, the numeric value of the quantification limit shall be recorded.

The field blank values shall be calculated on the analogy to Clause 8 and Clause 9 and shall be referred to the respective sampling volume. The results of the field blank values shall be documented individually for all analytes. They are not used as correction of the results but only for a better interpretation of the measured values.

Table 5 — Example for an average laboratory blank value and background value (ambient air) during indoor air sampling by means of Tenax® TA tubes

Compound	Average laboratory blank value ng absolute	Background value ng absolute	Background value relative to 70 l µg/m³
DMP	<0,5	<0,5	<0,007
DEP	<0,5	<0,5	<0,007
DPP	<0,5	<0,5	<0,007
DiBP	<0,5	0,8	0,011
DBP	<0,5	<0,5	<0,007
BBP	<0,2	<0,2	<0,003
DCHP	<0,1	<0,1	<0,001
DEHP	2,0	4,4	0,063
Internal standards: D_4-DBP, D_4-BBP, D_4-DEHP.			

10.3 Reproducibility standard deviation and repeatability standard deviation

An interlaboratory test was performed for the validation of the two analytical methods for indoor air described in this document[4]. The samples for the interlaboratory test consisted of either:

a) a solution containing four phthalates for spiking the Tenax® thermal desorption tubes, or

b) a Florisil® adsorption tube spiked with four phthalates;

c) or both.

The thermal desorption tube was analysed according to 5.2 and the Florisil® adsorption tube was analysed according to 5.3. The results are compiled in Table 6. The results prove the comparability of the two methods. Although one of the methods was always applied by the laboratories for the first time, the comparison of the reference values demonstrates the practicability of both methods and the correctness of the results within an acceptable variance.

Table 6 — Results of the interlaboratory test analysis with reference value, average value, relative standard deviation and median

Compound	Reference value		Average value		S_R		S_r		Median		Number of laboratories	
	mg/l		mg/l		%		%		mg/l			
	TD	SE	TD	SE	TD	SE	TD	SE	TD	SE	TD	SE
DiBP	175	175	186	181	23	60	2,9	5,4	176	176	6	8
DBP	175	175	191	184	26	62	2,6	4,5	178	178	7	8
BBP	150	150	131	129	42	35	7,5	5,2	145	121	7	8
DEHP	200	200	175	163	31	31	6,0	4,1	182	183	7	8

Key

S_R relative reproducibility standard deviation

S_r average relative repeatability standard deviation

TD thermal desorption

SE solvent extraction

An interlaboratory test for phthalate analysis was performed in 2005 by the State Health Office of Baden-Württemberg, Germany, where a phthalate solution of unknown concentration was forwarded.

The 28 participants analysed the samples according to the respective internal methods; the results are shown in Table 7. In addition, a mixed dust sample of different house dusts sieved to ≤63 µm was analysed by 26 participants. These results are shown in Table D.2.

Table 7 — Results from an interlaboratory test for phthalate analysis in solution

Compound	Reference value mg/l	Average value mg/l	Median mg/l	Relative standard deviation %
DMP	10	10,53	10,33	15,39
DEP	110	110,04	108,62	12,66
DPP	80	82,19	82,22	9,15
DBP	70	72,70	72,80	12,43
DCHP	60	62,53	59,47	22,16
BBP	40	45,92	39,88	65,13

NOTE Number of laboratories, N = 28.

[a] The results refer to experiments with *n*-compounds.

SOURCE: Reference [2]. Reproduced with the permission of the authors.

Table 7 *(continued)*

Compound	Reference value mg/l	Average value mg/l	Median mg/l	Relative standard deviation %
DEHP	50	50,75	49,97	20,83
DNP[a]	90	88,08	88,33	11,50
DDP[a]	120	114,34	113,52	20,53

NOTE Number of laboratories, N = 28.

[a] The results refer to experiments with *n*-compounds.

SOURCE: Reference [2]. Reproduced with the permission of the authors.

11 Quality assurance

11.1 Method verification and determination of blanks

11.1.1 General

Due to the ubiquitous distribution especially of the plasticizers DiBP, DBP, DEHP and since the measured values are frequently in the range of the quantification limit, the blank values play a significant role for phthalates analysis. It is therefore recommended to measure the results of the field blank values continuously and to make a record by, for example, a control chart in order to identify blank value changes. Problems during the determination of blank values are discussed in Annex I.

11.1.2 Field blank value of the indoor air

The entire method shall be verified regularly and with each sample series by the determination of field blank values. A field blank sample of the indoor air is a sample that is obtained in an identical manner as the actual sample, however, without sucking air through the sampling equipment. The adsorbent agents shall not be exposed to the ambient air for a longer time than the exchange of the sampling head requires. In this way, the field blank value enables, among other things, also statements with regard to contaminations during transport, to the sampling set-up and to the entire course of the analysis. Field blank values are not subtracted from the sample result.

11.1.3 Analytical laboratory blank value

In addition, a laboratory blank value of all analytes shall be determined after larger changes of the analytical method by means of a blank value sample that covers the entire analytical method including extraction, cleaning and quantification. This procedure is also recommended following the analysis of a sample with values that exceed the previous concentration levels by a factor of 10.

11.2 Measures for blank value minimization

The following measures have been proven successful for minimization of the blank values that significantly influence the quantification limit:

— sealing (e.g. aluminium foil) the operating materials after heating to minimize dust intrusion,

— blank value verification of chemicals and operating materials, especially solvents,

— fitting and airtight sealing of the sampling media in the laboratory,

— transportation and storage of the samples and sampling media in phthalate-free containers (aluminium foil, glass bottles with grinded glass plugs, screw-cap flasks without synthetic seals),

— avoidance of plastic gloves, labels, hand creams, paper containers especially of waste paper, etc.,

— use of phthalate-free equipment and materials, e.g. cotton gloves, PTFE droppers (e.g. Burky Multipette), storage of the injection needles in solvents free of blank values, septum-free injection (e.g. Merlin Microseal).

11.3 Documents

The questionnaire in ISO 16000-1:2004, Annex D should be used for indoor air studies. An example of a sampling protocol is shown in Annex J as additional sampling documentation.

12 Interferences

During sampling, transport and analysis of phthalates, it shall be borne in mind that numerous materials and operating materials are equipped with the investigated analytes and can thus lead to a significant contribution to the blank values. The measures for minimization of blank values are described in Clause 11.

The varying composition of the commercially available reference materials of the isomer mixtures constitutes a specific problem. The uncertainties during identification and quantification of isomer mixtures are described in 7.1.

Annex A
(informative)

General information on phthalates

A.1 Properties and occurrence

Phthalates are various, predominantly aliphatic diesters of the ortho-phthalic acid (1,2-benzene dicarbon acid; see Figure A.1). A recent overview of production, application, substance properties and legal regulations can be found in Reference [10] and more recently by industry organizations[11] and in reviews[12]. Approximately one million tons of phthalates are produced annually in Western Europe. More than 90 % are used as plasticizers of soft PVC. In 2004, the market share of phthalate-free plasticizers in Western Europe was 7 %. Flexible PVC consists on average of 30 % to 35 % of plasticizers. Products of or with soft PVC are found in almost all households: floorings, artificial leather, wallpaper, shower curtains, electric cables, wrapping materials, shoes, sports and leisure articles as well as interior panelling of motor vehicles can thus contain phthalates. Numerous medical products such as blood bags and hoses also consist of soft PVC.

The five most frequently used phthalates were traditionally DiDP, DiNP, DEHP, DBP and BBP. An overview of the most important phthalates, their acronyms and several relevant substance properties can be found in Table A.1. These phthalates can be determined in indoor air, solvent wipe test or house dust by means of the analytical methods specified in this document.

DEHP was been the most frequently used phthalate for a long time. Consumption in Western Europe was approximately 460 000 t in 1999; corresponding to nearly 42 % of the total plasticizer consumption. This share dropped to 22 % in 2004 at an almost steady overall plasticizer consumption and since its designation as a substance of very high concern (SVHC) under the EU REACH regulation[13] in 2009 on account of its revised classification under the EU Classification, Labelling and Packaging regulation[14] as Category 1B toxic to reproduction, its use is now subject to authorization. However, since flexible PVC is utilized in many medium and long-life applications (e.g. flooring, automotive leather) it can be expected to be present in such articles for several years to come even though its use in the fabrication of new articles is now exceedingly limited. The same applies to both butylbenzyl phthalate and di-butyl phthalate.

DiNP and DiDP are isomer mixtures, potentially also containing common isomers. DiNP is a mixture from esters of the o-phthalic acid with C8-C10- alcohols (C9-rich). Owing to different production procedures, two DiNP mixtures differing in their isomer content are commercially available. In the case of DiDP, the isomer mixture contains esters of the o-phthalic acid with C9-C11-alcohols (C10-rich). The exact content of the mixtures is known neither for DiNP nor for DiDP. DiNP and DiDP are by now the most utilized phthalates in Europe. DiNP and DiDP are classed as high molecular weight phthalates those phthalates with 7-13 carbon atoms in their backbone. Their common share of these plasticizers of the European market was more than 50 % in 2020[11], corresponding to over 500,000 tons consumption.

Both phthalates are predominantly utilized in PVC applications and have partially substituted DEHP in recent years.

BBP, di-isobutylphthalate and di-butyl phthalate are also considered as substances of very high concern in Europe but, unlike DEHP, no authorization have been applied for. While this means that no new articles have been produced using these substances since 21st February 2015, they can still appear in articles manufactured before that date.

Table A.2 provides examples for phthalate contents in indoor air samples from an exposure survey with no reference to a particular occasion[15]. Sampling and analysis by thermal desorption GC-MS is done according to 5.2.

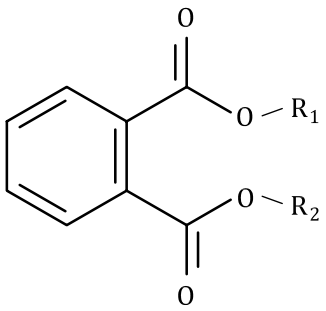
Table A.1 — Most important phthalates and selected physical properties

Compound	Acronym	CAS RN®[a]	Chemical formula	Boiling point[b] °C
Dimethyl phthalate	DMP	131–11–3	$C_{10}H_{10}O_4$	281 to 284
Diethyl phthalate	DEP	84–66–2	$C_{12}H_{14}O_4$	298 to 302
Di-*n*-propyl phthalate	DPP	131–16–8	$C_{14}H_{18}O_4$	317,5
Diisobutyl phthalate	DiBP	84–69–5	$C_{16}H_{22}O_4$	296,5
Di-*n*-butyl phthalate	DBP	84–74–2	$C_{16}H_{22}O_4$	340
Benzyl-*n*-butyl phthalate	BBP	85–68–7	$C_{19}H_{20}O_4$	370
Dicyclohexyl phthalate	DCHP	84–61–7	$C_{20}H_{24}O_4$	436
Di(2-ethyl hexyl) phthalate	DEHP	117–81–7	$C_{24}H_{38}O_4$	385
Di(*n*-octyl) phthalate	DOP	117–84–0	$C_{24}H_{38}O_4$	385
Diphenyl phthalate	DPhP	84–62–8	$C_{20}H_{14}O_4$	405
Diisononylphthalate (isomeric mixture)	DiNP	28553–12–0 68515–48–0	$C_{26}H_{42}O_4$	270 to 280 (at 27 hPa)
Diisodecylphthalate (isomeric mixture)	DiDP	26761–40–0 68515–49–1	$C_{30}H_{50}O_4$	
Diallyl phthalate[c]	DAIP	131–17–9	$C_{14}H_{14}O_4$	320
D_4-dimethyl phthalate[c]	D_4-DMP	93951–89–4	$C_{10}H_6D_4O_4$	284
D_4-diethyl phthalate[c]	D_4-DEP	93952–12–6	$C_{12}H_6D_4O_4$	298 to 299
D_4-di-*n*-butyl phthalate[c]	D_4-DBP	93952–11–5	$C_{16}H_{18}D_4O_4$	340
D_4-benzyl-*n*-butyl phthalate[c]	D_4-BBP	93951–88–3	$C_{19}H_{16}D_4O_4$	370
D_4-di(2-ethylhexyl) phthalate[c]	D_4-DEHP	93951–87–2	$C_{24}H_{34}D_4O_4$	384
D_4-di(*n*-octyl) phthalate[c]	D_4-DOP	93952–13–7	$C_{24}H_{34}D_4O_4$	384

[a] CAS Registry Number® is a trademark of the American Chemical Society (ACS). 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.

[b] SOURCE: DCHP: www.chemicalbook.com; labelled standards: C/D/N ISOTOPES Inc., Quebec, Canada, http://www.cdnisotopes.com; other compounds: GESTIS database.[16]

[c] These are internal standards.



Key

R_1 aliphatic substituents

R_2 aromatic substituents

Figure A.1 — Basic structure of phthalates

A.2 Release and environmental behaviour

Table A.2 — Phthalate contents in indoor air samples (n = 34)

Compound	Number of samples greater than LOQ	Average value µg/m³	Median µg/m³	Minimum µg/m³	Maximum µg/m³	95 % percentile
DMP	34	0,34	0,17	0,03	1,80	1,50
DEP	34	0,36	0,32	0,11	0,90	0,77
DiBP	34	0,66	0,66	0,13	2,00	1,33
DBP	34	0,76	0,59	0,09	2,30	1,85
BBP	11	0,01	0,005	0,01	0,04	0,04
DEHP	34	2,64	2,15	0,26	11,0	9,65
The LOQ is always 0,01 µg/m³. The LOQ for DEHP is 0,06 µg/m³.						

Phthalates and other plasticizers are distributed within the polymer matrix, with dipole-dipole interactions between their polar centres and the polar groups on the PVC aiding their retention in the polymer matrix. However, they are not chemically bound by ionic or covalent bonds. Hence, phthalates can slowly but steadily diffuse out of the products during application and can volatilize in ambient air. With the exception of the volatile DMP, phthalates belong to the SVOC. Hence, they possess a specific potential to adsorb on particles in the air. Phthalates can therefore be found not only in indoor air[3],[17],[18],[15],[19],[20] but also in house dust.[17],[18],[7],[10],[20]

Moreover, during the production, processing and packing of food, the fat-soluble phthalates can get directly into the food chain. The exposure of the European population to eight phthalates is described in detail in Reference [21]. The main exposure of the general population to phthalates takes place via foodstuffs and inhalation. For DEP and DBP, the exposure of teenagers and adults to phthalates is dominated by dermal reception via body care products and cosmetics. With nurslings and infants reception of DEHP and DiNP takes place predominantly orally because plasticizers from toys and baby articles can be solved by the saliva. However, it is notable that six common phthalates have been restricted from use in toys in Europe for many years under the REACH regulation (restriction no. 51)[13]. Furthermore, oral reception of house dust plays a not negligible role. Phthalates arrive directly into the blood stream during application of medical products like hoses, probes and blood bags.

In addition to a direct spreading (e.g. of pesticides), the outdoor release of phthalates takes place also from materials by evaporation, washout and wear. Phthalates can be transported over long distances by air; hence, these substances are globally distributed. In the waters, phthalates adsorb on floating matter. DEHP and other phthalates are persistent under anaerobic conditions and are therefore intensely accumulated in sediments.

A.3 Regulatory background

In preparations like dyes and varnishes, which are passed to private end users, as well as in cosmetic products, DEHP, BBP and DBP are by now also prohibited throughout the EU. Plasticizer-free material alternatives already exist for most of the soft PVC products. Plastics on the basis of polyolefines such as PE or PP, as non-polar polymers, are generally free of plasticizers.

Annex B
(informative)

Sampling by adsorption with ODS solid phase disk or SDB copolymer cartridge

B.1 Apparatus, operating materials and chemicals

B.1.1 Sampling system, in accordance with Figures B.1 and B.2.

B.1.2 Pump, suitable for a volume flow of approximately 2 l/min or 10 l/min under the conditions of sampling, recommended sampling volume of approximately 2,88 m^3 to 14,4 m^3 in 24 h.

B.1.3 Gas volume meter, the maximal measurement inaccuracy shall not exceed 5 %.

B.1.4 ODS solid phase disk, 47 mm in diameter. The filter was rinsed with fresh acetone five times and dried on clean bench prior to use then installed in an aluminium holder.

B.1.5 SDB copolymer, (mesh 30/60; 400 mg) was cleaned and packed into glass tube (length is equal to 21 mm and the diameter is equal to 19 mm) before shipping, so that is can be used without further cleaning. The cartridge was installed in an aluminium holder.

B.1.6 Sampler holder, parts of the holder for the solid phase disk or cartridge that contact the sampler should comprise PTFE.

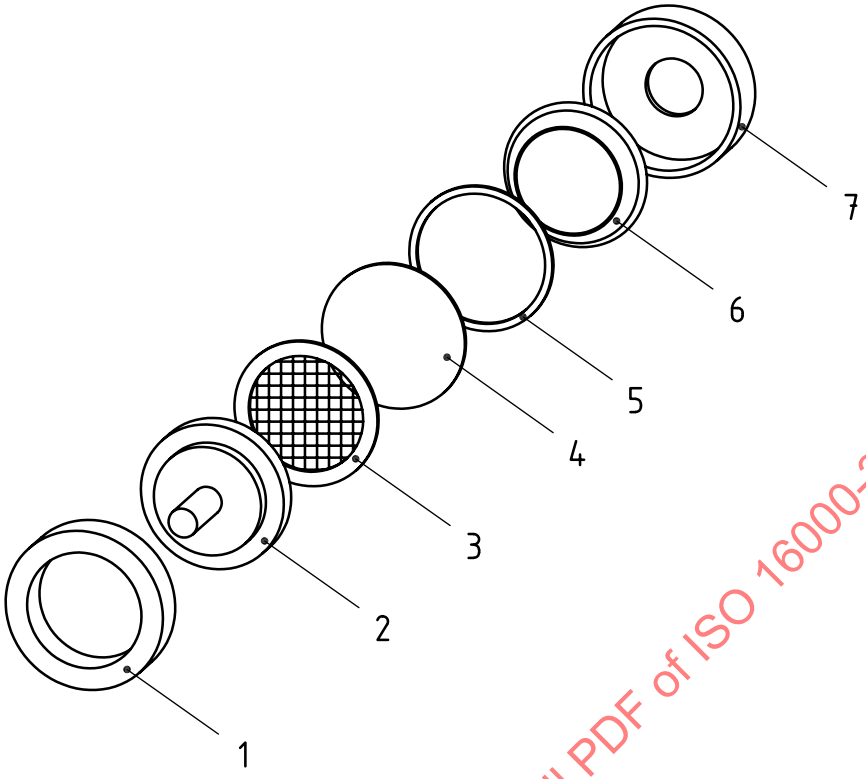
B.1.7 Glass centrifuge tube, 10 ml.

B.1.8 Laboratory sampling facilities, hygrometer, thermometer, barometer.

B.1.9 Solvent, acetone for residual agricultural chemical test, free of blank values (solvent shall be tested for the absence of phthalate blank values).

B.1.10 Internal standards, suitable are, e.g. the ring-deuterated compounds D_4-DMP, D_4-DEP, D_4-DBP, D_4-BBP, D_4-DEHP, D_4-DOP as well as the non-deuterated DAIP; see Clause 7 and Table 3.

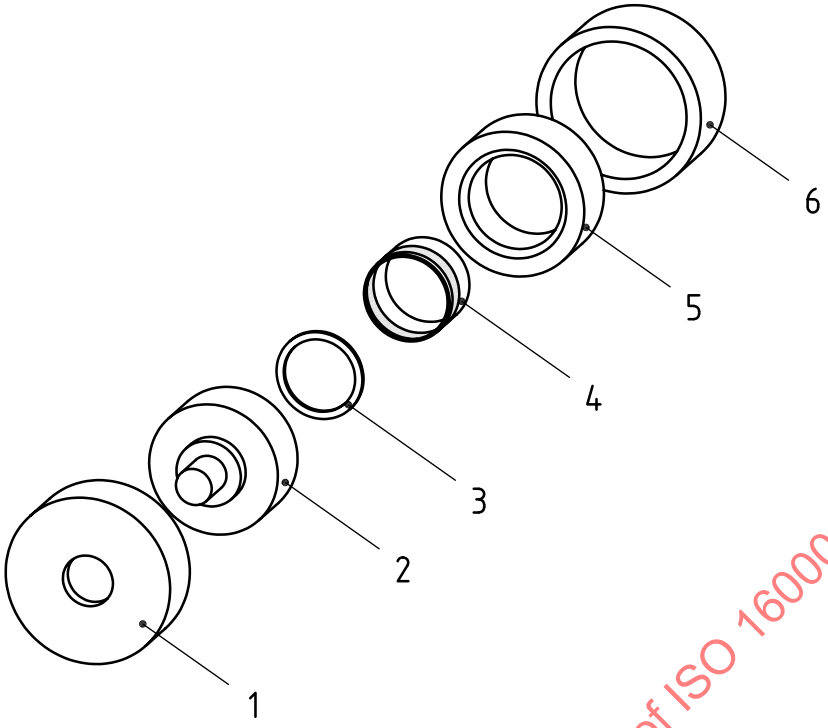
B.1.11 GC-MS, gas chromatographic system, fitted with a mass spectrometric detector.



Key

1 pump side cap (made of aluminium)
2 screen holder (made of PTFE)
3 support screen (made of PTFE)
4 ODS solid phase disc
5 O-ring (made of PTFE)
6 solid phase disc retainer (made of PTFE)
7 air sampling side cap (made of aluminium)

Figure B.1 — Scheme of holder for solid phase disc



Key

1	pump side cap (made of aluminium)	4	SDB copolymer cartridge
2	cartridge holder (made of PTFE)	5	cartridge retainer (made of PTFE)
3	O-ring	6	air sampling side cap (made of aluminium)

Figure B.2 — Scheme of cartridge holder

B.2 Sampling

After installing the solid phase disc or cartridge in the sampler holder, wrap the entire holder assembly with aluminium foil, put in a closed metal container and carry to the measurement site. Then, prepare two identical holders separately, one for the operation blank (to be kept in the analysis facilities until sampling is completed), the other for transport to the measurement site and intended as the travel blank.

For sampling, place the holder 1,2 m to 1,5 m above the measurement site and connect it to the suction pump. Run the suction pump and collect the sample air at a flow rate of 2 l/min to 10 l/min for 8 h to 24 h.

After sampling, detach the holder from the suction pump, wrap in aluminium foil, store in a closed metal container and transport back to the analysis facilities. The holder for the travel blank test should be handled in the same manner as the sampling holders, minus the air sampling procedure.

In addition, the weather conditions at the time of the measurement (e.g. air temperature, air humidity and air pressure) as well as the details of the sampling (e.g. start and end of sampling, volume of sampled air) shall be recorded.

For the solid phase disc holder, disassemble the parts into pieces, place them in a metal bucket or glass beaker before use, perform ultrasonic cleaning in acetone for 10 min, air dry and assemble the cleaned solid-phase disc. At that time, use a pincette that has been ultrasonically cleaned in acetone for 10 min. Cartridge holders do not require cleaning before use. When mounting the cartridge in the holder, wash your hands with soap and be careful not to directly touch the air sampling side of the cartridge.

The operation blank test is performed to confirm the extent of contamination from the environment in the preparation of the test solution.

The purpose of the travel blank test is to confirm the extent of contamination during the time from sampling to sample solution analysis. In the case the travel blank value is equal to or lower than the operation blank value, it is confirmed that there is no contamination during transfer. If the travel blank value is larger than the operation blank value, contamination occurred during transport and the origin of contamination should be pursued. Measures should be taken to prevent contamination during the retest. In calculating the concentration in air, the travel blank value is subtracted from the measured value.

B.3 Test solution preparation

Remove the solid phase disc from the holder and fold it into a glass centrifuge tube. Remove the cartridge from the holder and transfer the internal SDB copolymer resin to a glass centrifuge tube. Add 5 ml of acetone and 5 µl of internal standard solution to the centrifuge tube extract ultrasonically for 20 min and centrifuge at 2,500 rpm for 10 min; then, use the supernatant as the test solution.

B.4 Blank test

In the blank test with ODS solid phase disk and SDB copolymer cartridge, DEP, DBP and DEHP were detected from all adsorbents (see Table B.1), while the two other target phthalates – DiBP and BBP – were not detected.

Table B.1 — Blank values of phthalates in each adsorbent (n = 3)

Analyte	ODS disc A ng ± sd	ODS disc B ng ± sd	SDB cartridge ng ± sd
DEP	2,0 ± 0,10	2,6 ± 0,20	1,3 ± 0,20
DiBP	<0,2	<0,2	<0,2
DBP	23,6 ± 3,0	30,1 ± 4,5	10,1 ± 1,5
BBP	<1,0	<1,0	<1,0
DEHP	23,0 ± 5,6	32,7 ± 4,4	13,7 ± 2,8
Internal standards are D_4-DBP, D_4-BBP, D_4-DEHP.			

B.5 Recovery test

Recovery test was performed using the deuterated phthalates. Each adsorbent was spiked with 0,5 µg of D_4-DEP, D_4-DBP, D_4-BBP and D_4-DEHP. Then, indoor air was passed through at a flow rate of 2 l/min or 10 l/min for 24 h (corresponding to an air volume of 2,88 m^3 or 14,4 m^3; n = 3). After air was passed through, the adsorbents were extracted by ultrasonication for 10 min using 10 ml of acetone. A 5-ml aliquot of the extract was then concentrated under nitrogen to 0,5 ml. The internal standards that were added the 5 ml extract before concentration were D_{10}-fuloranthen for the recovery test. After GC-MS analysis, the percentage recoveries were calculated.

Table B.2 shows the recovery of deuterated phthalates spiked to the adsorbents, after passing through indoor air (2,88 m^3 or 14,4 m^3). The percentage recoveries were in the range 89,7 % to 95,5 % at the air sampling of 2,88 m^3 and 85,9 % to 100 % at the air sampling volumes of 14,4 m^3, indicating that the deuterated phthalates were almost quantitatively recovered from any of the adsorbents.

Table B.2 — Recovery of deuterated phthalates (n = 3)

Analyte	ODS disc A ng ± sd	ODS disc B ng ± sd	SDB cartridge ng ± sd
Air volume: 2,88 m³ (2 l/min for 24 h)			
D_4-DEP	95,5 ± 1,9	94,2 ± 4,8	93,3 ± 8,6
D_4-DBP	94,8 ± 4,7	92,1 ± 6,8	92,1 ± 7,8
D_4-BBP	93,1 ± 1,5	92,0 ± 3,4	91,0 ± 6,8
D_4-DEHP	91,8 ± 3,4	91,8 ± 4,5	89,7 ± 6,6
Air volume: 14,4 m³ (10 l/min for 24 h)			
D_4-DEP	96,5 ± 2,6	90,2 ± 6,8	94,6 ± 4,2
D_4-DBP	98,6 ± 3,9	92,1 ± 5,4	93,8 ± 2,8
D_4-BBP	92,8 ± 4,2	92,0 ± 3,4	92,3 ± 5,8
D_4-DEHP	100 ± 5,0	90,6 ± 4,8	85,9 ± 4,5
The internal standard is D_{10}-fluoranthene.			

B.6 Interlaboratory validation study

To establish the method performance characteristics, an interlaboratory validation study was carried out[22].

Accuracy, which was determined by the recovery study, was evaluated by preparing two kinds of adsorbents (ODS filters and SDB cartridges) spiked with 4 ug of DBP and DEHP. Table B.3 shows the results of intra- (within) and inter- (between) reproducibility in the recovery test.

In the case of DBP, the recoveries were between 85,3 and 107,9 % (ODS filters), and 92,1 and 105,0 % (SDB cartridges). In the case of DEHP, the recoveries were between 84,5 and 107,3 % (ODS filters), and 73,3 and 103,3 % (SDB cartridge).

The intralaboratory reproducibility, relative standard deviations (RSD_r), of DBP were 2,1 % to 13,6 % for ODS filters and 2,0 % to 7,5 % for SDB cartridges. RSD_r of DEHP were 4,0 % to 20,7 % for ODS filters and 0,8 % to 8,1 % for SDB cartridge. On the other hand, the interlaboratory reproducibility, relative standard deviation (RSD_R), of DBP was 8,6 % for ODS filters and 5,1 % for SDB cartridges, while RSD_R of DEHP was 9,7 % for ODS filters and 13,1 % for SDB cartridges.

The interlaboratory reproducibility (RSD_R) values were compared with the predicted levels of precision obtained from the Horwitz equation. The predicted RSD_R was calculated to be 16,55 %, according to the Horwitz equation. The HorRat value—the ratio of RSD_R (measured) to the predicted RSD_R (Horwitz)—gives a comparison between the actual precision and the precision predicted by the Horwitz equation. The HorRat values ranged from 0,31 to 0,79 (see Table B.3).

Table B.3 — Recovery, repeatability and reproducibility of the method calculated using two adsorbents spiked with DBP and DEHP (n = 5)

			Lab A	Lab B	Lab C	Lab D	Lab E
DBP	ODS filter	Recovery (%)	103,5	101,1	107,9	85,3	101,6
		Repeatability (within-lab) RSD_r (%)	3,0	2,1	2,8	8,4	13,6
		Reproducibility (between-lab) RSD_R (%)	8,6				
		Horwitz ratio (HorRat) value	0,52				
	SDB cartridge	Recovery (%)	96,3	102,0	100,1	92,1	105,0
		Repeatability (within-lab) RSD_r (%)	6,9	2,0	7,5	4,5	2,3
		Reproducibility (between-lab) RSD_R (%)	5,1				
		Horwitz ratio (HorRat) value	0,31				
DEHP	ODS filter	Recovery (%)	107,3	104,8	95,0	91,7	84,5
		Repeatability (within-lab) RSD_r (%)	4,2	4,0	4,8	6,7	20,7
		Reproducibility (between-lab) RSD_R (%)	9,7				
		Horwitz ratio (HorRat) value	0,59				
	SDB cartridge	Recovery (%)	96,6	103,3	85,4	97,9	73,3
		Repeatability (within-lab) RSD_r (%)	6,6	1,9	8,1	2,3	0,8
		Reproducibility (between-lab) RSD_R (%)	13,1				
		Horwitz ratio (HorRat) value	0,79				

Annex C
(informative)

Screening phthalates in solvent wipe tests

C.1 Measurement strategy

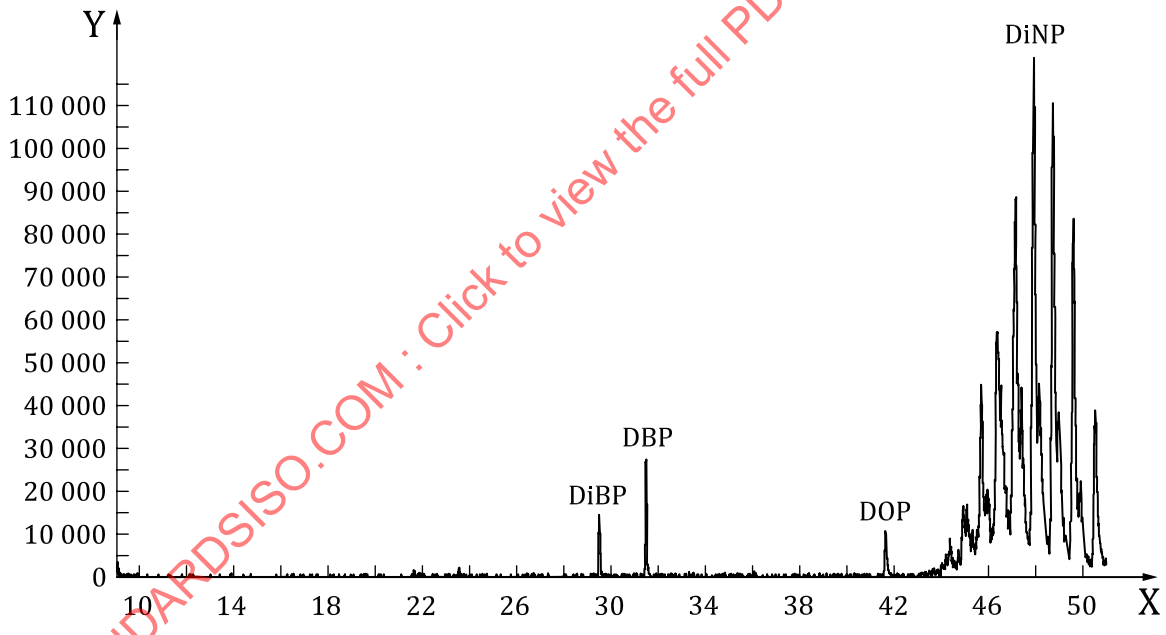
The reason for investigations by solvent wipe samples can be, for example:

— screening examinations towards localization and identification of sources (see Figure C.1),

— detection of possible surface contaminations,

— fogging problems ("black dust").

The phthalate concentrations in the solvent wipe samples from surfaces of inert phthalate-free materials frequently range from approximately 1 µg/m^2 to 1 000 µg/m^2. With fogging samples, concentrations higher by an order of magnitude can occur (especially for DEHP partially >10 mg/m^2). Due to this extensive concentration range, the following processing instruction and the practical example are purely indicative (see Table C.1).



Key

X retention time

Y strength of the signal

Figure C.1 — Ion trace chromatogram (m/z = 149) of a wipe sample of a phthalate containing wall coating (screening analysis without IS)

C.2 Selection of a surface for sampling

The selection of the sampled surface shall be accurately justified and documented. Solvent wipe samples should preferably be performed on non-absorptive surfaces (glass, metal, ceramics, plastics, etc.). The

sampled surface is dependent on the measurement task and the anticipated concentration. It should be approximately 10 cm × 10 cm.

It is recommended to test the surface selected for the examination for solvent resistance prior to sampling.

C.3 Sampling and conditioning of a wipe sample of solvents

C.3.1 Sampling

Sampling shall take place using phthalate-free substrates. Aluminium oxide wool sterilized by heating or pre-extracted wiping cloths have been proven suitable. The substrate is moistened with a suitable solvent (TBME, toluene, ethanol) depending on the solvent resistance of the surface. The selected surface is wiped with the moistened material three times forming slightly overlapping courses using cleaned tweezers or metal pliers (see Figure C.2). The process is repeated on the same surface, if necessary, with a second solvent. Likewise, unloaded substrates that have been moistened in the same way are taken as blank value samples. The samples are securely packed (e.g. in aluminium foil or glass bottles) in order to avoid contamination.

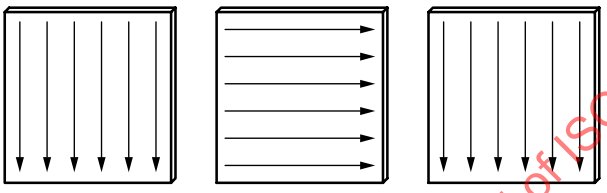


Figure C.2 — Sampling of solvent wipe samples

Table C.1 — Phthalate contents in solvent wipe samples form a windowpane (450 cm^2) during a measurement with no reference to a particular occasion

Compound	Sample 1 µg/m^2	Sample 2 µg/m^2	Sample 3 µg/m^2
DMP	< LOQ	< LOQ	> LOQ
DEP	< LOQ	< LOQ	< LOQ
DBP	< LOQ	< LOQ	< LOQ
BBP	< LOQ	< LOQ	< LOQ
DEHP	12	58	7,7
DOP	< LOQ	< LOQ	< LOQ
The limit of quantification is 1 µg/m^2.			

C.3.2 Example of extraction and analysis

If the substrates have been packed after sampling in glass bottles, it is recommended to perform the extraction directly in these bottles and not to transfer the substrates to any other vessels. Alternatively, the samples are transferred to the laboratory to glass flasks or glass bottles (volume 50 ml) and mixed with 20 ml solvent and with 10 µl of the internal standard solution with concentration of 100 mg/l. The flasks or bottles are closed, effectually shaken and treated in an ultrasonic bath for 30 min. 10 ml of the supernatant is reduced to 0,5 ml under vacuum control. Attention should be paid in this process not to reduce to dryness. The concentration of the internal standard in the concentrated extract amounts to 1,0 mg/l. The concentrated extracts are then analysed.

The practical example described here is suitable for a concentration range from 5 µg/m^2 to 1 000 µg/m^2 for a sampled surface of 10 cm × 10 cm. If even higher concentrations are found or anticipated in the wipe samples, then the amount of the internal standard and the solvent as well as the supernatant thickening shall be adjusted.

If very high phthalate concentrations are expected in the wipe samples, as it can be the case with, e.g. the "fogging" problems, then the substrates can initially also be extracted with (e.g. 20 ml) solvent without addition of an internal standard. Subsequently, a small sample of the supernatant (maximally 100 µl) is then taken for the analysis and the approximate concentration is calculated. The required quantity of the internal standard and the solvent, as well as the concentration factor, can then be determined based on this information. However, after addition of the internal standard, the sample shall again be effectually shaken and treated for 30 min in the ultrasonic bath. This procedure is particularly advisable in case of anticipated very high concentrations in wipe samples; the volume error occurring thereby is negligible.

C.4 Calculation of the result

Provided the intercept is not significantly different from zero, then Formula (C.1) is valid:

$$m = v_{PA} / b \tag{C.1}$$

where

m is the analyte mass in the sample extract in µg;

v_{PA} is the calculated peak area ratio;

b is the slope of the calibration function in μg^{-1}.

The final result, the concentration, c_A, of the investigated compound on the sampled surface, is calculated by Formula (C.2):

$$c_A = m / A \tag{C.2}$$

where

c_A is the concentration of the investigated compound on the sampled surface in $\mu g/m^2$;

m is the analyte mass in the sample extract in µg;

A is the sampled surface in m^2.

Annex D
(informative)

Screening phthalates in house dust

D.1 Characterization of house dust

Dust originates from a number of natural and anthropogenic sources and therefore, varies considerably in chemical and biological composition. In addition, the physical properties of dust are of importance, of which the size of the individual particles is by far the most important. Particles up to an aerodynamic diameter of about 30 µm are mainly encountered as suspended particulate matter in air, whereas larger particles are generally sedimented in the form of dust precipitation.

In the context of this document, the term "house dust" is intended to mean all types of particles which are encountered indoors in deposited form in order to delimit this term from "suspended particulate matter". The dust can be solids of the most varied inorganic or organic materials which can be of natural or synthetic origin. The term includes not only fractions which originate indoors themselves, but also those which are introduced from the outside.

The finer constituents consist, *inter alia*, of skin flakes and hairs of animals and humans, the abrasion of textiles and fittings (e.g. fibres from clothing and carpets), inorganic materials such as sand, loam and clay, food crumbs, soot particles and dusts from combustion processes (smoke), microorganisms, fungal spores, and pollen are also present. Coarser constituents consist, *inter alia*, of plant parts such as leaves and needles, hairs, stones and sand. House dust thus includes equally particles having diameters in the sub-millimetre range and in the range of several millimetres having round, polygonal or fibrous shape.

In addition to the size distribution of the particles, the content of the organic and inorganic material in house dust also varies. The house dust from kindergartens frequently consists almost completely of inorganic materials such as sand, loam and clay from sand pits. House dust from the residences of animal owners having at the same time heavy abrasion of carpets can consist virtually solely of organic material. Thus, the content of organic matter (measured using the loss on ignition) in house dust can be between <5 % and >95 %[23]. With regard to the analyses of phthalates in house dust, special attention shall be paid to the fact that plastic particles within the dust sample can lead to increased phthalate contents (false-positive results).

Particularly, the "age" of the house dust, that is the time for which the dust has laid on the ground, affects the contents level of substances, since the substances originating from the most varied sources accumulate with time in the dust. In this document, a distinction is made between old dust and fresh dust. Old dust is dust of unknown age as can frequently be found on surfaces of fittings (cupboards etc.). Fresh dust is defined here as dust whose age is determined by the measurement planning and is known exactly (usually one week).

Also, employing differing sampling methods influences the results of the study of house dust and its constituents. With respect to a later study of constituents in the collected house dust, it should be taken into account, for example, that during sampling of a surface by vacuuming, losses can occur for substances which have a sufficiently high vapour pressure due to vaporization from the matrix during sampling.

D.2 Measurement strategy

The reason for the investigation of house dust samples can be, for example:

— screening examinations for the pre-assessment of the contamination,

— orienting measurements for qualitative determination of the phthalate spectrum.

Dust sampling serves in particular the determination of semi-volatile compounds, which are preferentially accumulated in dust. It serves as a screening method for the definition of the phthalate spectrum and can indicate the existence of sources. During the investigation of old dust, it shall be taken into account that the pollution can be caused by sources that are no longer existing.

During sampling of house dust, the ubiquitous distribution of phthalates shall be considered in order to avoid contamination of the sample. The hints in Clause 11 shall thereby be particularly observed. For these reasons, the following preparation specification and the practical example are purely indicative (see Table D.1). Table D.1 provides examples for typical phthalate concentrations in unsieved dust samples[20]. The primary sources of DEHP, DBP and BBP can be identified by means of solvent wipe samples. The measured dust concentrations prove that source identification by means of dust analysis is hardly possible.

At least one internal standard compound is required for air samples; at least two internal standard compounds are required for house dust samples and solvent wipe samples.

D.3 Apparatus, operating materials and chemicals for sampling and analysis

D.3.1 Filter, glass fibre filter, diameter 50 mm to 80 mm (adapted to the sampling system), free of binder, conditioned as follows: heating to 500 °C for 2 h, cooling in the transport vessel, weighing (precision of ±0,1 mg), storing in the transport vessel.

D.3.2 Transport container for filters, suitable vessel, free of phthalates, for example, petri dish made of glass with suitable diameter.

D.3.3 Ground glass tube, for dust sample intake for further extraction.

D.3.4 Solvent, e.g. TBME or toluene, free of blank values, for residue analysis.

D.3.5 Ultrasonic bath.

D.3.6 Centrifuge.

D.4 Preparation of the room for sampling

Before fresh dust is sampled, at a defined time interval (e.g. one week) all of the area to be sampled later is cleaned thoroughly by wet wiping off. This thorough cleaning serves to produce a reproducible initial state. In the time between the thorough cleaning and sampling, the area to be sampled should not be cleaned further by the occupants. If analytical results relevant to a decision are required, the thorough cleaning shall be performed by the measurement institute. The selection of the area to be sampled should be made carefully on site with respect to the greatest possible representativeness taking into account the particular problem, and the selection made shall be documented. The material obtained is stored as a reference sample for any control purposes.

Alternatively, a sampling area free of contamination can be prepared by carpeting with aluminium foil that can be examined after a defined time interval (e.g. one week).

D.5 Sampling

Sampling can take place by dust suction using a suitable sampling attachment on vacuum cleaners (e.g. modified sampling heads equipped with 5 cm to 8 cm glass fibre filters) or using flat filter systems.

The sampling area should at least be 2 m^2 and is slowly vacuumed in a lamellar way. Only smooth floorings and surfaces free of phthalates are suitable for sampling. When house dust is sampled from floorings, depending on the condition of the floor covering, during the vacuuming process not only particles from the surface of the floor covering, but also particles from any open joints and intermediate spaces of the floor can also be taken up. This is of importance particularly if the material of the floor foundation contains

substances which are to be determined in the house dust. Indication of the sampling location as well as material and condition of the sampling surface is essential for the test report (see Annex J).

The minimal weighted sample of the dust quantity used for extraction should amount to approximately 50 mg. Typical foreign matter such as paper clips, foil rests or similar are sorted out with tweezers.

The possibility of contamination by the used vacuum cleaner and/or the material of the vacuum cleaner bag cannot be avoided for the analysis of sent vacuum cleaner bags. Even if the unused material of the vacuum cleaner bags is examined, in parallel, an additional blind value caused, for example, by the vacuum cleaner is possible. For this reason, the examination of sent vacuum cleaner bags regarding phthalates and other plasticizers is not reasonable.

D.6 Apparatus blank value for sampling of house dust

For the house dust sampling, field blank values are in a strict sense hardly realizable due to the high fluctuation width. The establishment of an apparatus blank value is, however, required for validation of the sampling system in case of a new application or change of a system component (e.g. also for vacuum cleaner bags). Such apparatus blank value is gained in an identical manner as the actual sample. A suitable amount of a phthalate-free powder (e.g. silica gel or bentonite) from an inert surface is sucked instead of house dust.

D.7 Sample preparation

The exposed glass fibre filter is re-weighted (precision of ±0,1 mg). Afterwards, the glass fibre filter and the dust are transferred completely to the extraction vessel. The sample is spiked with a suitable quantity of internal standard and mixed with sufficient solvent[17],[2]. Further, the sample is effectually shaken for thorough wetting, extracted for 15 min in an ultrasonic bath and subsequently centrifuged (if required). An aliquot of the extract is transferred to an auto sampler vial and used for the GC-MS analysis (see Clause 7). A typical concentration of the internal standard in the extract is, for example, 1 mg/l.

The phthalates of lower concentration are determined from this raw extract by means of GC-MS analyses according to Clause 7. For example, DEHP generally requires an additional dilution.

TBME and toluene have been proven as suitable extraction solvents. The use of another slightly polar solvent is possible. Non-polar solvents (e.g. hexane) are not suitable. However, it shall be guaranteed that the same solvent is used for calibration and gas chromatographic determination of the sampling solution.

The use of automatic extractors (e.g. ASE) is possible. The advantage consists in the limited solvent volumes and the repeatable blank value. A precondition is the incorporation of phthalate-free connections and hoses. During the analysis of house dust, it shall be taken into account that plastic particles found in the house dust can be solved by the solvents and can irreversibly clog the transfer capillaries.

NOTE The extraction in Soxhlet is not advisable due to the problems related to blank values.

Table D.1 — Phthalate concentration in unsieved dust samples

	Compound						
	DMP	DEP	DBP	DiBP	BBP	DEHP	DiNP
Rooms with identified primary sources of DEHP, DBP and BBP (n = 5)							
Average value mg/kg	0,7	32	68	12	36	126,8	331
Absolute standard deviation	0,6	17	56	9	42	101,5	406
Rooms without any identified primary source of DEHP, DBP and BBP (n = 5)							
Average value mg/kg	0,35	17	18	2	10	123,2	193
Absolute standard deviation	0,07	17	20	1,4	2	199	192

D.8 Presentation of results

The contents of the dust constituents are usually reported on a mass basis in mg/kg of dust, but report on an area basis in mg/m^2 is also possible if the area is precisely defined. Furthermore, the result may also be presented related to the deposition rate in mg/(m^2 d).

Table D.2 — Results from an interlaboratory test for phthalate analysis in a non-spiked ≤63 µm-mixed dust sample

Compound	Average value µg/ml	Median µg/ml	Relative standard deviation %
DEP	13,5	11,1	107
DBP	30,6	26,7	55,0
BBP	49,5	32,5	163
DEHP	527	515	42,3
NOTE N = 26 where N is the number of laboratories.			