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**Safety of toys —**

Part 6:

**Certain phthalate esters in toys and  
children's products**

*Sécurité des jouets —*

*Partie 6: Jouets et produits pour enfants — Dosage de certains  
phtalates d'esters dans les jouets et produits pour enfants*





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# Contents

Page

|  |           |
|--|-----------|
| <b>Foreword</b> .....  | <b>iv</b> |
| <b>Introduction</b> .....                                      | <b>v</b>  |
| <b>1 Scope</b> .....   | <b>1</b>  |
| <b>2 Terms and definitions</b> .....                           | <b>1</b>  |
| <b>3 Principle</b> .....                                       | <b>2</b>  |
| <b>4 Reagents</b> .....  | <b>2</b>  |
| <b>5 Apparatus</b> .....                                       | <b>3</b>  |
| <b>6 Selection of test portion</b> .....                       | <b>4</b>  |
| <b>7 Procedure</b> .....                                       | <b>4</b>  |
| 7.1 Sample weighing.....                                       | 4         |
| 7.2 Extraction.....  | 4         |
| 7.3 Sample solution for analysis.....                          | 5         |
| 7.4 Determination.....   | 5         |
| <b>8 Calculation</b> .....                                     | <b>8</b>  |
| 8.1 External Standard (ES) calculation.....                    | 8         |
| 8.2 Internal Standard (IS) calculation.....                    | 8         |
| <b>9 Quality control</b> .....                                 | <b>9</b>  |
| 9.1 Limit of quantification (LOQ).....                         | 9         |
| 9.2 Method blank.....  | 9         |
| 9.3 Recovery.....  | 9         |
| 9.4 Calibration check.....                                     | 9         |
| <b>10 Precision</b> .....                                      | <b>9</b>  |
| <b>11 Test report</b> .....                                    | <b>9</b>  |
| <b>Annex A (normative) Phthalate esters</b> .....              | <b>10</b> |
| <b>Annex B (informative) Extraction apparatus</b> .....        | <b>11</b> |
| <b>Annex C (informative) Example of GC-MS conditions</b> ..... | <b>13</b> |
| <b>Annex D (informative) Precision of the method</b> .....     | <b>16</b> |
| <b>Annex E (informative) Composite test</b> .....              | <b>20</b> |
| <b>Annex F (informative) Background and rationale</b> .....    | <b>24</b> |
| <b>Bibliography</b> .....                                      | <b>27</b> |

## 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](http://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](http://www.iso.org/patents)).

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

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

The committee responsible for this document is Technical Committee ISO/TC 181, *Safety of toys*.

ISO 8124 consists of the following parts, under the general title *Safety of toys*:

- *Part 1: Safety aspects related to mechanical and physical properties*
- *Part 2: Flammability*
- *Part 3: Migration of certain elements*
- *Part 4: Swings, slides and similar activity toys for indoor and outdoor family domestic use*
- *Part 6: Toys and children's products — Determination of certain phthalate esters in toys and children's products*

The following parts are under preparation:

- *Part 5: Determination of total concentration of certain elements in toys*
- *Part 7: Finger paints — Requirements and test methods*
- *Part 8: Age determination guidelines*

## Introduction

This part of ISO 8124 is largely based upon the existing Chinese national standard GB/T 22048-2008. Relevant standards of some countries and regions are referred to as well.

Considering the diversity of laws and regulations in different countries, this International Standard has not set out limits for phthalate esters. It is intended to be used as a method standard in conformity assessment. The user of this part of ISO 8124 is therefore advised to be aware of relevant national requirements.

Whereas in some countries, phthalate ester requirements for toys are also applicable to children products and whereas children product materials are generally similar to those of toys, this part of ISO 8124 whose scope covers various materials can be applicable to both toys and children products.

[Annex A](#) is normative and [Annex B](#), [Annex C](#), [Annex D](#), [Annex E](#), and [Annex F](#) are for information purposes only, but they are crucial and helpful for the correct interpretation of this part of ISO 8124.



# Safety of toys —

## Part 6:

# Certain phthalate esters in toys and children's products

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

**IMPORTANT** — It is absolutely essential that tests conducted in accordance with this International Standard be carried out by suitably trained staff.

## 1 Scope

This part of ISO 8124 specifies a method for the determination of di-*n*-butyl phthalate (DBP), benzyl butyl phthalate (BBP), *bis*-(2-ethylhexyl) phthalate (DEHP), di-*n*-octyl phthalate (DNOP), di-*iso*-nonyl phthalate (DINP), and di-*iso*-decyl phthalate (DIDP) (see [Annex A](#)) in toys and children's products.

This part of ISO 8124 is applicable to toys and children's products which are made of plastics, textiles, and coatings, etc. This International Standard has been validated for polyvinylchloride (PVC) plastics, polyurethane (PU) plastics, and some representative paint coatings (see [Annex D](#)). It might also be applicable to other phthalate esters and other products materials provided that adequate validation is demonstrated.

## 2 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

### 2.1

#### **laboratory sample**

toy or children's product in the form in which it is marketed or intended to be marketed

### 2.2

#### **base material**

material upon which coatings can be formed or deposited

### 2.3

#### **coating**

all layers of material formed or deposited on the base material of toys or children's products, including paints, varnishes, lacquers, inks, polymers, or other substances of a similar nature, whether they contain metallic particles or not, no matter how they have been applied to the toy or children's product, and which can be removed by scraping with a sharp blade

### 2.4

#### **scraping**

mechanical removal of coatings down to but not including the base material

### 2.5

#### **test portion**

portion of homogeneous material taken from a corresponding part of the laboratory sample for analysis

2.6

**composite test portion**

mixed test portion formed by physically mixing several test portions of similar material

Note 1 to entry: This term excludes the compositing of dissimilar materials, for example, compositing textiles and paint coatings are not permitted.

2.7

**composite test**

test performed on the composite test portion

2.8

**limit of quantification**

**LOQ**

lowest amount of the analyte in the sample that can be quantitatively determined with defined precision under the stated experimental conditions

2.9

**method blank**

aliquot of solvents that is treated exactly as a sample including exposure to glassware, apparatus, and conditions used for a particular test, but with no added sample

Note 1 to entry: Method blank data are used to assess contamination from the laboratory environment.

### 3 Principle

The test portion of a toy or children's product is mechanically cut into small pieces which are then extracted through a Soxhlet extractor or solvent extractor (see [Annex B](#)) with dichloromethane; after which, the phthalate esters in the extract are determined qualitatively and quantitatively by gas chromatograph-mass spectrometer (GC-MS).

### 4 Reagents

**4.1 Dichloromethane**, CAS No. 75-09-2, analytical grade or higher, free of phthalate esters.

**4.2 Phthalate reference substances**, DBP, BBP, DEHP, DNOP, DINP, and DIDP (see [Annex A](#)), minimum of 95 % purity.

**4.3 Stock solution**, 100 mg/l of DBP, BBP, DEHP, DNOP each, and 500 mg/l of DINP, DIDP each in dichloromethane ([4.1](#)).

Stock solution should be properly stored at 0 °C to 4 °C to prevent change of concentration. It is recommended to prepare the solution at least every three months.

**4.4 External Standard (ES) calibration solutions.**

A series of calibration standard solutions (of at least five equidistant calibrations in the range of 0,4 mg/l to 10 mg/l for DBP, BBP, DEHP, and DNOP, 2 mg/l to 50 mg/l for DINP and DIDP) is prepared by transferring 0,2 ml to 5 ml of the stock solution ([4.3](#)) to a 50 ml volumetric flask and making up to the mark with dichloromethane.

Calibration standard solutions should be properly stored at 0 °C to 4 °C to prevent change of concentration. It is recommended to prepare the solution at least monthly.



#### 4.5 Internal Standard (IS) calibration solutions.

**4.5.1 Internal reference substances**, benzyl benzoate (BB, CAS No.120-51-4) or di-*n*-amyl phthalate (DAP, CAS No.131-18-0) [also known as di-*n*-pentyl phthalate (DPP)], minimum of 95 % purity.

The internal reference substances should not be present in the test portion matrix. Other compounds such as isotopically labelled phthalates can be used as alternative internal reference substances.

**4.5.2 Internal stock solution**, 250 mg/l of BB or DAP or others, in dichloromethane.

IS solutions should be properly stored at 0 °C to 4 °C to prevent change of concentration. It is recommended to prepare these solutions at least every three months.

#### 4.5.3 Internal Standard calibration solutions.

A series of calibration standard solutions (of at least five equidistant calibrations in the range of 0,4 mg/l to 10 mg/l for DBP, BBP, DEHP and DNOP, 2 mg/l to 50 mg/l for DINP and DIDP) is prepared by transferring 0,2 ml to 5 ml of the stock solution (4.3) to a 50 ml volumetric flask and adding 2 ml of the IS stock solution (4.5.2) before making up to the mark with dichloromethane, each of the calibration standards containing 10 mg/l IS.

IS calibration solutions should be properly stored at 0 °C to 4 °C to prevent change of concentration. It is recommended to prepare these solutions at least monthly.

## 5 Apparatus

Phthalate esters are common contaminants which can affect the test result even at a low level of concentration. In order to prevent interference and cross-contamination, any type of plastic apparatus that could affect the analysis should be avoided, and glassware and equipment should be scrupulously cleaned before use.

**5.1 Normal laboratory glassware.**

**5.2 Gas chromatography-mass spectrometer (GC-MS)**, with a capillary column coupled to a mass spectrometric detector (electron ionization, EI) used for the analysis. See 7.4.1.

**5.3 Soxhlet extractor**, see [Figure B.1](#).

**5.4 Solvent extractor**, see [Figure B.2](#).

**5.5 Extraction thimble**, cellulose.

**5.6 Cotton wool**, for extraction thimble.

**5.7 Analytical balance**, capable of measuring to an accuracy of 0,001 g.

**5.8 Concentration apparatus**, for example, a rotary evaporator.

**5.9 Solid phase extraction (SPE) cartridge**, 1000 mg silica gel/6 ml tubes, or equivalent.

**5.10 Volumetric flasks**, of 5 ml, 10 ml, 25 ml, 50 ml, and 100 ml nominal capacity.

**5.11 Pipettes**, of 0,5 ml, 1 ml, 2 ml, 5 ml, and 10 ml nominal capacity.

**5.12 Polytetrafluoroethylene (PTFE) membrane filter**, of pore size 0,45 µm.

## 6 Selection of test portion

Use a scalpel or other appropriate cutting utensils to cut a representative portion from the laboratory sample into small pieces. For coatings, remove each different coating from the laboratory sample by scraping. Extra care shall be taken to minimize the inclusion of the base material. Each piece shall, in the uncompressed condition, have no dimension greater than 5 mm and be mixed uniformly.

A test portion of less than 10 mg from a single laboratory sample shall not be tested.

NOTE Different countries or regions might have different legislation requirements for the minimum sample mass.

Composite test can be used for screening. See [Annex E](#).

## 7 Procedure

### 7.1 Sample weighing

Weigh, to the nearest 1 mg, approximately 1 g of the test portion into an extraction thimble ([5.5](#)). If 1 g test portion cannot be obtained from a single laboratory sample, sampling as much as possible from more than one laboratory samples, but 0,1 g should be a minimum test portion.

### 7.2 Extraction

Two optional extraction methods are described in the following, and the laboratory can select the most suitable one at its discretion.

#### 7.2.1 Method A

Place the thimble with test portion into the 150-ml Soxhlet extractor ([5.3](#)). In order to prevent the sample from floating, add cotton wool ([5.6](#)) to the top of the thimble.

Add 120 ml of dichloromethane ([4.1](#)) into the 150-ml flask. Reflux for 6 h with no less than four reflux cycles per hour.

After cooling, reduce the volume of the dichloromethane to about 10 ml using a suitable concentration apparatus ([5.8](#)). Take care to avoid reduction to dryness.

When using a rotary evaporator, it is recommended that the temperature of the water bath is in the range of 40°C to 50°C with a constant pressure between 30 kPa and 45 kPa.

NOTE During the refluxing and concentration steps, careful temperature control is necessary in order to avoid loss of phthalate esters.

#### 7.2.2 Method B

Place the thimble with test portion into the solvent extractor ([5.4](#)). In order to prevent the sample from floating, add cotton wool ([5.6](#)) to the top of the thimble.

Add 80 ml of dichloromethane ([4.1](#)) into the receiver. Immerse for 1,5 h at about 80 °C and reflux for 1,5 h. At the end, concentrate the dichloromethane extract to about 10 ml.

NOTE During the refluxing and concentration steps, careful temperature control is necessary in order to avoid loss of phthalate esters.

### 7.3 Sample solution for analysis

Filter the solution (7.2.1 or 7.2.2), which is obtained after the dichloromethane extract has been treated according to the procedure specified in 7.3.1 or 7.3.2 where appropriate, with PTFE membrane filter (5.12) for GC-MS (5.2) analysis.

If necessary, e.g. when the concentrated extract exhibits turbidity, before the filtering above, purify the solution (7.2.1 or 7.2.2) with a pretreated SPE (5.9). Rinse the cartridge with 3 ml of dichloromethane three times and collect the eluate.

NOTE Pretreat the SPE cartridge with approximate 10 ml of dichloromethane before purification. Discard the effluent.

#### 7.3.1 For quantification by External Standard calibration

Transfer the extract or the eluate into a 25-ml volumetric flask and make up to the mark with dichloromethane.

NOTE The volume of the final solution can be adjusted according to the test specimen mass and concentration.

#### 7.3.2 For quantification by Internal Standard calibration

Transfer the extract or the eluate and 1 ml of the IS stock solution (4.5.2) into a 25-ml volumetric flask and make up to the mark with dichloromethane. The final solution contains 10 mg/l of IS.

NOTE The volume of both IS solution and the final solution can be adjusted according to the test specimen mass and concentration. The concentration of IS in the final test solution should be the same as that of standard calibration solutions (4.5.3).

### 7.4 Determination

#### 7.4.1 GC-MS conditions

Due to the variation of instruments in different laboratories, no universal applicable instructions can be provided for chromatographic analysis. The following general GC-MS operating conditions have been found suitable, and an example of operating conditions is given in Annex C.

- a) Column: capillary column, non-polar (phenylarylene polymer equivalent to 5 % phenylmethyl polysiloxane), or equivalent.
- b) Oven temperature program.
- c) Carrier gas: helium or hydrogen, constant flow.
- d) Injector system: split or splitless.
- e) Ionization method: electron ionization (EI), 70 eV.
- f) Determination: Identification by full scan mode, quantification by selected ion monitoring (SIM) mode simultaneously.

#### 7.4.2 Identification

Identify the compound by matching both retention times and relative intensities of the diagnostic ions of test solution and standard solution.

The target compound is considered to be identified in the test solution if the following criteria are fulfilled:

- a) the ratio of the retention time of the analyte to that of the IS, i.e. the relative retention time of the analyte, corresponds to that of the calibration solution at a tolerance of  $\pm 0,5$  %;

- b) the diagnostic ions (see [Table C.1](#)) are present at the substance-specific retention time;
- c) the relative intensities of the diagnostic ions (refer to [Table C.1](#)) in full scan, expressed as a percentage of the intensity of the most intense ion, shall correspond to those of the calibration standard at comparable concentrations, measured under the same conditions, within the tolerances in [Table 1](#).

**Table 1 — Maximum permitted tolerances for relative ion intensities using a range of mass spectrometric techniques**

| Relative intensity (% of base peak) | Maximum permitted tolerances (relative intensity) |
|-------------------------------------|---|
| >50 %                               | ±10 %   |
| >20 % to 50 %                       | ±15 %   |
| >10 % to 20 %                       | ±20 %   |
| ≤10 %                               | ±50 %   |

NOTE Some isomers of DINP or DIDP can interfere with the identification of DINP or DIDP. For example, Di-propylheptyl phthalate (DPHP, CAS No. 53306-54-0) is one of the isomers of DIDP, it is theoretically difficult to separate DPHP from DIDP, but they can be recognized through the feature of peak, retention time, and abundance ratio.

### 7.4.3 Calibration

#### 7.4.3.1 General

Two optional calibration methods, External Standard (ES) ([7.4.3.2](#)) and Internal Standard (IS) ([7.4.3.3](#)), are described in the following. Either ES or IS can be used for calibration. Laboratories can choose the suitable calibration method according to their best practice (see [Annex F](#)).

A calibration curve shall be established for either method. A minimum of five equidistant calibration standard solutions ([4.4](#) or [4.5.3](#)) shall be prepared. Quantification is based on the measurement of the peak area. The correlation coefficient ( $r$ ), of each calibration curve shall be at least 0,995.

The isomers of DINP and DIDP shall be quantified using baseline integration.

NOTE 1 DINP and DIDP are available as different isomeric mixtures under different CAS numbers. Since the chromatogram of the GC-MS is different for each mixture, the laboratory should choose the reference substance that matches as closely as possible the isomeric ratio to the phthalates in the test portion and report the CAS No. of the reference material used in accordance with 11 f).

NOTE 2 Due to the existence of inseparable isomers, the peaks of DNOP, DINP and DIDP are partially overlapped. The interference of this can be minimized effectively when  $m/z = 279$  (DNOP),  $m/z = 293$  (DINP), and  $m/z = 307$  (DIDP) are selected as quantification ions respectively.

#### 7.4.3.2 External Standard (ES) calibration

Integrate the peak areas of the target quantification ions (see [Table C.1](#)) in the chromatograph by ES calibration.

To establish the calibration curve, the response  $A$  is plotted against the concentration  $C$  in accordance with Formula (1):

$$A = (a_1 \times C) + b_1 \quad (1)$$

where

$A$  is the peak area or sum of peak areas of the individual phthalate in the calibration solution;

$a_1$  is the slope of the calibration curve;

$C$  is the concentration of the individual phthalate in the calibration solution, in mg/l;

$b_1$  is the ordinate intercept of the calibration curve.

### 7.4.3.3 Internal Standard (IS) calibration

Integrate the peak areas of the target quantification ions (see [Table C.1](#)) in the chromatograph by IS calibration.

To establish the calibration curve, the response  $A/A_{IS}$  is plotted against the concentration ratio  $C/C_{IS}$  in accordance with Formula (2):

$$\frac{A}{A_{IS}} = \left( a_2 \times \frac{C}{C_{IS}} \right) + b_2 \quad (2)$$

where

$A$  is the peak area or sum of peak areas of the individual phthalate in the calibration solution;

$A_{IS}$  is the peak area of the IS in the calibration solution;

$a_2$  is the slope of the calibration curve;

$C$  is the concentration of the individual phthalate in the calibration solution, in mg/l;

$C_{IS}$  is the concentration of the IS in the calibration solution in mg/l;

$b_2$  is the ordinate intercept of the calibration curve.

NOTE It is common practice to set the IS concentration ( $C_{IS}$ ) to 1 mg/l for the IS methods when the amount and concentration of IS added to the test portion and calibrants prior to injection are the same.

## 8 Calculation

### 8.1 External Standard (ES) calculation

Calculate the mass fraction of the individual phthalate in the test portion by using Formula (3) after solving Formula (1):

$$w_S = \frac{(A - b_1)}{a_1} \times \frac{V}{m} \times D \times \frac{1}{10\,000} \quad (3)$$

where

- $w_S$  is the concentration of the individual phthalate found in the test portion, in %;
- $A$  is the peak area or sum of peak areas of the individual phthalate in the test solution;
- $b_1$  is the ordinate intercept of the calibration curve, obtained from Formula (1);
- $a_1$  is the slope of the calibration curve, obtained from Formula (1);
- $V$  is the volume of the final solution, in ml;
- $m$  is the mass of the test portion, in g;
- $D$  is the dilution factor.

The result shall be expressed in percentage by weight (%) and reported to three significant figures.

The response value of the tested phthalate in the calibration solution and test solution should be within the instrument detection linear range. If necessary, further diluted solution with dichloromethane should be prepared.

### 8.2 Internal Standard (IS) calculation

Calculate the mass fraction of the individual phthalate in the test portion by using Formula (4) after solving Formula (2):

$$w_S = \left( \frac{A}{A_{IS}} - b_2 \right) \times \frac{C_{IS}}{a_2} \times \frac{V}{m} \times D \times \frac{1}{10\,000} \quad (4)$$

where

- $w_S$  is the concentration of the individual phthalate found in the test portion, in %;
- $A$  is the peak area or sum of peak areas of the individual phthalate in the test solution;
- $A_{IS}$  is the peak area of the IS in the test solution;
- $b_2$  is the ordinate intercept of the calibration curve, obtained from Formula (2);
- $C_{IS}$  is the concentration of the IS, in the calibration solution, in mg/l;
- $a_2$  is the slope of the calibration curve, obtained from Formula (2);
- $V$  is the volume of the final solution, in ml;
- $m$  is the mass of the test portion, in g;
- $D$  is the dilution factor.

The result shall be expressed in percentage by weight (%) and reported to three significant figures.

The response value of the tested phthalate in the calibration solution and test solution should be within the instrument detection linear range. If necessary, further diluted solution with dichloromethane should be prepared.

## 9 Quality control

### 9.1 Limit of quantification (LOQ)

LOQ for DBP, BBP, DEHP, DNOP: 0,001 %;

LOQ for DINP, DIDP: 0,005 %.

### 9.2 Method blank

A method blank (2.9) shall be prepared for each batch of samples by following the steps in [Clause 7](#) and [8](#) but without using a sample. The method blank can be used to assess the contamination in the test process, which should be less than the LOQ (9.1).

### 9.3 Recovery

One spiked blank per batch shall be prepared by adding 1 ml of stock solution (4.3) in the method blank; then treat it in the same way as described in [Clause 7](#) and [8](#). The recovery of each phthalate should be 80 % to 120 % of the expected value.

### 9.4 Calibration check

A mid-point calibration check solution without extraction should be re-injected after every 20 samples and at the end of the run to demonstrate the stability of the GC-MS. The deviation of each phthalate should be within 15 % of the expected value.

## 10 Precision

The precision of this part of ISO 8124 is shown in [Annex D](#).

## 11 Test report

The test report shall contain at least the following information:

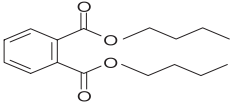
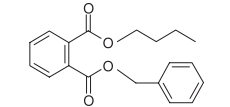
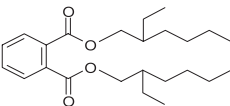
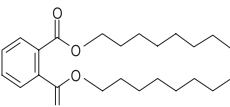
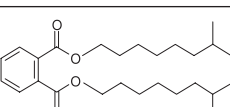
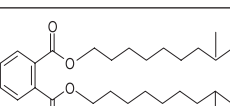
- a) a reference to this part of ISO 8124 (i.e. ISO 8124-6:2014);
- b) a complete identification of the sample;
- c) a reference to the extraction procedure used (method A or method B);
- d) a reference to the calculation method used (External Standard or Internal Standard);
- e) the results of the individual quantitative phthalate analysis, expressed as percentage by weight (%);
- f) the CAS No. of the used DINP or DIDP reference substance;
- g) any deviations from the procedure specified;
- h) any unusual features observed during the test;
- i) date of the test.



## Annex A (normative)

### Phthalate esters

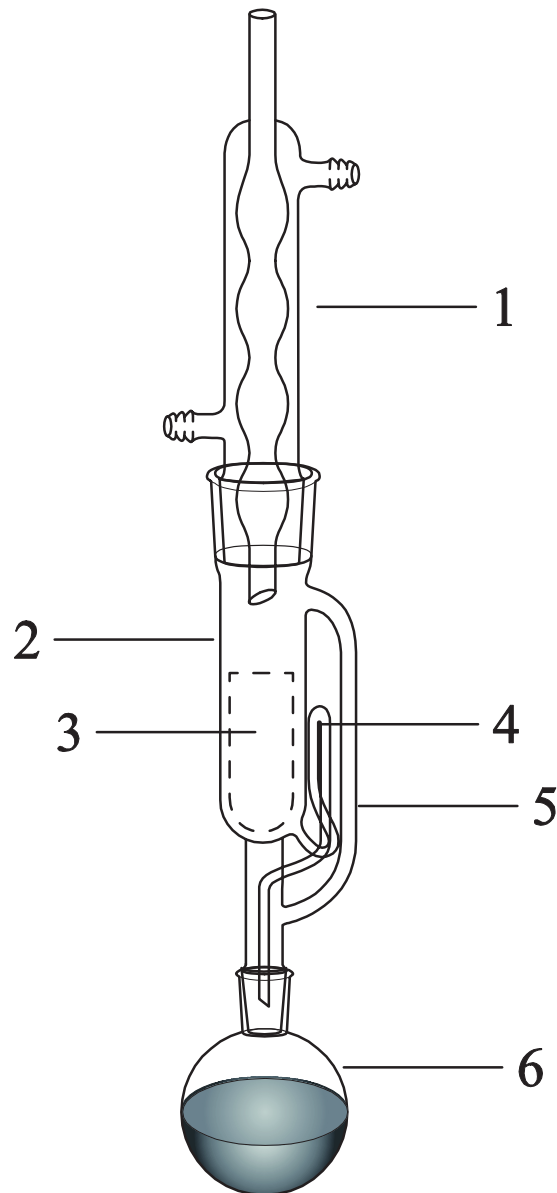
Table A.1 — Phthalate esters

| No.          | Phthalate esters (Initialism)   | CAS No.                 | Structure formula <sup>a</sup>   | Molecular formula                              |
|--------------|---|-------------------------|--|--|
| 1            | Di- <i>n</i> -butyl phthalate (DBP)   | 84-74-2                 |    | C <sub>16</sub> H <sub>22</sub> O <sub>4</sub> |
| 2            | Benzyl butyl phthalate (BBP)  | 85-68-7                 |    | C <sub>19</sub> H <sub>20</sub> O <sub>4</sub> |
| 3            | <i>Bis</i> -(2-ethylhexyl) phthalate (DEHP)   | 117-81-7                |    | C <sub>24</sub> H <sub>38</sub> O <sub>4</sub> |
| 4            | Di- <i>n</i> -octyl phthalate (DNOP)  | 117-84-0                |  | C <sub>24</sub> H <sub>38</sub> O <sub>4</sub> |
| 5            | Di- <i>iso</i> -nonyl phthalate (DINP)  | 28553-12-0 <sup>b</sup> |  | C <sub>26</sub> H <sub>42</sub> O <sub>4</sub> |
|              |   | 68515-48-0 <sup>c</sup> |  |  |
| 6            | Di- <i>iso</i> -decyl phthalate (DIDP)  | 26761-40-0 <sup>d</sup> |  | C <sub>28</sub> H <sub>46</sub> O <sub>4</sub> |
|              |   | 68515-49-1 <sup>e</sup> |  |  |
| <sup>a</sup> | The structure formulas of DINP and DIDP are only one of their isomeric compounds.                   |                         |  |  |
| <sup>b</sup> | CAS No. 28553-12-0 is a mixture of esters of o-phthalic acid with C9 alkyl alcohols.                |                         |  |  |
| <sup>c</sup> | CAS No. 68515-48-0 is a mixture of esters of o-phthalic acid with C8-C10 (C9 rich) alkyl alcohols.  |                         |  |  |
| <sup>d</sup> | CAS No. 26761-40-0 is a mixture of esters of o-phthalic acid with C10 alkyl alcohols.               |                         |  |  |
| <sup>e</sup> | CAS No. 68515-49-1 is a mixture of esters of o-phthalic acid with C9-C11 (C10 rich) alkyl alcohols. |                         |  |  |



## Annex B (informative)

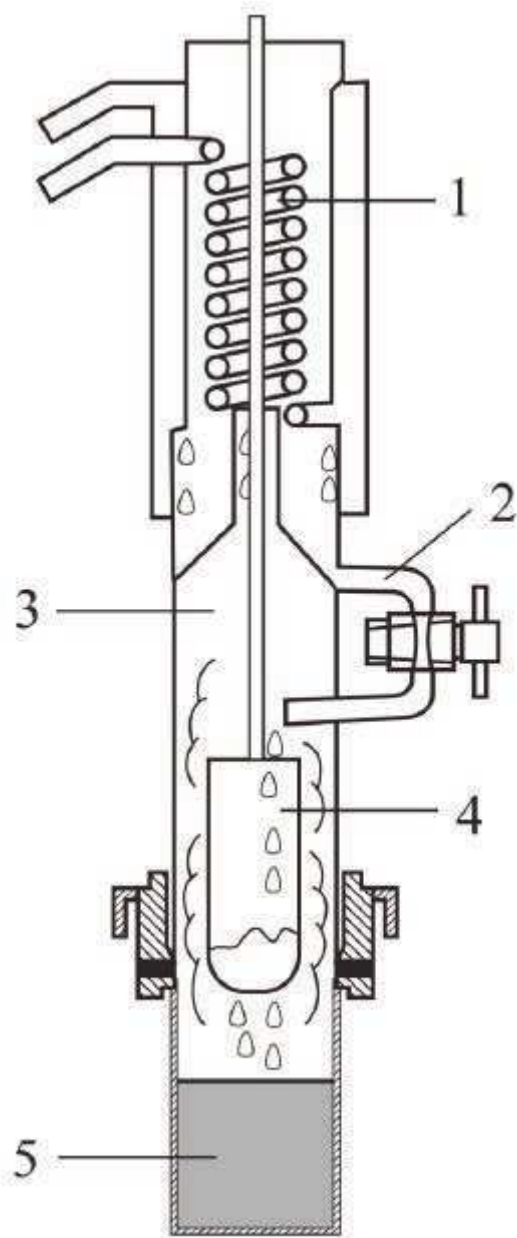
### Extraction apparatus



#### Key

- 1 condenser
- 2 extraction chamber
- 3 thimble
- 4 siphon tube
- 5 distillation path
- 6 boiling flask

Figure B.1 — Soxhlet extractor



**Key**

- 1 condenser
- 2 solvent feed
- 3 extraction chamber
- 4 thimble
- 5 receiver

**Figure B.2 — Solvent extractor**

## Annex C (informative)

### Example of GC-MS conditions

Due to the variation of instruments in different laboratories, no generally applicable instructions can be provided for chromatographic analysis. The following parameters have been tested and used successfully. Retention time and diagnostic ions of the phthalate esters are specified in [Table C.1](#) and the chromatograms are shown in [Figure C.1](#), [Figure C.2](#), [Figure C.3](#), and [Figure C.4](#).

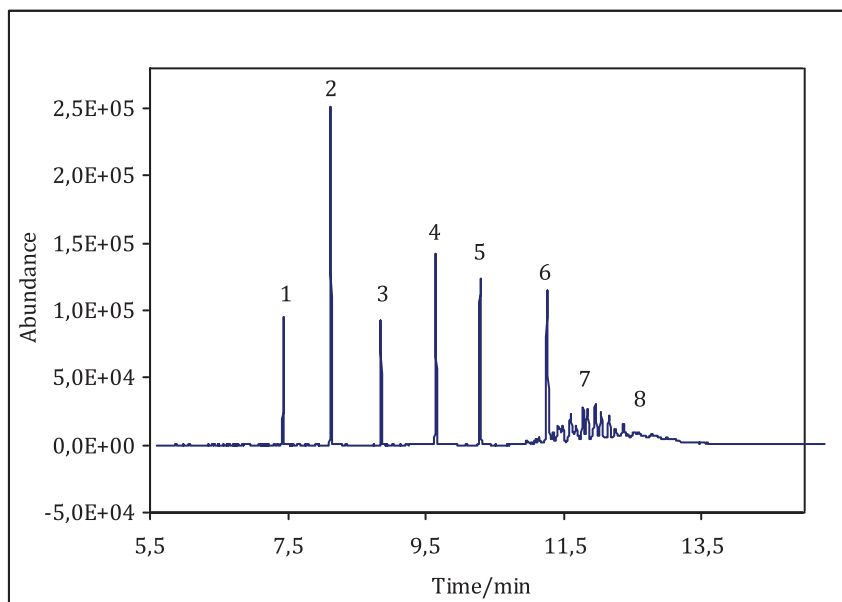
- a) Column: DB-5MS capillary column 30 m × 0,25 mm (ID) × 0,25 μm (film thickness)
- b) Oven program: 80 °C  $\xrightarrow[0,5 \text{ min}]{25 \text{ °C/min}}$  300 °C (4,5 min)
- c) Carrier gas: helium, 1 ml/min, constant flow
- d) Injector temperature: 300 °C
- e) Injection: 1,0 μl, 20:1 Split
- f) Transfer line temperature: 290 °C
- g) Ionization mode: electron ionization (EI), 70 eV; ion source temperature: 230 °C
- h) Mass filter: quadruple mass filter
- i) Determination: Identification by full scan mode ( $m/z = 50-500$ ), quantification by selected ion monitoring (SIM) mode simultaneously, refer to [Table C.1](#) and [Figure C.1](#), [Figure C.2](#), [Figure C.3](#), and [Figure C.4](#).

**Table C.1 — Retention time and diagnostic ions for chemicals**

| No. | Chemicals | Retention time<br>min | Diagnostic ions<br>$m/z$           | Relative intensity |
|-----|-----------|-----------------------|------------------------------------|--------------------|
| –   | BB (IS)   | 7,4                   | <u>105</u> , 91, 212, 194          | 100:46:17:09       |
| 1   | DBP       | 8,1                   | <u>149</u> , 150, 223, 205         | 100:09:05:04       |
| –   | DAP (IS)  | 8,9                   | <u>149</u> , 150, 237, 219         | 100:10:06:03       |
| 2   | BBP       | 9,6                   | <u>149</u> , 091, 206, 238         | 100:72:23:03       |
| 3   | DEHP      | 10,3                  | <u>149</u> , 167, 279, 150         | 100:50:32:10       |
| 4   | DNOP      | 11,3                  | 149, <u>279</u> , 150, 261         | 100:18:10:03       |
| 5   | DINP      | 10,7–13,0             | 149, <u>127</u> , <u>293</u> , 167 | 100:14:09:06       |
| 6   | DIDP      | 11,0–14,5             | 149, <u>141</u> , <u>307</u> , 150 | 100:21:16:10       |

Underlined: the first quantification ions.

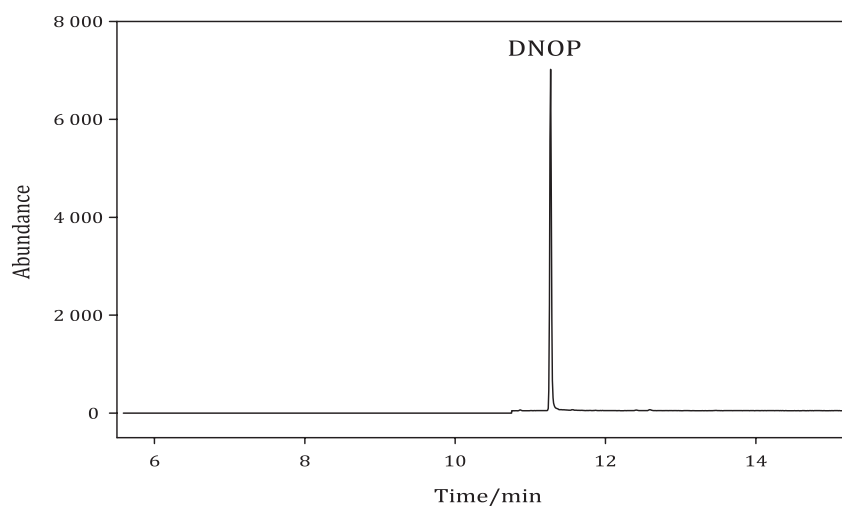
Italic: the second quantification ions.



**Key**

- 1 BB
- 2 DBP
- 3 DAP
- 4 BBP
- 5 DEHP
- 6 DNOP
- 7 DINP
- 8 DIDP

**Figure C.1 — Total ion chromatogram (BB, DBP, DAP, BBP, DEHP, DNOP 10 mg/l, DINP, DIDP 50 mg/l)**



**Figure C.2 — Extracted ion chromatogram of DNOP standard ( $m/z = 279$ )**

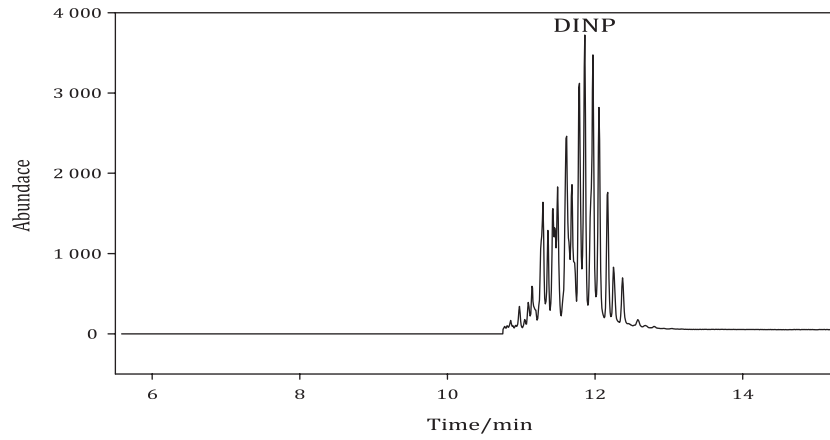


Figure C.3 — Extracted ion chromatogram of DINP standard ( $m/z = 293$ )

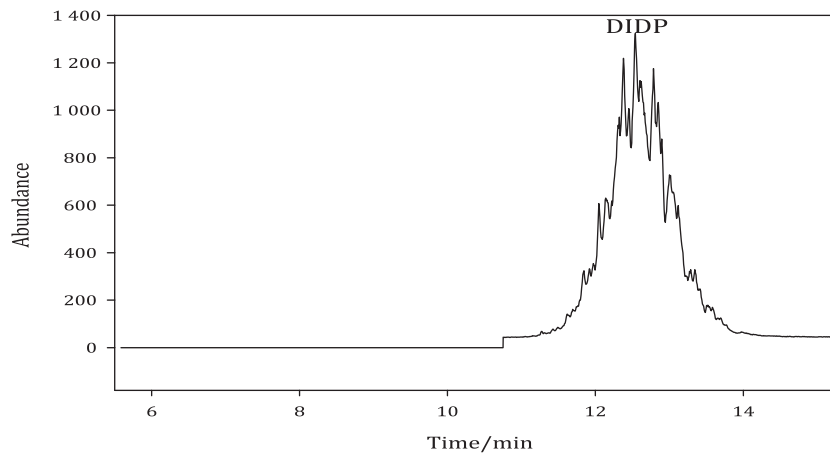


Figure C.4 — Extracted ion chromatogram of DIDP standard ( $m/z = 307$ )

## Annex D (informative)

### Precision of the method

The first inter-laboratory collaborative trial test was organized in 2010 with 122 laboratories participating in the determination of 6 phthalate esters in PVC toys with one concentration level.

The second inter-laboratory collaborative trial test was organized in 2011 with 12 laboratories participating in the determination of 6 phthalate esters in polyurethane (PU) plastic and coatings with base resin of PVC, polyacrylic acid (PAA), and nitrocellulose (NC) with two concentration levels.

The third inter-laboratory collaborative trial test was organized in 2012 with 8 laboratories participating in the determination of 2 phthalate esters in polyurethane (PU) plastic with low concentration level.

All the precision data are shown in [Table D.1](#) to [D.6](#) for reference.

**Table D.1 — Summary of the results of the inter-laboratory trial test on PVC plastic**

| Phthalate esters | Method                      | <i>l</i> | <i>o</i> | <i>M</i> | <i>s<sub>r</sub></i> | <i>CV<sub>r</sub></i> | <i>r</i> | <i>s<sub>R</sub></i> | <i>CV<sub>R</sub></i> | <i>R</i> |
|------------------|-----------------------------|----------|----------|----------|----------------------|-----------------------|----------|----------------------|-----------------------|----------|
|                  |                             |          | %        | mg/kg    | mg/kg                | %                     | mg/kg    | mg/kg                | %                     | mg/kg    |
| DBP              | Method A and ES calibration | 94       | 6,0      | 2 442    | 72                   | 2,9                   | 201      | 207                  | 8,5                   | 579      |
|                  | Method A and IS calibration | 15       | 0        | 2 441    | 52                   | 2,1                   | 146      | 178                  | 7,3                   | 499      |
|                  | Method B and ES calibration | 7        | 0        | 2 451    | 62                   | 2,5                   | 173      | 90                   | 3,7                   | 253      |
| BBP              | Method A and ES calibration | 93       | 7,0      | 2 024    | 64                   | 3,2                   | 179      | 170                  | 8,4                   | 477      |
|                  | Method A and IS calibration | 15       | 0        | 2 005    | 62                   | 3,1                   | 174      | 179                  | 8,9                   | 501      |
|                  | Method B and ES calibration | 7        | 0        | 2 024    | 83                   | 4,1                   | 233      | 150                  | 7,4                   | 421      |
| DEHP             | Method A and ES calibration | 96       | 4,0      | 3 737    | 107                  | 2,9                   | 301      | 310                  | 8,3                   | 867      |
|                  | Method A and IS calibration | 15       | 0        | 3 694    | 91                   | 2,5                   | 255      | 302                  | 8,2                   | 846      |
|                  | Method B and ES calibration | 7        | 0        | 3 888    | 72                   | 1,9                   | 203      | 266                  | 6,8                   | 744      |

Table D.1 (continued)

| Phthalate esters | Method                      | <i>l</i> | <i>o</i> | <i>M</i> | <i>s<sub>r</sub></i> | <i>CV<sub>r</sub></i> | <i>r</i> | <i>s<sub>R</sub></i> | <i>CV<sub>R</sub></i> | <i>R</i> |
|------------------|-----------------------------|----------|----------|----------|----------------------|-----------------------|----------|----------------------|-----------------------|----------|
|                  |                             |          | %        | mg/kg    | mg/kg                | %                     | mg/kg    | mg/kg                | %                     | mg/kg    |
| DNOP             | Method A and ES calibration | 57       | 1,7      | 2 153    | 83                   | 3,9                   | 233      | 313                  | 14,5                  | 877      |
|                  | Method A and IS calibration | 9        | 0        | 2 103    | 50                   | 2,4                   | 139      | 197                  | 9,4                   | 552      |
|                  | Method B and ES calibration | 5        | 0        | 2 286    | 113                  | 5,0                   | 317      | 252                  | 11,0                  | 704      |
| DINP             | Method A and ES calibration | 53       | 8,6      | 3 100    | 91                   | 2,9                   | 256      | 637                  | 20,6                  | 1 784    |
|                  | Method A and IS calibration | 8        | 0        | 3 297    | 203                  | 6,1                   | 567      | 509                  | 15,4                  | 1 424    |
|                  | Method B and ES calibration | 5        | 0        | 3 126    | 192                  | 6,1                   | 536      | 773                  | 24,7                  | 2 165    |
| DIDP             | Method A and ES calibration | 51       | 12,1     | 2 244    | 80                   | 3,6                   | 224      | 360                  | 16,0                  | 1 007    |
|                  | Method A and IS calibration | 8        | 0        | 2 445    | 119                  | 4,9                   | 333      | 343                  | 14,0                  | 961      |
|                  | Method B and ES calibration | 5        | 0        | 2 374    | 116                  | 4,9                   | 325      | 476                  | 20,1                  | 1 333    |

Explanation of symbols:

- l* is the number of laboratories after outlier rejection;
- o* is the percentage of outliers;
- M* is the median value of the results;
- s<sub>r</sub>* is the standard deviation of repeatability;
- CV<sub>r</sub>* is the coefficient of variation of repeatability;
- r* is the repeatability,  $r = 2,8 \times S_r$ ;
- s<sub>R</sub>* is the standard deviation of reproducibility;
- CV<sub>R</sub>* is the coefficient of variation of reproducibility;
- R* is the reproducibility,  $R = 2,8 \times S_R$ .

Table D.2 — Summary of the results of the inter-laboratory trial test on PU plastics

| Phthalate esters | <i>l</i> | <i>o</i> | <i>M</i> | <i>s<sub>r</sub></i> | <i>CV<sub>r</sub></i> | <i>r</i> | <i>s<sub>R</sub></i> | <i>CV<sub>R</sub></i> | <i>R</i> |
|------------------|----------|----------|----------|----------------------|-----------------------|----------|----------------------|-----------------------|----------|
|                  |          | %        | mg/kg    | mg/kg                | %                     | mg/kg    | mg/kg                | %                     | mg/kg    |
| DBP              | 11       | 8,3      | 724      | 46                   | 6,3                   | 129      | 77                   | 10,7                  | 216      |
|                  | 12       | 0        | 2 839    | 106                  | 3,7                   | 297      | 277                  | 9,8                   | 777      |

For definitions of symbols, see [Table D.1](#).

Table D.2 (continued)

| Phthalate esters | <i>l</i> | <i>o</i> | <i>M</i> | <i>s<sub>r</sub></i> | <i>CV<sub>r</sub></i> | <i>r</i> | <i>s<sub>R</sub></i> | <i>CV<sub>R</sub></i> | <i>R</i> |
|------------------|----------|----------|----------|----------------------|-----------------------|----------|----------------------|-----------------------|----------|
|                  |          | %        | mg/kg    | mg/kg                | %                     | mg/kg    | mg/kg                | %                     | mg/kg    |
| BBP              | 12       | 0        | 923      | 48                   | 5,2                   | 135      | 100                  | 10,8                  | 279      |
|                  | 12       | 0        | 4 586    | 208                  | 4,5                   | 581      | 325                  | 7,1                   | 911      |
| DEHP             | 11       | 8,3      | 968      | 60                   | 6,2                   | 169      | 93                   | 9,6                   | 259      |
|                  | 12       | 0        | 4 023    | 146                  | 3,6                   | 408      | 467                  | 11,6                  | 1 308    |
| DNOP             | 12       | 0        | 869      | 39                   | 4,5                   | 109      | 124                  | 14,3                  | 348      |
|                  | 12       | 0        | 3 717    | 88                   | 2,4                   | 246      | 523                  | 14,1                  | 1 465    |
| DINP             | 11       | 8,3      | 1 039    | 78                   | 7,5                   | 219      | 166                  | 16,0                  | 464      |
|                  | 11       | 8,3      | 3 760    | 206                  | 5,5                   | 578      | 729                  | 19,4                  | 2 040    |
| DIDP             | 12       | 0        | 1 161    | 86                   | 7,4                   | 240      | 121                  | 10,5                  | 340      |
|                  | 12       | 0        | 4 715    | 242                  | 5,1                   | 678      | 1005                 | 21,3                  | 2 813    |

For definitions of symbols, see [Table D.1](#).

Table D.3 — Summary of the results of the inter-laboratory trial test on PVC coatings

| Phthalate esters | <i>l</i> | <i>o</i> | <i>M</i> | <i>s<sub>r</sub></i> | <i>CV<sub>r</sub></i> | <i>r</i> | <i>s<sub>R</sub></i> | <i>CV<sub>R</sub></i> | <i>R</i> |
|------------------|----------|----------|----------|----------------------|-----------------------|----------|----------------------|-----------------------|----------|
|                  |          | %        | mg/kg    | mg/kg                | %                     | mg/kg    | mg/kg                | %                     | mg/kg    |
| DBP              | 11       | 8,3      | 1 014    | 57                   | 5,6                   | 159      | 109                  | 10,8                  | 306      |
|                  | 12       | 0        | 10 084   | 251                  | 2,5                   | 703      | 993                  | 9,9                   | 2 781    |
| BBP              | 11       | 8,3      | 999      | 48                   | 4,8                   | 134      | 66                   | 6,6                   | 185      |
|                  | 12       | 0        | 10 822   | 366                  | 3,4                   | 1 026    | 1 071                | 9,9                   | 2 999    |
| DEHP             | 11       | 8,3      | 1 012    | 37                   | 3,7                   | 105      | 102                  | 10,1                  | 286      |
|                  | 12       | 0        | 10 754   | 446                  | 4,2                   | 1 250    | 992                  | 9,2                   | 2 778    |
| DNOP             | 11       | 8,3      | 897      | 49                   | 5,5                   | 137      | 93                   | 10,4                  | 261      |
|                  | 11       | 8,3      | 10 660   | 688                  | 6,4                   | 1 925    | 1 013                | 9,5                   | 2 836    |
| DINP             | 11       | 8,3      | 1 306    | 102                  | 7,8                   | 286      | 220                  | 16,9                  | 617      |
|                  | 12       | 0        | 10 622   | 552                  | 5,2                   | 1 546    | 1 568                | 14,8                  | 4 391    |
| DIDP             | 12       | 0        | 1 242    | 82                   | 6,6                   | 231      | 224                  | 18,1                  | 628      |
|                  | 12       | 0        | 11 653   | 890                  | 7,6                   | 2 492    | 1 733                | 14,9                  | 4 852    |

For definitions of symbols, see [Table D.1](#).

Table D.4 — Summary of the results of the inter-laboratory trial test on PAA coatings

| Phthalate esters | <i>l</i> | <i>o</i> | <i>M</i> | <i>s<sub>r</sub></i> | <i>CV<sub>r</sub></i> | <i>r</i> | <i>s<sub>R</sub></i> | <i>CV<sub>R</sub></i> | <i>R</i> |
|------------------|----------|----------|----------|----------------------|-----------------------|----------|----------------------|-----------------------|----------|
|                  |          | %        | mg/kg    | mg/kg                | %                     | mg/kg    | mg/kg                | %                     | mg/kg    |
| DBP              | 11       | 8,3      | 1 022    | 40                   | 3,9                   | 112      | 87                   | 8,5                   | 243      |
|                  | 12       | 0        | 9 476    | 346                  | 3,7                   | 969      | 851                  | 9,0                   | 2 382    |
| BBP              | 11       | 8,3      | 1 069    | 57                   | 5,3                   | 159      | 121                  | 11,3                  | 339      |
|                  | 12       | 0        | 10 484   | 363                  | 3,5                   | 1 017    | 864                  | 8,2                   | 2 419    |
| DEHP             | 11       | 8,3      | 1 105    | 86                   | 7,8                   | 242      | 129                  | 11,7                  | 361      |
|                  | 12       | 0        | 10 762   | 452                  | 4,2                   | 1 266    | 1 037                | 9,6                   | 2 905    |

For definitions of symbols, see [Table D.1](#).



Table D.4 (continued)

| Phthalate esters | <i>l</i> | <i>o</i> | <i>M</i> | <i>s<sub>r</sub></i> | <i>CV<sub>r</sub></i> | <i>r</i> | <i>s<sub>R</sub></i> | <i>CV<sub>R</sub></i> | <i>R</i> |
|------------------|----------|----------|----------|----------------------|-----------------------|----------|----------------------|-----------------------|----------|
|                  |          | %        | mg/kg    | mg/kg                | %                     | mg/kg    | mg/kg                | %                     | mg/kg    |
| DNOP             | 11       | 8,3      | 1 186    | 44                   | 3,7                   | 123      | 139                  | 11,7                  | 389      |
|                  | 12       | 0        | 10 727   | 343                  | 3,2                   | 960      | 1 110                | 10,4                  | 3 109    |
| DINP             | 10       | 16,7     | 1 456    | 106                  | 7,3                   | 297      | 238                  | 16,3                  | 666      |
|                  | 12       | 0        | 10 996   | 960                  | 8,7                   | 2 689    | 1 252                | 11,4                  | 3 507    |
| DIDP             | 10       | 16,7     | 1 377    | 100                  | 7,2                   | 279      | 176                  | 12,8                  | 493      |
|                  | 12       | 0        | 11 093   | 804                  | 7,3                   | 2 252    | 1 844                | 16,6                  | 5 163    |

For definitions of symbols, see [Table D.1](#).

Table D.5 — Summary of the results of the inter-laboratory trial test on NC coatings

| Phthalate esters | <i>l</i> | <i>o</i> | <i>M</i> | <i>s<sub>r</sub></i> | <i>CV<sub>r</sub></i> | <i>r</i> | <i>s<sub>R</sub></i> | <i>CV<sub>R</sub></i> | <i>R</i> |
|------------------|----------|----------|----------|----------------------|-----------------------|----------|----------------------|-----------------------|----------|
|                  |          | %        | mg/kg    | mg/kg                | %                     | mg/kg    | Mg/kg                | %                     | mg/kg    |
| DBP              | 12       | 0        | 985      | 62                   | 6,3                   | 174      | 119                  | 12,0                  | 332      |
|                  | 12       | 0        | 9 596    | 507                  | 5,3                   | 1 421    | 943                  | 9,8                   | 2 640    |
| BBP              | 12       | 0        | 1 046    | 53                   | 5,1                   | 149      | 129                  | 12,3                  | 361      |
|                  | 12       | 0        | 10 555   | 512                  | 4,8                   | 1 433    | 1 034                | 9,8                   | 2 894    |
| DEHP             | 12       | 0        | 1 038    | 65                   | 6,2                   | 181      | 138                  | 13,3                  | 387      |
|                  | 12       | 0        | 10 015   | 469                  | 4,7                   | 1 313    | 822                  | 8,2                   | 2 301    |
| DNOP             | 12       | 0        | 1 205    | 71                   | 5,9                   | 198      | 145                  | 12,0                  | 405      |
|                  | 11       | 8,3      | 10 948   | 384                  | 3,5                   | 1 074    | 898                  | 8,2                   | 2 514    |
| DINP             | 12       | 0        | 1 501    | 78                   | 5,2                   | 218      | 310                  | 20,6                  | 867      |
|                  | 12       | 0        | 11 345   | 603                  | 5,3                   | 1 690    | 1 082                | 9,5                   | 3 031    |
| DIDP             | 11       | 8,3      | 1 379    | 79                   | 5,7                   | 220      | 176                  | 12,7                  | 492      |
|                  | 12       | 0        | 11 654   | 956                  | 8,2                   | 2 676    | 1 933                | 16,6                  | 5 413    |

For definitions of symbols, see [Table D.1](#).

Table D.6 — Summary of the results of the inter-laboratory trial test on PU plastic in low concentration

| Phthalate esters | <i>l</i> | <i>o</i> | <i>M</i> | <i>s<sub>r</sub></i> | <i>CV<sub>r</sub></i> | <i>r</i> | <i>s<sub>R</sub></i> | <i>CV<sub>R</sub></i> | <i>R</i> |
|------------------|----------|----------|----------|----------------------|-----------------------|----------|----------------------|-----------------------|----------|
|                  |          | %        | mg/kg    | mg/kg                | %                     | mg/kg    | Mg/kg                | %                     | mg/kg    |
| DEHP             | 7        | 12,5     | 171      | 11                   | 6,5                   | 31       | 20                   | 11,8                  | 56       |
| DINP             | 7        | 12,5     | 375      | 24                   | 6,5                   | 68       | 53                   | 14,1                  | 149      |

For definitions of symbols, see [Table D.1](#).

## Annex E (informative)

### Composite test

#### E.1 Introduction

Composite testing of similar materials is a general strategy to reduce testing cost but obstacles such as the complexity of the test matrix, interpretation of analytical results, unexpected chemical reactions between different test portions, etc., often lead to inconclusive results. Composite testing is only allowed in the case where a qualitative result is enough for judging the compliance with requirements. The composite test described in this annex is only used for a screening purpose.

It is important to note that composite testing cannot be used for the purpose of solving the lack of test portion's mass. If a test portion's mass is not enough to perform a single test, it is not possible to get a representative result through composite testing either.

#### E.2 Preparation of a composite test portion

A composite test portion shall meet all of the following conditions:

- 1) Up to three test portions can be combined to form a composite test portion.
- 2) Only similar materials can be combined to form a composite test portion. The compositing of dissimilar materials is not appropriate (e.g. compositing plastics and coatings).
- 3) Similar mass shall be used for each constituent test portion, i.e. the mass between any two constituent test portions should not differ by over 10 %, and the mass of each constituent test portion in the composite test shall be within 100 mg to 500 mg.

#### E.3 Test procedure

The test procedure specified in [Clause 7](#) of this part of ISO 8124 can also be applied to composite test.

#### E.4 Calculation

The average mass fraction of the target phthalate in the composite test portion ( $w_{\text{avg}}$ ) and the maximum mass fraction of the target phthalate in the individual test portions ( $w_{\text{max}}$ ) can be calculated through Formulae (E.1) and (E.2) respectively, regardless of whether ES or IS calibration is used or not.

$$w_{\text{avg}} = C \times \frac{V}{m_{\text{tot}}} \times D \times \frac{1}{10\,000} \quad (\text{E.1})$$

$$w_{\max} = C \times \frac{V}{m_{\min}} \times D \times \frac{1}{10\,000} \quad (\text{E.2})$$

where

$w_{\text{avg}}$  is the average mass fraction of the target phthalate in the composite test portion, in %;

$w_{\max}$  is the maximum mass fraction of the target phthalate in the individual test portions, in %;

$C$  is the concentration of the target phthalate in the composite test portion solution, in mg/l;

$V$  is the volume of the final solution, in ml;

$m_{\text{tot}}$  is the total mass of the composite test portion, in gram;

$m_{\min}$  is the minimum mass of the individual test portions, in gram;

$D$  is the dilution factor.

NOTE When calculating  $w_{\max}$ , it is based on a worst-case assumption that all of the phthalate came from the test portion with the minimum mass.

## E.5 Judgment of next action

When the average mass fraction of the target phthalate in the composite test portion ( $w_{\text{avg}}$ ) and the maximum mass fraction of the target phthalate in the individual test portions ( $w_{\max}$ ) has been calculated, the next action should be introduced according to the results obtained. In consideration of the next action from the composite test portion, it is imperative that a sufficient “safety factor” is applied to account for the uncertainty of the composite test to ensure that non-conforming materials are correctly identified.

The next action should be judged according to Formula (E.3)

$$L_{\text{act}} = L \times F \quad (\text{E.3})$$

where

$L_{\text{act}}$  is the action limit, in %;

$L$  is the regulated limit, in %;

$F$  is the safety factor, between 0 % and 100 %.

When  $w_{\max} < L_{\text{act}}$ , no further action is needed.

When  $w_{\max} \geq L_{\text{act}}$ , further action including individual testing is needed

where

$w_{\max}$  is the maximum mass fraction of the target phthalate in the individual test portions, in %.

Taking into consideration that the testing capability and uncertainty among different laboratories and the material tested are variables, it is up to the laboratory to decide the best fit safety factor based on their experience and history data accumulated. It is recommended to apply 60 % as a safety factor based on practical phthalates analysis experience.

### E.6 Test report

In addition to the information listed in [Clause 11](#), the test report shall contain the following:

- 1) a reference to the composite test portion used;
- 2) the average test result for the individual phthalate in the composite test portion (based on the total mass), in %;
- 3) the maximum test results for the individual phthalate in the composite test portion (based on the lowest mass), in %.

### E.7 Example

Assume that a composite test portion is formed by physically mixing three PVC plastic test portions which are designated as A, B, and C respectively. The mass for A, B, and C is 0,305 4 g, 0,312 5 g, and 0,325 0 g respectively and the final volume for the extraction solution of the composite test portion is 25 ml while the test result for DEHP in the extracted solution of the composite test portion is 5,90 mg/l.

Formula (E.1) is used to calculate the average mass fraction of the target phthalate in the composite test portion:

$$w_{avg} = \frac{5,90 \times 25}{0,3054 + 0,3125 + 0,3250} \times \frac{1}{10\ 000} = 0,0156 \%$$

Formula (E.2) is used to calculate the maximum mass fraction of the target phthalate in the individual test portions:

$$w_{max} = \frac{5,90 \times 25}{0,3054} \times \frac{1}{10\ 000} = 0,0483 \%$$

- If the regulated limit for the DEHP is 0,1 % and the safety factor is set at 60 %
  - the maximum DEHP content in one of the test portions (0,0483 %) is below the action limit 0,1 % × 0,6 = 0,06 %. No further action is needed, and
  - the test results can be reported as follows.

**Table E.1 — Test report of the composite test**

| Composite test portion no. | Test item | Regulated limit in % | Action limit <sup>a</sup> in % | w <sub>avg</sub> in % | w <sub>max</sub> in % | Conclusion |
|----------------------------|-----------|----------------------|--------------------------------|-----------------------|-----------------------|------------|
| 1. PVC A/PVC B/PVC C       | DEHP      | 0,1                  | 0,06                           | 0,015 6               | 0,048 3               | Pass       |

<sup>a</sup> Action limit is calculated with set “safety factor” at 60 %.

- If the regulated limit for the DEHP is 0,05 % and the safety factor is set at 60 %
  - the maximum DEHP content in one of the test portions (0,0483 %) is above the action limit 0,05 % × 0,6 = 0,03 %. Each constituent test portion should be tested, and
  - the test results can be reported as following.

Table E.2 — Test report of the composite test

| Composite test portion no.  | Test item | Regulated limit in % | Action limit <sup>a</sup> in % | $w_{avg}$ in % | $w_{max}$ in % | Conclusion      |
|---|-----------|----------------------|--------------------------------|----------------|----------------|-----------------|
| 1. PVC A/PVC B/<br>PVC C  | DEHP      | 0,05                 | 0,03                           | 0,015 6        | 0,048 3        | Individual test |
| <sup>a</sup> Action limit is calculated with set "safety factor" at 60 %. |           |                      |                                |                |                |                 |

## **Annex F** **(informative)**

### **Background and rationale**

#### **F.1 Introduction**

Plastics, such as polyvinyl chloride (PVC), are widely used in toys and children's products. During the production of PVC, softeners such as phthalate esters can be added to increase the plasticity. Due to increasing concern regarding the potential hormonal effect of phthalates to female hormones, and with environmental oestrogens which can accumulate in organisms along the food chain, starting from 1999, some countries and regions began to impose regulations on the use of some phthalate esters. Several phthalate test methods have thus been developed to meet the requirements of such regulations. However, these methods differ quite a lot from each other.

In the absence of a universal standard for determination of phthalate esters in toys and children's products, and the presence of phthalate esters in materials other than PVC (e.g. PU plastics, textiles, paint coatings, etc.), this part of ISO 8124 provides a phthalate determination method that covers most of these materials.

#### **F.2 Other phthalate esters in toys and children's products**

This part of ISO 8124, provided that adequate validation has been demonstrated, can be applied to toys and children's products containing phthalate esters other than DBP, BBP, DNOP, DEHP, DINP, and DIDP. It is also important to note that additional phthalate esters can be regulated in specific countries/regions.

#### **F.3 Sample preparation, extraction, and determination methods**

When sampling, the sample can alternatively be milled or ground into a representative powder, but interference and cross-contamination should be avoided.

Several extraction methods, such as the soxhlet extraction, solvent extraction, microwave assisted extraction, ultrasonic extraction etc., can be used to extract phthalates from toys and children's products. Soxhlet extraction is a traditional method which is the most commonly used to extract organic substances from samples, and the apparatus is commercially available. The solvent extractor used in this method is a modification of the classical soxhlet extraction to provide an easier and faster approach for sample extraction. These two methods have been proven to be effective for phthalate extraction. Other extraction techniques can be alternatively employed provided that the extraction efficiency is verified to be comparable to that of the method described in this part of ISO 8124.

Certain other instrument determination techniques, such as LC-MS, can be used if such alternative technique methods have been validated and provide comparable results.

#### **F.4 ES and IS Calibration**

Either ES or IS can be used for calibration. Generally, IS calibration for GC-MS analysis provides repeatable results with better precision but lengthens the operation procedure. However, in some cases the IS may be interfered by substances present in the sample. ES calibration for GC-MS analysis is relatively simple, but extra attention should be paid on maintaining the stabilities of GC-MS conditions between the analyses of calibration solutions and test solutions.

Laboratories can choose the suitable calibration method in accordance with their best practise. When ES calibration is used, the laboratory should ensure and demonstrate the stability of instrument conditions between the analyses of calibration solutions and test solutions. The calibration solution and test solution should, as far as possible, be injected alternately in the same condition and in the same time to eliminate the instability of the GC-MS. When IS calibration is used, the internal reference substance should not be present in the test portion. Otherwise, another internal reference substance, or isotopically labelled phthalates, should be used to avoid the interference.

## F.5 Materials that might contain phthalate esters

Phthalates can be found in plastics, textiles, coatings or paints, etc., in toys and children's products. Being a plasticizer, phthalates often exist in PVC as well as other plastics including polyvinyl acetate (PVA), polyvinylidene chloride (PVDC), and polyurethane (PU). PVC is used in toys, children's products and many other consumer products in the form of wire and cable insulation, etc. Phthalates might also be used as solvents and/or plasticizers in paints, inks, adhesives, sealants, air fresheners, and scented products, but are more likely to be used when the finished product shall be flexible, such as a printed design on apparel, or in paints, adhesives, or sealants on flexible substrates.

Certain plastics, such as polyethylene and polypropylene, usually do not contain plasticizers, but surface coatings and adhesives on them can contain phthalates. Even though some plastics do not need plasticizers, phthalates are still added, which means that phthalates can be found in some elastomers or synthetic rubbers. Most natural and synthetic fibres and textiles are not expected to contain phthalates but printed designs, coatings, surface treatments, and elastic components can contain phthalates.

Examples of materials that can contain phthalates are

- PVC and related polymers, such as polyvinylidene chloride (PVDC) and polyvinyl acetate (PVA),
- soft or flexible plastics, except polyolefins,
- soft or flexible rubber, except silicone rubber and natural latex,
- foam rubber or foam plastic, such as PU,
- surface coatings, non-slip coatings, finishes, decals, and printed designs,
- elastic materials in apparel, such as sleepwear,
- adhesives and sealants, and
- electrical insulation.

Examples of materials that do not normally contain phthalates:

- unfinished metal;
- natural wood, except for coatings and adhesives added to wood;
- textiles made of natural fibres, such as cotton or wool, except for printed decorations, waterproof coatings or other surface treatments, back coatings, and elastic materials (especially sleepwear);
- textiles made of common synthetic fibres, such as polyester, acrylic, and nylon, except for printed decorations, waterproof coatings or other surface treatments, and elastic materials except for any textiles containing PVC or related polymers;
- polyethylene and polypropylene (polyolefins);
- silicone rubber and natural latex;
- mineral products such as play sand, glass, and crystal.

All the information above can be used to determine which materials in toys and children's products need to be tested or not.



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