厚生労働行政推進調査事業費補助金（化学物質ﾘｽｸ研究事業）
分担研究報告書

室内空気環境汚染化学物質の標準試験法の国際規格化

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厚生労働省のシックハウス（室内空気汚染）問題に関する検討会が開催され、指針値の見直しや、新たな規制汚染物質が検討されている。また、フタル酸エステル類について改正指針値に対応可能な標準試験法が提案され、日本薬学会編　衛生試験法・注解 2015：追補 2019 にて国内規格化や、国際規格にも新規案として提案されてる。本分担研究では、国内に規格化されたフタル酸エステル類の測定・分析方法に対する国際規格化や、室内における新たな汚染物質の放散源の探索のため、マイクロチャンバーを用いた仕上げ材からの SVOC 物質の放散速度を測定した。国内のフタル酸エステル類の測定・分析方法を国際規格化するために ISO/TC146/SC6 の国際会議の状況を総括した。フタル酸エステル類の測定と分析方法は WG20 に該当するが、2019 年度は WG20 の会議が予定されなかったため、SC6 の総会で日本のフタル酸エステル類の測定・分析方法を紹介した。その結果、発表資料は WG20 の Document 資料として登録された。また、2019 年度 12 月末まで国内のフタル酸エステル類の測定・分析方法を ISO-16000-33(フタル酸エステル類分析方法)の改正案として作成し、WG 委員長に提出した。今現在は改正案が検討されている。建材からの SVOC 放散速度を測定した。測定対象建材は、接着剤 5 種類、床材 4 種類、水性ペイント 3 種類、壁紙 2 種類であった。DBP、DOA、DEHP、TXIB はすべての建材から検出された。床材からは特に 2E1H と DEHP の放散速度が高く、また、水性ペイントからは 2EH、DEHP、TEXANOL、TXIB の放散速度が高く測定された。今後、水性ペイントの使用が多い学校や病院における実態調査や、実験室実験による放散速度と気中濃度との相関性を把握する必要があると考えられる。

A. 研究目的

最近、厚生労働省のシックハウス検討会では指針値設定・改定候補物質に対する意見と方針が検討され、キシレン(200[μg/m^3])、DBP(17[μg/m^3])、DEHP(100[μg/m^3])の指針値が改正された。しかし、新規物質としては 2-エチル-1-ヘキサノ-ル(2E1H)、2,2,4-トリメチル-1,3-ペンタンジオ-ルモノイソブチレ-ト(別名:Texanol)、2,2,4-トリメチル-1,3-ペンタンジオ-ルジイソブチレ-ト(別名:TXIB)が提案されたが、科学的な根拠やリスク評価等、更なる知見が必要であることで指針値には追加されなかった。

また、DBP、DEHP は最新の分析技術を基に汎用性が高い標準試験法が開発され、日本薬学会編　衛生試験法・注解 2015：追補 2019 にて国内規格化される予定である。この試験法を国際規格に含むことが検討されている。

本分担研究では、マイクロチャンバーを用いて建材からの SVOC 放散速度を測定することで、既存の規制物質である DBP、DEHP のみではなく、新たに検討されている SVOC 物質の汚染源を把握することとした。また、国内のフタル酸エステル類の測定・分析方法を ISO/TC146(大気の質)/SC6(室内空気)、ISO 16000-33：2017「Determination of phthalates with gas chromatography/mass spectrometry (GC/MS)」に新規提案するための進捗情報を報告する。

B. 研究方法

B-1　建材からのSVOC放散速度測定

1)測定概要

測定対象建材は、接着剤 5 種類、床材 4 種類、水性ペイント 3 種類、壁紙 2 種類である。これらの建材はホームセンターにて購入したものであり、一般によく使用されている。表 1 に測定対象建材の種類とサンプリング名を、図 1 に試験片の写真を示す。接着剤 5 種類については、アルミニウム板に 2 回塗った後、昨年度測定の床材 F-4(2018)を接着し、1 週間以上乾燥させてから測定を行った。接着剤の種類は、AF4-1 がアクリル樹脂エマルション系、AF4-2 がアクリル樹脂系、AF4-3 が酢酸ビニル樹脂溶剤形、AF4-4 がクロロプレンゴム溶剤形、AF4-5 がニトリルゴム系溶剤形である。床材 4 種類については、すべて塩化ビニルを使用している PVC 建材である。水性ペイント 3 種類については、アルミニウム板に 2 回塗った後、1 週間以上乾燥させてから測定を行った。水性ペイントの種類は、P-1 が水性アクリルエマルション塗料、P-2 が水性シリコンアクリルエマルション樹脂、P-3 が高性能シリコンアクリル樹脂である。また、標準塗り面積は、P-1 が 11～14 ㎡（1 回塗り）、P-2 が 11～15 ㎡（1 回塗り）、P-3 が 11～15 ㎡（1 回塗り）である。壁紙 2 種類については、W-1 がポリビニルアルコール、W-2 が塩化ビニル樹脂である。

2)測定方法

図2にマイクロチャンバー外観を示す。図3にマイクロチャンバー測定方法の工程図を示す。マイクロチャンバーの容積は630ml（±5%）であり、入口直前にベントラインを設けることにより蓋と建材の隙間から外気がチャンバーの中に入らないようにコンタミ対策をしている。測定開始前にマイクロチャンバーの解体し、マイクロチャンバーを水で洗浄した。その後、チャンバー内に残存する化学物質を揮発させるために加熱装置を用いて、1時間220℃で加熱処理を行った。加熱処理後、マイクロチャンバーを常温まで冷却させた。

試験片をマイクロチャンバーの蓋と容器の間に挟んで、試験片表面からのSVOC物質放散測定を行った。マイクロチャンバー内に試験片を設置した時点で放散試験の開始になる。放散試験は28℃の恒温槽で24時間行った。放散試験後には加熱

脱着試験を行った。放散試験に使用した試験片をチャンバーから取り外した後、加熱脱着装置にマイクロチャンバーを設置し、チャンバー内表面に付着しているSVOCを加熱脱着した。加熱脱着は220℃、1時間行った。加熱脱着されたSVOC物質はTenax TA捕集管を用いて回収した。建材からのSVOC放散速度は放散捕集と加熱脱着捕集の結果を合算して総捕集量とした。表2に放散捕集試験の測定条件を、表3に加熱脱着試験の測定条件を示す。

3)分析方法

分析対象物質は、2EH(2-エチルヘキサノール)、D6(ドデカメチルシクロヘキサシロキサン)、BHT(ジブチルヒドロキシトルエン)、DEP(フタル酸ジエチル)、C16(ヘキサデカン)、TBP(リン酸トリブチル)、TCEP(リン酸トリス(2-クロロエチル)、DBA(アジピン酸ジブチル)、DBP(フタル酸ジ-n-ブチル)、C20(n-イコサン)、TPP(リン酸トリフェニル)、DOA(アジピン酸ジオクチル)、DEHP(フタル酸-2-エチルヘキシル)、2EHA(2-エチルヘキシルアクリレート)、TEXANOL(テキサノール)、TXIB(2,2,4-トリメチル-1,3-ペンタンジオール ジイソブチラート)、DNOP(フタル酸ジ-n-オクチル)、DINP(フタル酸ジイソノニル)、DIDP(フタル酸ジイソデシル)の20種類の物質である。表4にTenax TA捕集管の加熱脱着条件、表5にGC/MSの分析条件を示す。

B-2　フタル酸エステル類の国際規格化

フタル酸エステル類の標準試験法を新たに開発し、改正指針値に対応可能な標準試験法を策定した。この試験法は日本薬学会編　衛生試験法・注解 2015：追補2019 にて国内規格化された。そこで、国内のフタル酸エステル類の測定・分析方法を ISO/TC146(大気の質)/SC6(室内空気)、ISO 16000-33 : 2017「Determination of phthalates with gas chromatography/mass spectrometry (GC/MS)」に新規提案することを目指し、ISO/TC146/SC6 の国際会議で本件を紹介した。今年度の進捗情報を報告した。

C.　研究結果

C-1　建材からの SVOC 放散速度の結果

新しい規制の候補となっている化学物質を含む 19 種類の化学物質を測定し、その内放散速度が高いものを昨年度の測定結果と合わせて図 4 から図 11 に示す。縦軸が放散速度、横軸が測定対象建材を示している。また、昨年度と今年度の測定結果を示している。

1)　2E1H

図 4 に 2E1H の放散速度測定結果を示す。2019 年度に測定した建材の中で放散速度が最も高かったのは、床材 F-2 であり、放散速度は 39.46 μg/(㎡・h)であった。接着剤 AF4-1 と A4F-2 の放散が高く測定されたが、床材 F-4 の測定結果より、放散速度の測定値が下回っており、接着剤からではなく、カーペットの F-4 の建材からの放散でいると考えられる。また、床材 F-1 の 17.36 μg/(㎡・h)、水性ペイント P-2 と P-3 の 15.00 μg/(㎡・h)、壁紙 W-2 の 28.41 μg/(㎡・h)がその他の建材に比べ、高い放散速度を示した。

2)　DBP

図 5 に DBP の放散速度測定結果を示す。2019 年度に測定した建材の中で放散速度が最も高かったのは、壁紙 W-1 の 0.87 μg/(㎡・h)であった。接着剤 AF4-2、AF4-4、AF4-5 は 0.51～0.53 μg/(㎡・h)であるが、2018 年度の床材 F-4 の測定結果が 0.61 μg/(㎡・h)であるため、接着剤からの放散ではなく、F-4 建材からの放散であることが考えられる。一方、接着剤 AF4-1 は 0.69 μg/(㎡・h)、AF4-3 は 0.66 μg/(㎡・h)であり、床材 F-4 のみではなく、接着材からの放散も考えられる。また、床材 F-1 の 0.35 μg/(㎡・h)、水性ペイント P-2 の 0.30 μg/(㎡・h) がその他の建材に比べ、高い値であった。

3)　C20

図 6 に C20 の放散速度測定結果を示す。2019 年度に測定した建材の中で放散速度が最も高かったのは、0.12 μg/(㎡・h)となった壁紙 W-1 である。接着剤は他の建材に比べ高い数値となっているが、2018 年度の床材 F-4 の測定結果が 0.55 μg/(㎡・h)であるため、接着材からの放散ではないと考えられる。また、床材 F-1 と F-4 の 0.11 μg/(㎡・h)、水性ペイント P-3 の 0.11 μg/(㎡・h)、壁紙 W-2 の 0.11 μg/(㎡・h)であった。

4)　DOA

図 7 に DOA の放散速度測定結果を示す。2019 年度に測定した建材の中で放散速度が最も高かったのは、水性ペイント P-2 であり、放散速度は 0.87 μg/(㎡・h)であった。また、水性ペイント P-1 の 0.46 μg/(㎡・h)、壁紙 W-2 の 0.54 μg/(㎡・h)がその他の建材に比べ、高く測定された。

5)　DEHP

図 8 に DEHP の放散速度測定結果を示す。2019 年度に測定した建材の中で放散速度が最も高かったのは、床材 F-3 であり、放散速度は 30.78 μg/(㎡・h)であった。また、床材 F-2 の 22.10 μg/(㎡・h)、床材 F-4 の 19.73 μg/(㎡・h)が測定された。

6)　2,2,4-トリメチルペンタン-1,3-ジオールモノイソブチラート（TEXANOL）

図 9 に TEXANOL の放散速度測定結果を示す。2019 年度に測定した建材の中で放散速度が最も高かったのは、水性ペイント P-2 と P-3 であり、放散速度が 47.4 μg/(㎡・h)以上となった。また、水性ペイント P-1 の放散速度は 14.2 μg/(㎡・h)であり、その他の建材に比べ、高い値であった。

7)　2,2,4-トリメチル-1,3-ペンタンジオールジイソブチレート（TXIB）

図 10 に TXIB の放散速度測定結果を示す。測定した建材の中で放散速度が最も高かったのは、水性ペイント P-1 であり、放散速度が 47.4 μg/(㎡・h)以上であった。である。また、接着剤 AF-3 の 18.15 μg/(㎡・h)、水性ペイント P-3 の 11.1 μg/(㎡・h)がその他の建材に比べ、高い値となっている。

8)　DINP

図 11 に DINP の放散速度測定結果を示

す。2019 年度に測定した建材の中で放散速度が最も高かったのは、10.3 μg/(㎡・h)となった壁紙 W-2 である。その他の建材からは検出されなかった。

C-2　フタル酸エステル類の国際化

ISO/TC146/SC6 の Working Group で議論を行った。国際会議は 2019 年 10 月 7 日～11 日まで、ドイツ・ザンクトアウグスティンで行われた。SC6 の中、フタル酸エステル類の分析方法は Working Group 20 に該当するが、今回は WG20 の会議が開催されなかったため、10 月 11 日の SC6 の総会で国内のフタル酸エステル類の測定・分析方法を紹介した。

その結果、SC6 で発表した ppt 資料は Working Group 20 の Document として認定された。また、掲載予定の英語論文も WG20 に提出することにした。以上の内容については WG20 のコンビーナーである Wensing 博士から了解を得た。英語論文の情報は以下に示す。 Tanaka-Kagawa T., Saito I., Onuki A., Tahara M., Kawakami T., Sakai S., Ikarashi Y., Oizumi S., Chiba M., Uemura H., Miura N., Kawamura I., Hanioka N., Jinno H. Method validation for the determination of phthalates in indoor air by GC-MS with solid-phase adsorption/solvent extraction using octadecyl silica filter and styrene–divinylbenzene copolymer cartridge. BPB Reports. 2019, **2** pp. 86–90

SC6 の総会で Resolution 456 として、以下の課題があった。国内のフタル酸エステル類の測定・分析方法を ISO 16000-33：2017「Determination of phthalates with gas chromatography/mass spectrometry (GC/MS)」に追加することを想定し、改正案を作成し、2019 年 12 月末に WG 主査に改正案を提出した。

D.　考察

D-1　建材からの SVOC 放散速度の測定

建材による化学物質の放散量を把握し、現在基準が設けられていない化学物質について新しい基準を制定するため、その根拠作りとして、マイクロチャンバー法により準揮発性有機化合物の放散速度の測定を行った。

DBP、DOA、DEHP、TXIB はすべての建材から検出された。一方、DEP、TBP、TCEP、DNOP、DIDP は全ての建材において検出限界値以下であった。床材からは特に 2E1H と DEHP の放散速度が高く、床材の使用が多い学校やオフィスビルにおける実態調査が必要であると考えられる。また、水性ペイントからは 2EH、DEHP、TEXANOL、TXIB の放散速度が高く、水性ペイントの使用が多い学校や病院における実態調査が必要である。

D-2　フタル酸エステル類の国際規格化

ISO 16000-33：2017「Determination of phthalates with gas chromatography/mass spectrometry (GC/MS)」には、空気、ハウスダスト、表面のフタル酸エステル類濃度の測定方法や、分析方法が規格されている。特に、空気中フタル酸エステル類の測定は加熱脱着方法と溶媒抽出方法が掲載されている。

国内のフタル酸エステル類の測定・分析方法の規格は溶媒抽出方法であるため、ISO 16000-33 規格の中、4 Sampling methods

and analytical apparatus、4.3　Sampling by adsorption and subsequent solvent extraction の項目を用いて、4.4 として、国内のフタル酸エステル類の測定・分析方法を追加することが考えられる。また、詳細な情報などが必要な場合は、Annex X を作成することが必要である。以上の考察から日本のフタル酸エステル類の測定・分析方法を ISO 16000-33：2017「Determination of phthalates with gas chromatography/mass spectrometry　(GC/MS)」に追加し、改正案を作成した。改正案を付録に添付する。

E. 結論

E-1　建材からの SVOC 放散速度の測定

室内で使用している建材から 20 種類の化学物質に対する放散測定を行った。2E1H は全ての建材から放散された。また、TXIB、TEXANOL は水性ペイント、PVC 建材、カーペットや断熱材から放散され、今後室内の汚染物質として調査が必要である。特に、TXIB、TEXANOL は水性ペイントから放散速度が高かったため、一般住宅より水性ペイントをよく使用している教育施設、オフィス、病院施設などの実態調査が必要であることや、実験室実験などによる放散速度と気中濃度との相関性を把握することが大事であると考えられる。

E-2　フタル酸エステル類の国際規格化

国内のフタル酸エステル類の測定・分析方法を国際規格化のために国際会議に参加した。国内のフタル酸エステル類の測定・分析方法を ISO 16000-33：2017「Determination of phthalates with gas chromatography/mass spectrometry (GC/MS)」に追加するため、新草案を作成している。2020 年度前半に WG20 の資料として提出される予定である。また、審議内容の確認と Resolution については、2020 年度 9 月末にフランス・パリで行われる ISO/TC146/SC6 で確認する。

F. 研究発表

1.論文発表

なし

2.学会発表

1) Hyuntae Kim, Shin-ichi TANABE, Makoto Koganei, The emission rate of newly regulated chemical substances from building materials, IAQVEC 2019,10th INT. conference on Indoor Air Quality, Ventilation and Energy conservation in building, Bair Italy USB #120、2019.9

2）小谷菜緒、金　炫兌、田辺新一、小金井真、建材から発生する未規制物質の放散速度に関する調査、日本建築学会中国支部研究発表会、2020.3(予定)

G. 知的所有権の取得状況

1.特許取得

なし

2.実用新案登録

なし

3.その他

なし

表一覧

表 1　測定対象建材

建材	商品名	サンプリング名
接着剤	ウッドシール	AF4-1
	ボンドコークホワイト	AF4-2
	ボンド K120	AF4-3
	速乾ボンド G10Z	AF4-4
	ボンド G103	AF4-5
床材	リノベシート 白ペンキ木柄	F-1
	吸着クッションフロア	F-2
	クッションフロア KF504-S	F-3
	クッションフロア KF528-S	F-4
水性塗料	水性インテリアカラー	P-1
	水性建物用	P-2
	水性バリューコート	P-3
壁紙	プラスチック障子紙	W-1
	補修用カベ紙　HK-16	W-2

表 2　加熱脱着試験の測定条件(MSTD-258M)

加熱脱着温度	30℃（5min)-(20℃/min) -220℃（40min)
供給ガス流量(He)	90 ml/min
吸引流量	60 ml/min
サンプリング時間	60 min
捕集管	Tanex TA(60/80 mesh)

表 3　放散捕集試験の測定条件

チャンバー容積	630ml
時間	24h
吸引流量	30ml/s×24h=42.3L
ベント流量	15ml/s
MC 供給流量	15ml/s
捕集管	Tenax TA（60/80mesh）充填

表 4　加熱脱着の条件(GERSTEL TDS A)

加熱脱着条件	280 ˚C (10 min)
トラップ温度	-60 ˚C
注入温度	325 ˚C (5 min)

表 5　GC/MS の分析条件

使用機器(GC/MS)	Agilent 6890N / 5973 inert
カラム	Inert Cap 1MS　30m×0.25mm×0.25μmdf
GC オーブン温度	50˚C(2min)→10˚C/min→320˚C(5min)
スプリット比	低濃度：splitless、高濃度：50：1
測定モード	SCAN
SCAN パラメータ	m/z 29(Low)~550(High)
検出器温度	230˚C

図一覧

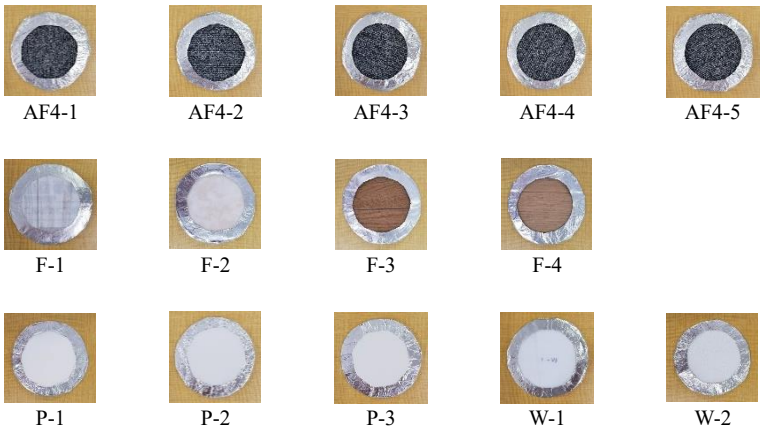

図 1　試験片一覧

図 2　マイクロチャンバー外観

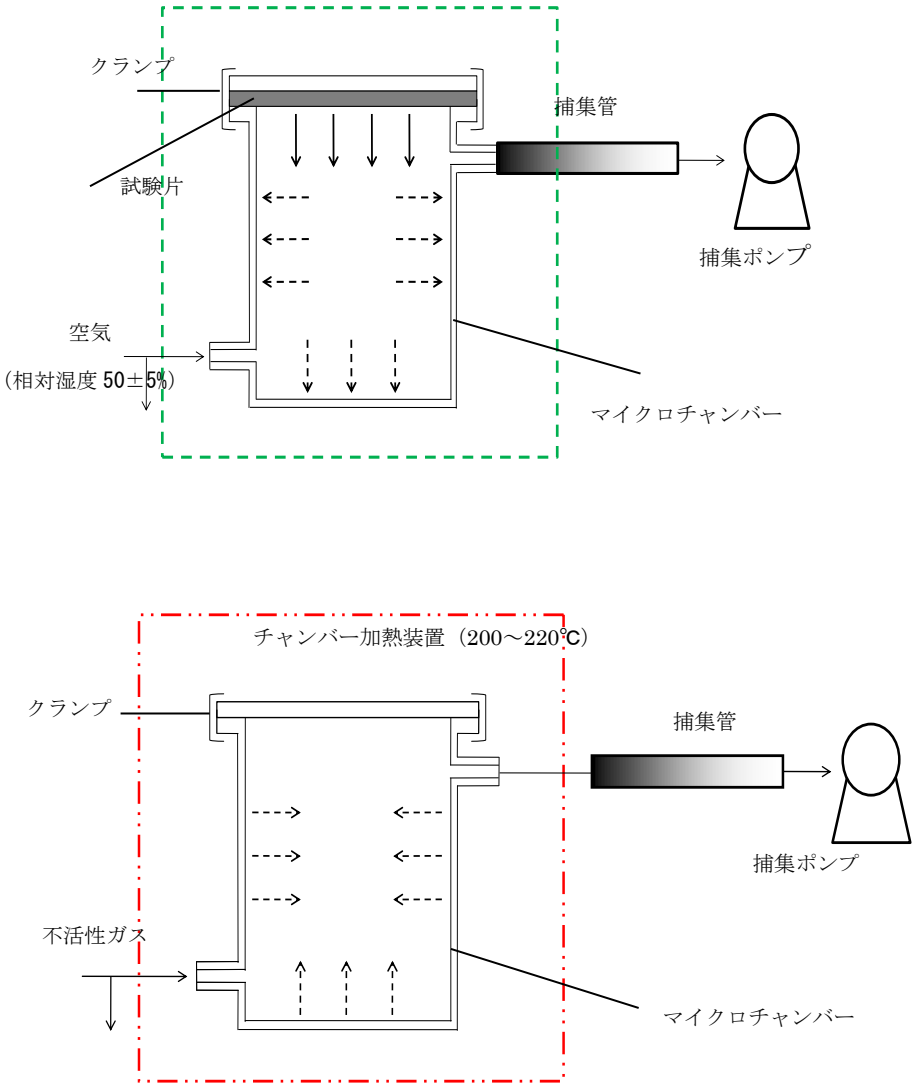

図 3　マイクロチャンバー測定方法の工程図

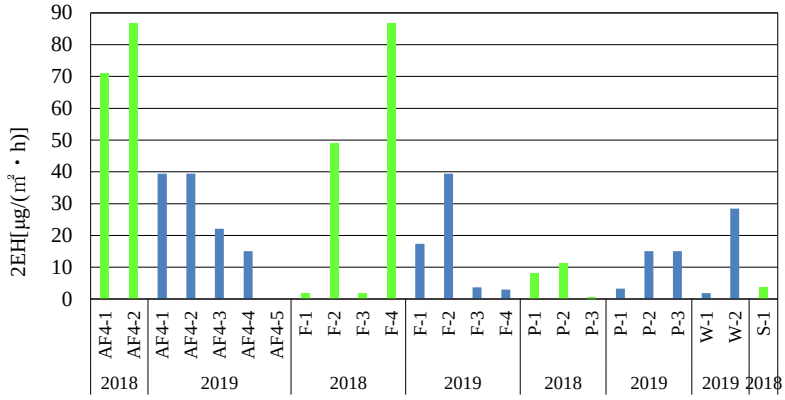

図4　2EH放散速度結果

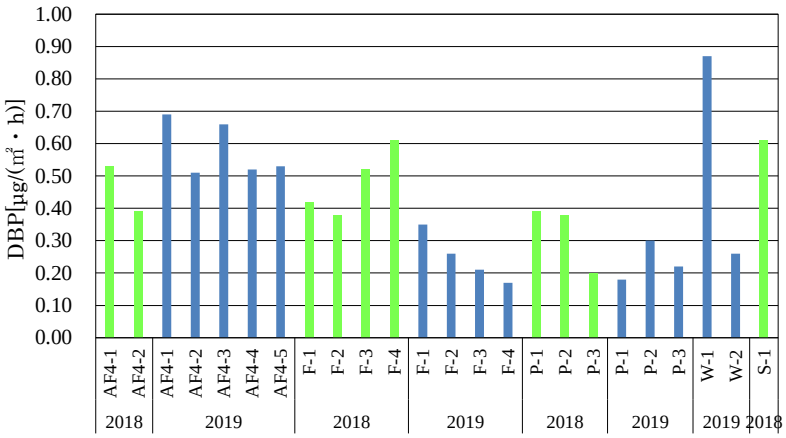

図5　DBP放散速度結果

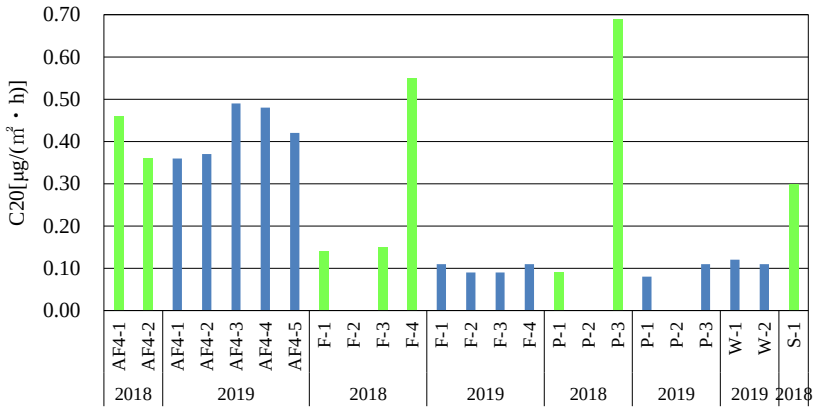

図6　C20放散速度結果

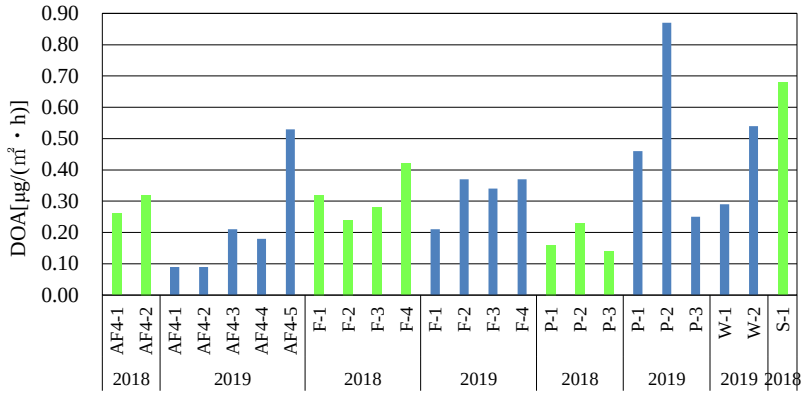

図7　DOA放散速度結果

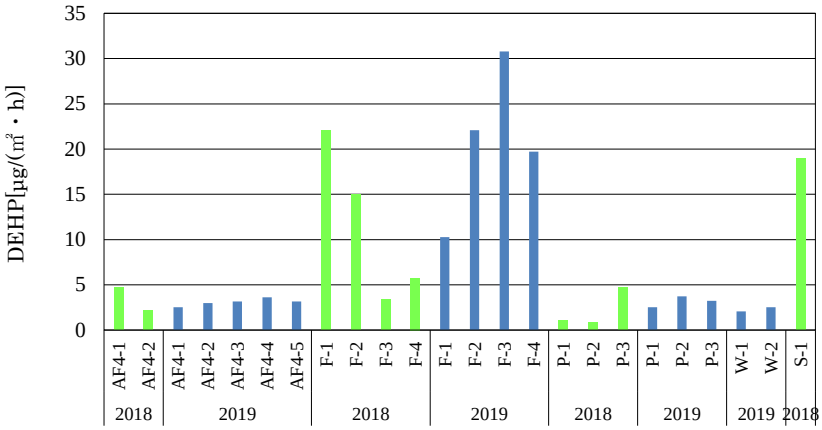

図8　DEHP放散速度結果

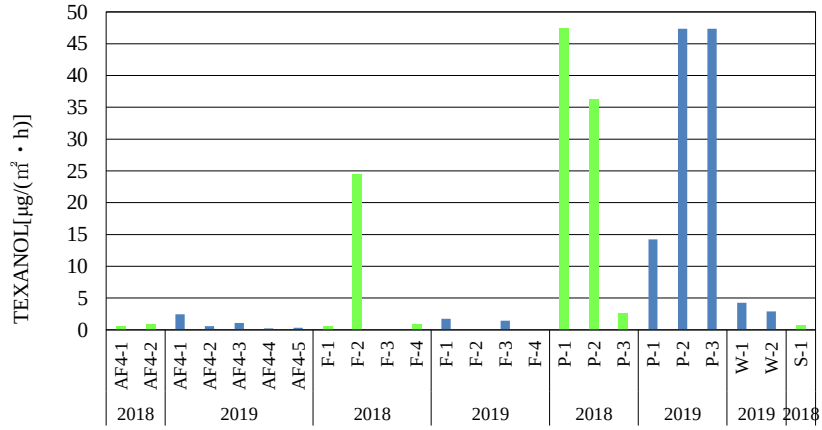

図9　TEXANOL放散速度結果

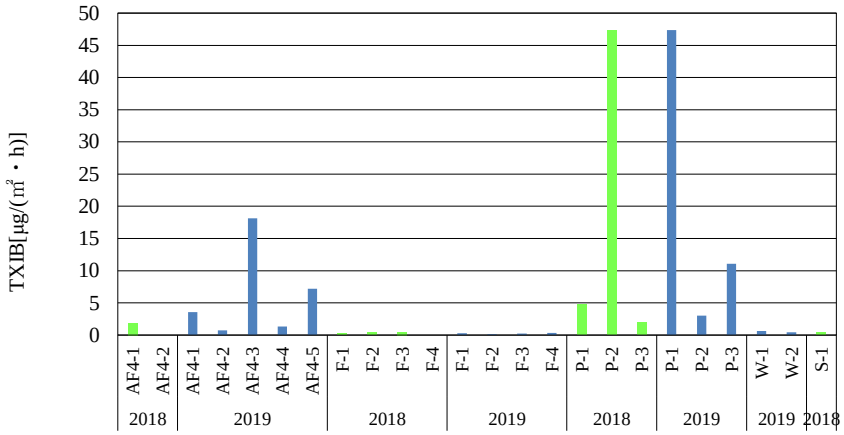

図10　TXIB放散速度結果

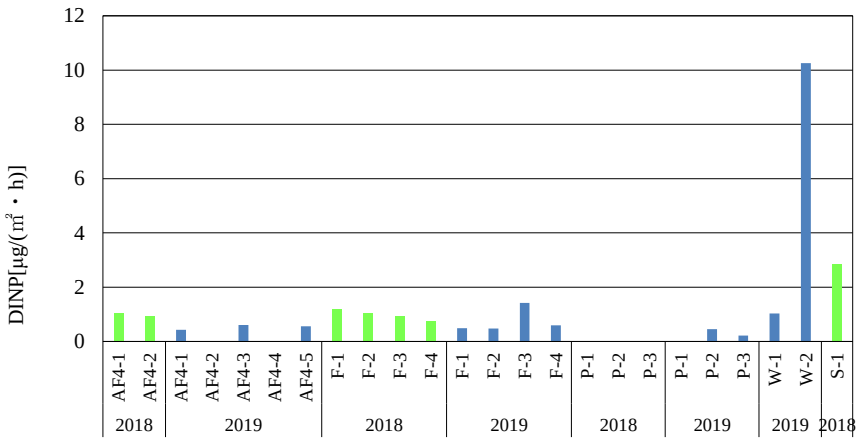

図11　DINP放散速度結果

［付録］

Meeting of ISO/TC 146/SC 6
"Indoor air"

Sankt Augustin (Germany)
11 October 2019

Resolutions

Resolution 456
ISO/TC 146/SC 6 agrees that the Japanese delegation should prepare the documents on "Determination of phthalates with gas chromatography/mass spectrometry (GC/MS)" for further discussion and send them to the secretariat by the end of this year. The secretariat will distribute it to WG 20.

DRAFT Ver. 1.1

ISO

16000-33

Indoor air —

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

Air intérieur —
Partie 33: Détermination des phtalates par chromatographie en phase gazeuse/spectrométrie de masse (CPG/SM)

Contents

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).

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

For an explanation on the 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 the following URL: www .iso .org/ iso/ foreword .html.

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

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

Introduction

The different parts of ISO 16000 describe 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 (see Foreword).

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 dicarbon 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. The five most frequently used phthalates are diisodecylphthalate (DiDP), diisononylphthalate (DiNP), di(2-ethylhexyl)-phthalate (DEHP), di-n-butyl-phthalate (DBP), and benzyl-n-butyl-phthalate (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 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.

Two alternative sampling and processing methods, whose comparability has been proven in a round robin test, are specified for indoor air[5]. Sampling can take place using sorbent tubes with subsequent thermal desorption and GC-MS analysis. Alternatively, sampling can take on other types of sorbent tubes that are subsequently analysed by solvent extraction with GC-MS.

Depending on the sampling method, the compounds dimethyl phthalate to diisoundecylphthalate can be analysed in house dust as described in Annex C[9]. 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 B. 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, 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 16000-6:2011, *Indoor air — 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*

3 Terms and definitions

No terms and definitions are listed in this document.

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

− IEC Electropedia: available at http:// www .electropedia .org/

− ISO Online browsing platform: available at http:// www .iso .org/ obp

4 Sampling methods and analytical apparatus

4.1 General

Sampling of indoor air takes place either by adsorption on a thermal desorption tube filled with quartz wool and Tenax® TA[1)] on adsorbents such as Florisil®[2)], octadecyl silica (ODS), and styrene–divinylbenzene copolymer (SDB) with subsequent solvent extraction[5][6][X]. 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 round robin 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[5].

NOTE The experiences from the round robin 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 the respective clauses. Further hints to quality assurance and problems related to blank values that shall be considered are listed in Clause 10.

4.2 Sampling by adsorption with subsequent thermal desorption

Use the apparatus, reagents and materials described in ISO 16000-6 (including the informative annex on semi-volatile compounds) with the following additional specific requirements:

4.2.1 Apparatus, operating materials and chemicals

4.2.1.1 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 at least 200 mg of adsorbent, e.g. Tenax® TA[1)] 20/35 (see ISO 16000-6:2011, Annex D).

4.2.1.2 Sampling system, according to Figure 1.

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

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

4.2.1.5 Laboratory sampling facilities, hygrometer, thermometer, barometer.

4.2.1.6 Internal standards, required as quality control measure of the whole analytical process including sampling; suitable examples include: the ring-deuterated compounds D4-DMP, D4-DEP, D4-DBP, D4-BBP, D4-DEHP, D4-DOP as well as the non-deuterated diallyl phthalate (DAlP), see Clause 5 and Table 3. Standards shall be prepared in phtalate-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.

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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 U.S. 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.

4.2.1.7 Thermal desorption unit, coupled to GC-MS for the two-stage thermal desorption of the sorbent tubes and transfer of desorbed vapours via an inert gas flow into a gas chromatographic (GC) system, fitted with a mass spectrometric (MS) detector.

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

4.2.2 Preparation of the thermal desorption tube

The use of a tube packed with quartz wool and Tenax® TA[1)] presupposes 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 200 mg sorbent 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[1)]), 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 16000-6:2011, 7.1).

Sampling should take place as soon as possible after conditioning. If sampling is not possible within approximately 14 days after conditioning, then the tube shall be reconditioned for 15 min at approximately 300 °C before sampling. In order to avoid contamination, the thermal desorption tubes should be touched only with cotton gloves. 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. If the selected analytical system does not do this, tubes shall only be handled using clean cotton gloves, in the field and laboratory, to minimize contamination.

Tubes should be indelibly and individually labelled but without attaching adhesive labels which might jam or discolour during thermal desorption.

4.2.3 Sampling

Prior to sampling, the conditioned tubes are spiked with maximal 1 µl 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 and shall be free of leaks. The pump is connected to the non-sampling end of the sorbent tube by means of polyethylene or polytetrafluoroethylene (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 doubled sampling of the indoor air is recommended.

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

4.3 Sampling by adsorption with Florisil®[2)] and subsequent solvent extraction

4.3.1 Apparatus, operating materials and chemicals

4.3.1.1 Sampling system, according to Figure 1.

4.3.1.2 Pump, suitable for a volume flow 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.

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

4.3.1.4 Muffle furnace.

4.3.1.5 Flat, heat resistant evaporating dish, for heating Florisil®[2)].

4.3.1.6 Florisil®[2], 60 to 100 mesh.

4.3.1.7 Glass wool, silanized.

4.3.1.8 Glass flask, with screw-cap and polytetrafluoroethylene (PTFE) sealing, 50 ml.

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

4.3.1.10 Laboratory sampling facilities, hygrometer, thermometer, barometer.

4.3.1.11 Solvent, e.g. tertiary butyl methyl ether (TBME) or toluene, free of blank values (solvent shall be tested for the absence of phthalate blank values).

4.3.1.12 Internal standards, suitable are, e.g. the ring-deuterated compounds D4-DMP, D4-DEP, D4-DBP, D4-BBP, D4-DEHP, D4-DOP as well as the non-deuterated diallyl phthalate (DAlP); see Clause 5 and Table 3.

4.3.1.13 GC-MS, gas chromatographic (GC) system, fitted with a mass spectrometric (MS) detector.

[Figure 1 is omitted]

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

[Figure 2 is omitted]

Figure 2 — Filling of the glass tube

Key

1 Florisil®[2)]

2 glass wool

4.3.2 Preparation of Florisil®[2)] and the adsorption tubes

Florisil®[2)] 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 Florisil®[2)] and 150 µl water are given to a 50 ml glass flask with a screw-cap and polytetrafluoroethylene (PTFE) sealing. After closing the flask, Florisil®[2)] shall be mixed for approximately 45 min until a uniformly flowing powder has formed again. The deactivated Florisil®[2)] 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®[2)] 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 DFG method [16].

4.3.3 Hints to the application of Florisil®[2)]

Each charge of Florisil®[2)] newly heated and deactivated according to 4.3.2 shall be examined for blank values. Charges 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 up to six months. After expiration of this period, unused tubes shall be emptied and the Florisil®[2)] shall be treated again according to 4.3.2.

Other adsorbents such as Chromosorb 106 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.

4.3.4 Sampling

A defined volume (e.g. 10 µl) of the internal standard solution (e.g. 100 mg/l, this 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 D (for thermal desorption method) and in Annex E (for solvent extraction method using Florisil®[2)]).

The internal standard is added, e.g. 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 5 are suitable as internal standards.

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

[Table 1 is omitted]

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.

4.3.5 Sample conditioning

The Florisil®[2)] 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 polytetrafluoroethylene (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.

5 ml of the supernatant are then extracted by a dropper and reduced to 0,2 ml. Reduction to dryness leads to considerable substance loss, especially of the volatile phthalates. 100 µl of this concentrated extract is transferred to the auto sampler vials and used for the CG/MS analysis (Clause 6). Under application of the specifications described in 4.3.4, the concentration of the internal standard in the concentrated extract amounts to 1 mg/l.

4.4 Sampling by adsorption with ODS solid phase disk or SDB copolymer cartridge and subsequent solvent extraction

4.4.1 Apparatus, operating materials and chemicals

4.4.1.1 Sampling system, according to Figure 1.

4.4.1.2 Pump, suitable for a volume flow of approximately 2 l/min or 10 l/min under the conditions of the sampling, recommended sampling volume of approximately 2.88 m^3 to 14.4 m^3 in 24 h.

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

4.4.1.4 ODS solid phase disk, 47 mm in diameter.

4.4.1.5 SDB copolymer cartridge.

4.4.1.6 Sampler holder, parts of the holder for the solid phase disk or cartridge that contact the sampler should comprise Teflon®.

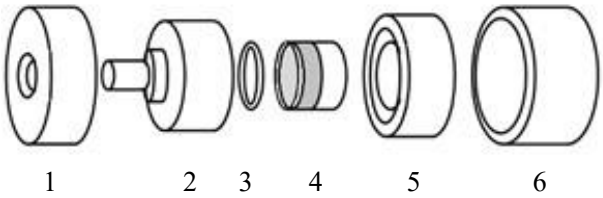
4.4.1.7 Glass centrifuge tube, 10 ml.

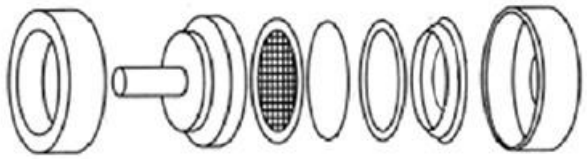
4.4.1.8 Laboratory sampling facilities, hygrometer, thermometer, barometer.

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

4.4.1.10 Internal standards, suitable are, e.g. the ring-deuterated compounds D4-DMP, D4-DEP, D4-DBP, D4-BBP, D4-DEHP, D4-DOP as well as the non-deuterated diallyl phthalate (DAlP); see Clause 5 and Table 3.

4.4.1.13 GC-MS, gas chromatographic (GC) system, fitted with a mass spectrometric (MS) detector.





Key

1 Pump side cap (made of aluminium)
2 Screen holder (made of Teflon®)
3 Support screen (made of Teflon®)
4 Solid phase disc
5 O-ring (made of Teflon®)
6 Solid phase disc retainer (made of Teflon®)
7 Air sampling side cap (made of aluminium)

Figure X — Scheme of holder for solid phase disk

Key

1 Pump side cap (made of aluminium)
2 Cartridge holder (made of Teflon®)

3 O-ring
4 SDB copolymer cartridge
5 Cartridge retainer (made of Teflon®)
6 Air sampling side cap (made of aluminium)

Figure X — Scheme of cartridge holder

4.4.2 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 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 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.

Furthermore, record the weather conditions at the time of measurement (such as air temperature, humidity and pressure) and the sampling details (such as start and end time of air sampling and volume of air sampled).

NOTE 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.

4.4.3 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.

5 Calibration

5.1 General

Phthalates present in indoor environments tend to undergo gas-particle-partitioning which is mainly characterized by the vapour pressure of the individual compound. Phtalates 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 B and Annex C, respectively. Table 2 gives an overview for a range of phthalates and their occurrence in air samples or in house dust as well as wipe samples.

Table 2 — Ascertainable phthalates in the various media

[Table 2 is omitted]

A calibration shall be performed in order to specify the concentration and working range to be determined, respectively. A multiple calibration (at least a 5-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 3-point calibration) shall be performed for the validation of the calibration function.

The ring-deuterated compounds listed in 4.2.2 as well as the non-deuterated diallyl phthalate (DAIP) are suitable as internal standards (based on ISO 18856).

5.2 Calibration of the thermal desorption method

A minimum 5-point thermal desorption GC-MS calibration shall be performed by desorbing a blank tube and preparing standard tubes at 4 or more different levels covering the work range. Methanol is used as solvent. A detailed example for a calibration procedure is given in Annex D.

5.3 Calibration of the solvent extraction method

A minimum 5-point solvent extraction GC-MS calibration shall be performed by desorbing a blank tube and preparing standard tubes at 4 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 E.

6 Identification and quantification

6.1 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, e.g. 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)

[Table 3 is omitted]

When DAIP is used as 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) [17][18][19] (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 [17]. Two different approaches can be attempted to identify the mixtures and to quantify them by approximation:

[Figure 3 is omitted]

a) Mass trace m/z = 149

b) Mass trace m/z = 307

Key

X retention time

Y strength of the signal

NOTE Source: personal communication R. Nagorka.

Figure 3 — Superimposed GC-MS chromatograms of a DiNP standard and a DiDP standard

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 (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.

The selected quantification method shall be recorded in the test report. Yet, another problem is that the suppliers of analytical standards are far from covering the band width of the commercially used semivolatile phthalates. More importantly, these analytical standards can have a substantially different composition as exemplified 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.

[Figure 4 is omitted]

a) Producer A

b) Producer B

NOTE Source: personal communication R. Nagorka.

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

Figure 5 shows a typical chromatogram of an air sample with a laboratory blank value and calibration exemplified by a Florisil®[2)] processing.

[Figure 5 is omitted]

a) Chromatogram of a laboratory blank value from a Florisil®2) tube spiked with the IS and concentrated. IS (DAlP): 17,02 min, DiBP: 19,22 min, DBP: 20,85 min, DEHP: 29,65 min

b) Chromatogram of a calibration standard of 1 mg/l 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) Chromatogram of a processed air sample. 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

7 Establishment of calibration curves and calculation of the analyte mass

7.1 Establishment of calibration curves

A calibration curve is established by using calibration solutions. The calibration procedure is described in Annex D for the thermal desorption method and in Annex E 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 parameters s_a, s_b, r, and $s_{y,x}$

where

s_a is the standard deviation of the intercept;

s_b is the standard deviation of the slope;

r is the linear correlation coefficient;

$s_{y.x}$ is the standard deviation of the regression (standard deviation of the estimate);

n denotes the number of measurement points.

7.2 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, the rearrangement of Formula (2) gives:

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

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

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

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

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

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 zero hypothesis H_0: a=-α (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 ˆt-value is then compared with the tabulated t-value: $t_{tab} = t_{95\ \%,n-2}$ (see Table 4).

If the calculated ˆt-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

[Table 4 is omitted]

8 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/m³;

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

V_A is the sampling volume in m³.

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/m³;

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

V_A is the sampling volume in m³ under sampling conditions.

9 Performance characteristics

9.1 Detection limit

The analytical detection limit (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.

9.2 Quantification limit and problems related to the blank values

The analytical quantification limit (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 are generally dependent 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 10.1). 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 7 and Clause 8 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 average laboratory blank value and background value (ambient air) during indoor air sampling by means of Tenax® TA[1)] tubes

[Table 5 is omitted]

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

Table X — Blank values of phthalates in each adsorbent (n=3; ng ± s.d.)

Analyte	ODS disk A	ODS disk B	SDB cartridge
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: D_4-DBP, D_4-BBP, D_4-DEHP			

9.3 Reproducibility standard deviation and repeatability standard deviation

A round robin test was performed for validation of the two analytical methods for indoor air described in this document [5]. The samples for the round robin test consisted of:

a) a solution containing four phthalates for spiking the Tenax®[1] thermal desorption tubes, and/or
b) a Florisil®[2] adsorption tube spiked with four phthalates.

The thermal desorption tube was analysed according to 4.2 and the Florisil®[2] adsorption tube was analysed according to 4.3. 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 analysis of the round robin test with the respective reference value, average value, relative standard deviation and median

[Table 6 is omitted]

A round robin 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 C.2.

Table 7 — Results from a round robin test for phthalate analysis in a solution [2]

[Table 7 is omitted]

10 Quality assurance

10.1 Method verification and determination of blanks

Due to the ubiquitous distribution especially of the plasticizers DiBP, DBP and 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, e.g. a control chart in order to identify blank value changes. Problems to determine blank values are discussed in Annex H.

10.1.1 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.

10.1.2 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.

10.2 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, polytetrafluoroethylene (PTFE) droppers (e.g. Burky Multipette), storage of the injection needles in solvents free of blank values, septum-free injection (e.g. Merlin Microseal).

10.3 Documents

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

11 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 10.

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 6.1.

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]. 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 %. Soft 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, baby articles, children's toys, 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 are 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 in house dust by means of the analytical methods specified by this document.

DEHP has 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. DEHP is utilized to approximately 97 % as plasticizer in PVC. Impacts on fertility, reproduction and offspring development have been proven for DEHP, and for BBP and DBP as well in experimental studies on animals with the result that these three phthalates have been classified according to EU Directive 67/548/EEC as reproduction toxic (reproduction endangering) and hence as hazardous substances.

DiNP and DiDP are isomer mixtures, potentially also containing common isomers. DiNP is a mixture from esters of the o-phthalic acid with C_8-C_{10}- alcohols (C_9-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 C_9-C_{11}-alcohols (C_{10}-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. Their common share of the plasticizer consumption amounted to 58 % in 2004. This corresponds to 580 000 t.

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

In 2004, the BBP consumption in Europe was almost 195 00 t. Almost 60 % are used as plasticizers of PVC. About 40 % are utilized in other polymers, e.g. in sealants on polysulfide, polyamide and acryl base, as well as in adhesives, dyes and varnishes.

Almost 260 00 t DBP were produced in Europe in 1998. Approximately 30 % of DBP goes into the production of dyes, dispersions, varnishes and adhesives. In addition, DBP as well as DEP is contained in some medicine capsules. Cosmetics continue to contain both DMP and DEP.

The phthalates DBP, DiBP, DEHP are contained in garbage and recycling products, especially in waste paper in the ppm range. The pollution of waste paper and the contamination risk related shall be considered during sampling and analysis.

Table A.2 provides examples for phthalate contents in indoor air samples from an exposure survey with no reference to a particular occasion [12]. Processing took place by thermal desorption according to 4.2.

Table A.1 — The most important phthalates and selected physical properties

[Table A.1 is omitted]

[Figure A.1 is omitted]

Key

R1 aliphatic substituents

R2 aromatic substituents

Figure A.1 — Basic structure of phthalates

A.2 Release and environmental behavior

Table A.2 — Phthalate contents in indoor air samples in µg/m³ (*n* = 34); limit of quantification LOQ always 0,01 µg/m³, LOQ for DEHP 0,06 µg/m³

[Table A.2 is omitted]

Phthalates and other plasticizers are distributed only physically within the polymer matrix, and are not chemically bound. 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 semivolatile organic compounds (SVOC). Hence,they possess a specific potential to adsorb on particles in the air. Phthalates can therefore be found in interior spaces not only in indoor air [6][7][8][12][13][14] but also in house dust [7][8][9][10][14]. 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 [15]. 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. 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

The phthalates DEHP, BBP and DBP in toys and baby articles are by now forbidden throughout the European Union (Directive 2005/84/EU dated 14.12.2005). Furthermore, the application of DiNP, DiDP and DOP is prohibited in toys and baby articles that can be taken in the mouth. 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 polyethylene (PE) or polypropylene (PP) are generally free of plasticizers.

Annex B
(informative)

Screening phthalates in solvent wipe tests

B.1 Measurement strategy

The reason for investigations by solvent wipe samples can be, e.g.:

- screening examinations towards localization and identification of sources (see Figure B.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 1000 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 B.1).

[Figure B.1 is omitted]

Key
X retention time
Y strength of the signal

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

B.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.

B.3 Sampling and conditioning of the wipe sample of solvents

B.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 by the use of cleaned tweezers or metal pliers (see Figure B.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 B.2 is omitted]

Figure B.2 — Sampling of solvent wipe samples

Table B.1 — Phthalate contents in µg/m2 in solvent wipe samples form a windowpane (450 cm^2) during a measurement with no reference to a particular occasion

[Table B.1 is omitted]

B.3.2 Extraction and analysis (Practical example)

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 a 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 here to 1,0 mg/l. The concentrated extracts are analysed.

The practical example described here is suitable for a concentration range from 5 µg/m^2 to 1000 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.

B.4 Computation of the result

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

$$m = v_{PA} / b \qquad \text{(B.1)}$$

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, are calculated by Formula (B.2):

$$c_A = m / A \qquad \text{(B.2)}$$

where

c_A is the concentration of the investigated compound on the sampled surface in µg/m^2;

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

A is the sampled surface in m^2.

Annex C
(informative)

Screening phthalates in house dust

C.1 Definition and 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 may 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 (for example, fibres from clothing and carpets), inorganic materials such as sand, loam and clay, food crumbs and soot particles and dusts from combustion processes (smoke) and 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 % [21]. 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 may 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.

C.2 Measurement strategy

The reason for the investigation of house dust samples can be, e.g.:

- 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 semivolatile 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 might 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 10 shall thereby be particularly observed. For these reasons, the following preparation specification and the practical example are purely indicative (see Table C.1). Table C.1 provides examples for typical phthalate concentrations in unsieved dust samples [14]. 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.

C.3 Apparatus, operating materials and chemicals for sampling and analyses

C.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 (accuracy ± 0,1 mg), storing in the transport vessel.

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

C.3.3 Ground glass tubes, for dust sample intake for further extraction.

C.3.4 Solvent, e.g. tertiary butyl methyl ether (TBME) or toluene, free of blank values, for residue analysis.

C.3.5 Ultrasonic bath.

C.3.6 Centrifuge.

C.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 of aluminium foil that can be examined after a defined time interval (e.g. one week).

C.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 m2 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 I).

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 e.g. by the vacuum cleaner is possible. For this reason, the examination of sent vacuum cleaner bags regarding phthalates and other plasticizers is not reasonable.

C.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.

C.7 Sample preparation

The exposed glass fibre filter is re-weighted (accuracy ± 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 [7][9]. 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 (Clause 6). A typical concentration of the internal standard in the extract is, e.g. 1 mg/l.

The phthalates of lower concentration are determined from this raw extract by means of GC-MS analyses according to Clause 6. For example, DEPH 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 C.1 — Phthalate concentration in unsieved dust samples in mg/kg

[Table C.1 is omitted]

C.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 C.2 — Results from a round robin test for phthalate analysis in a non-spiked ≤63 µm-mixed dust sample

[Table C.2 is omitted]

Annex D

(informative)

Practical example for the calibration of the thermal desorption method

D.1 Solutions of the internal standard

The solution is prepared as follows:

10 mg of one or more internal standards are solved in methanol and filled up to 10 ml. Afterwards, a further 1:50 dilution takes place. This procedure results in a solution with concentration 20 mg/l (= 20 µg/ml = 20 ng/µl). Commercially available solutions with the same concentration can be used as an alternative.

D.2 Stock solutions

The single compounds for preparation of stock solutions I recommended for air samples are shown in Table 2.

D.2.1 Stock solution I of the phthalates

The stock solutions I of the phthalates are prepared as follows:
50 mg of each of the above-mentioned phthalates (200 0 ng/µl) are solved in 25 ml methanol.

D.2.2 Stock solution II of the phthalates

Stock solution I is diluted with methanol by the factor of 8 (250 ng/µl).
1 µl of stock solution II and of the internal standard solution, respectively, are injected into a Tenax® TA[1)] tube for determination of the phthalate response factors.

D.3 Calibration solutions

The calibration solutions are prepared according to the scheme in Table D.1.

Methanol has been proven successful as solvent. The use of other solvents is possible. As long as other volatile organic compounds are determined with the same measurement system, possible contaminations by the used solvent (e.g. toluene, acetone) shall be considered.

Table D.1 — Scheme for preparation of the calibration solutions for the thermal desorption method

[Table D.1 is omitted]

Annex E
(informative)

Practical example for the calibration of the solvent extraction method using Florisil®[2)]

E.1 Solutions of the internal standard

The solution is prepared as follows:
10 mg of one or more internal standards are solved in TBME or toluene and are filled up to 100 ml. The result is a solution with concentration 100 mg/l (= 100 µg/ml = 100 ng/µl). Commercially available solutions with the same concentration can be used as alternative.

E.2 Stock solutions

The single compounds for preparation of stock solutions I recommended for the various media are shown in Table 2.

E.2.1 Stock solution I of the phthalates

The stock solutions I of the phthalates are prepared as follows:
50 mg of each of the above-mentioned phthalates are solved and filled up to 100 ml. The resulting solutions are each with concentrations of 500 mg/l.

E.2.2 Stock solution II of the phthalates

2 ml of each of the stock solutions I are pipetted together in a 100 ml graduated flask and filled up to 100 ml. The result is a solution with concentrations of the respective phthalates of 10 mg/l.

Due to the chromatographic overlapping of the peaks of the isomer mixtures of DiNP, DiDP and DiUP (see Clause 6) for the analysis of house dust and wipe samples, it is recommended not to add the solutions of these phthalates to the combined standard solution II, but to prepare for each of these three phthalates a separate stock solution IIa (DiNP), stock solution IIb (DiDP), stock solution IIc (DiUP).

E.3 Calibration solutions

The calibration solutions are prepared according to the scheme in Table E.1.

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.

Table E.1 — Scheme for preparation of calibration solutions for the solvent extraction method

[Table E.1 is omitted]

Annex F
(informative)

Practical example for the gas chromatography with thermal desorption

The settings and parameters of the thermal desorption unit and the temperature of the cryofocusing unit shall be adjusted in such manner as to enable determination of the relatively semivolatile DEPH in addition to the analytics of the volatile phthalates. Within the entire sample injection system (transfer line, connecting lines, etc.), it shall be guaranteed by means of inertness of the sampling path, sufficiently high temperature and linear velocity that the phthalates subject to examination (especially the higher boiling phthalates) are entirely transferred to the GC column and memory effects are avoided. The usual adjustments of the analytics of volatile organic compounds are not suitable for this purpose. Technical details are given in Annex F for the gas chromatography with thermal desorption and in Annex G for the gas chromatography following solvent extraction.

Thermal desorption unit	with back flush circuit
Injector	with an empty deactivated glass insert
Temperature programme TDS furnace	35 °C – 60 °C/min – 280 °C (10 min)
Injector (cryofocusing)	40 °C – 12 °C/s – 340 °C (10 min)

NOTE A reversal of the flow direction of the carrier gas is achieved with the optional back flush function of the thermal desorption unit during the opening of the TDS furnace for the tube exchange, which prevents penetration of ambient air containing phthalates into the injector system. The blank values originating during sample injection can thus be reduced.

Gas chromatograph (GC)	High resolution gas chromatographic system
Capillary column	DB-5MS, length 30 m, internal diameter 0,25 mm, film thickness 0,25 µm or another suitable capillary column of limited polarity, e.g. DB 5, HP5 MS, DB 170 3

Carrier gas	Helium 5.0
Temperature programme (GC)	35 °C (1 min) – 20 °C/min – 200 °C – 5 °C/min – 260 °C –20 °C/min – 340 °C (4 min), total time: 29 min
Mass spectrometer (MS)	quadrupole mass spectrometer
Transferline (MS)	320 °C

Annex G

(informative)

Practical example for the gas chromatography following solvent extraction

Gas chromatograph	High resolution gas chromatographic system
Capillary column	DB-5MS, length 30 m, internal diameter 0,25 mm, film thickness 0,25 µm or another suitable capillary column with low polarity, e.g. DB 5, HP5 MS, DB 170 3
Injector	Split/splitless injector with septum-free injection head
Temperature	280 ° C
Injection volume	1 µl, splitless injection
Temperature programme	90 °C (1 min) – 6 °C/min – 280 °C (7 min); total time: 40 min
Carrier gas	Helium 5,0
Mass spectrometer (MS)	Transmission quadrupole mass spectrometer
Transferline (MS)	290 °C

Annex H
(informative)

Problems related to the blank values

H.1 Practical example for the Tenax® TA[1)] method

Table 5 shows both the mean values of laboratory blank values as well as background values. If no blank values have been measurable, Table 5 will always indicate the quantification limit (signal-to-noise ratio 9:1 for the mass trace used for quantification) (<LOQ).

For determination of the laboratory blank values, eight conditioned Tenax® TA[1)] tubes were spiked with 1 µl internal standard solution each and subsequently analysed. For determination of the background value during a 24-h sampling session of indoor air (sampling volume 70 l), the ambient air was sucked one time simultaneously and at equal volumetric flow (50 ml/min) through two Tenax® TA[1)] tubes connected together in series.

H.2 Practical example for the Florisil®[2)] method

Due to the heated Florisil®[2)] used for sampling (see 4.3.2), the adsorption tubes filled with Florisil®2) are to a large extent phthalate-free if an elaborate operation method is employed. Special attention is thus assigned to the purity of the solvent used for extraction with this method. It should be taken into account that during sample processing an increase of the concentration of the sample extracts by a factor of 25 takes place. Hence, it is essential prior to application to examine the solvent provided for the extraction of Florisil®[2)] with regard to its phthalate content. Since the lower limit of the working range is 0,05 mg/l (see 4.3.4), the content of the investigated phthalates in the solvent, whose concentration is increased by the factor of 25, shall be at least smaller than this concentration. That is, the concentration of the individual investigated phthalates in the not yet concentrated solvent shall not exceed approximately 1 µg/l to 2 µg/l.

Based on experience, the phthalates content in the currently commercially available solvents is often significantly higher. Solvent cleaning by means of multiple (if required) distillation is a good aid. Hence, if an elaborate operation method is applied, it is possible to achieve blank value concentrations that are clearly below the concentrations of 0,05 mg/l in the concentrated extract. For a comparison,

reference should be made to the chromatogram of the laboratory blank value in Figure 5 a). The signals of DiBP, DBP and DEHP identifiable in addition to the peak of the internal standard correspond here to a concentration of approximately 0,02 mg/l in the concentrated extract. For a sampling volume of 1 m^3, a laboratory blank value of 0,02 mg/l DEHP would correspond to 0,04 µg/m^3.

Annex X
(informative)

Interlaboratory validation study for ODS filter method and SDB cartridge method

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

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 X.1 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 within-laboratory reproducibility, relative standard deviations (RSD_r), of DBP were 2.1–13.6% for ODS filters and 2.0–7.5% for SDB cartridges. RSD_r of DEHP were 4.0–20.7% for ODS filters and 0.8–8.1% 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 (Table X.1).

Table X.1. 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 I

(informative)

Example of a sampling protocol

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