INTERNATIONAL STANDARD

ISO 8124-6

Second edition
2018-11

Safety of toys —

Part 6: Certain phthalate esters in toys and children's products

Sécurité des jouets —

Partie 6: Dosage de certains esters de phtalates dans les jouets et produits pour enfants

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Foreword

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

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

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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

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

This document was prepared by Technical Committee ISO/TC 181, *Safety of toys*.

This second edition of ISO 8124-6 cancels and replaces the first edition (ISO 8124-6:2014), which has been technically revised.

The main changes to the previous edition are as follows:

— addition of di-*iso*-butyl phthalate (DIBP) in Clause 1 and Annex A;

— addition of liquid material in Clause 1, Clause 7 and Annex A;

— addition of a new Clause 2, *Normative references*, and renumbering of subsequent clauses;

— addition of a new method C, “ultrasonic bath method”;

— update and reorganization of the inter-laboratory collaborative trial test data in Annex B;

— addition of a new Annex E, *Ultrasonic bath performance check*, and renumbering of all annexes.

A list of all parts in the ISO 8124 series can be found on the ISO website.

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

Introduction

This document 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.

This document does not set out limits for phthalate esters. It is intended to be used as a method standard in conformity assessment. The user of this document is therefore advised to be aware of relevant national requirements.

In some countries phthalate ester requirements for toys are also applicable to children's products and children's product materials are generally similar to those of toys. This document, whose scope covers various materials, is therefore applicable to both toys and children's products.

Annex A and Annex E are normative, whereas Annex B, Annex C, Annex D, Annex F and Annex G are for information only. However, they are crucial and helpful for the correct interpretation of this document.

Safety of toys —

Part 6:
Certain phthalate esters in toys and children's products

WARNING — Persons using this document should be familiar with normal laboratory practice. This document 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.

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

1 Scope

This document specifies a method for the determination of di-*iso*-butyl phthalate (DIBP), di-*n*-butyl phthalate (DBP), benzylbutyl phthalate (BBP), bis-(2-ethylhexyl) phthalate (DEHP), di-*n*-octyl phthalate (DNOP), di-*iso*-nonylphthalate (DINP) and di-*iso*-decyl phthalate (DIDP) (as specified in Annex A) in toys and children's products.

This document is applicable to toys and children's products which are made of plastics, textiles, coatings and liquids. This document has been validated for polyvinylchloride (PVC) plastics, polyurethane (PU) plastics and some representative paint coatings (see Annex B). It might also be applicable to other phthalate esters and other product materials provided that adequate validation is demonstrated.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 2758, *Paper — Determination of bursting strength*

ISO 8124-1:2018, *Safety of toys — Part 1: Safety aspects related to mechanical and physical properties*

3 Terms and definitions

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

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

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

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

3.1
laboratory sample
toy or children's product in the form in which it is marketed or intended to be marketed

3.2
base material
material upon which coatings may be formed or deposited

[SOURCE: ISO 8124-3:2010, 3.1]

3.3
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

[SOURCE: ISO 8124-3:2010, 3.2, modified — 'toy' has been replaced with 'toy or children's product']

3.4
scraping
mechanical process for removal of coatings down to the base material

[SOURCE: ISO 8124-3:2010, 3.6]

3.5
test portion
portion of homogeneous material taken from a corresponding part of the laboratory sample for analysis

3.6
composite test portion
mixed test portion formed by physically mixing several test portions of similar materials

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

3.7
composite test
test performed on the composite test portion

3.8
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

3.9
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.

4 Principle

The test portion of a toy or children's product is extracted through a Soxhlet extractor, solvent extractor (see Annex C) or ultrasonic bath with dichloromethane. Phthalate esters in the extract are determined qualitatively and quantitatively by gas chromatography-mass spectrometry (GC-MS).

5 Reagents

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

5.2 Phthalate reference substances, DIBP, DBP, BBP, DEHP, DNOP, DINP and DIDP (as specified in Annex A), minimum of 95 % purity.

5.3 Stock solution, 100 mg/l of DIBP, DBP, BBP, DEHP, DNOP each, and 500 mg/l of DINP, DIDP each in dichloromethane (5.1).

5.4 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 DIBP, 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 (5.3) to a 50 ml volumetric flask and making up to the mark with dichloromethane.

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

5.5 Internal standard (IS) calibration solutions

5.5.1 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.

5.5.2 Internal stock solution

250 mg/l of BB, DAP or others, in dichloromethane.

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

5.5.3 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 DIBP, 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 (5.3) to a 50 ml volumetric flask and adding 2 ml of the IS stock solution (5.5.2) before making up to the mark with dichloromethane. Each of the calibration standards contains 10 mg/l IS.

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

6 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.

6.1 Normal laboratory glassware.

6.2 Gas chromatography-mass spectrometer (GC-MS), with a capillary column coupled to a mass spectrometric detector (electron ionization, EI) used for the analysis. See 8.4.1.

6.3 Soxhlet extractor, see Figure C.1.

6.4 Solvent extractor, see Figure C.2.

6.5 Extraction thimble, made of cellulose.

6.6 Cotton wool, for extraction thimble.

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

6.8 Concentration apparatus, for example, a rotary evaporator.

6.9 Solid phase extraction (SPE) cartridge, 1 000 mg silica gel/6 ml tubes, or equivalent.

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

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

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

6.13 Ultrasonic bath, thermostatically controlled internally or externally, with the effective ultrasonic power intensity ranging from 0,25 W/cm^2 to 2,0 W/cm^2. The performance check of the ultrasonic bath is performed as specified in Annex E.

EXAMPLE An ultrasonic bath with a total power consumption of 1 200 W including 200 W of effective ultrasonic power and 1 000 W of heating power, with an internal bath base area of 400 cm^2, will have an effective ultrasonic power intensity of 0,50 W/cm^2 (=200 W/400 cm^2).

6.14 Ultrasonic basket, usually supplied together with the ultrasonic bath. When hung on the ultrasonic bath, its lowest level is approximately 3 cm to 5 cm above the bottom of the bath.

6.15 Airtight glass reaction vessel, pressure resistant to at least 0,2 MPa and with a gross volume of 2 to 10 times the volume of dichloromethane. The reaction vessel should be tightly closed to prevent the evaporation of dichloromethane during ultrasonic extraction.

6.16 Centrifuge, capable of centrifuging at (5 000 ± 500) g.

7 Selection of test portion

For materials in solid form, use a scalpel or other appropriate cutting instrument 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.

For materials in liquid form, use appropriate apparatus, such as a pipette or syringe, to transfer a representative portion from the laboratory sample. Extra care shall be taken to minimize cross contamination.

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

The requirement does not preclude the taking of reference portions from toy or children's product materials in a different form, provided that they are representative of the relevant material specified above and the substrate upon which they are deposited.

A composite test can be used for screening. See Annex D.

8 Procedure

8.1 Sample weighing

Weigh, to the nearest 1 mg, approximately 1 g of the test portion into an extraction thimble (6.5) or reaction vessel (6.15). If 1 g test portion cannot be obtained from a single laboratory sample, sample as much as possible from more than one laboratory sample, but 0,1 g should be a minimum test portion.

8.2 Extraction

8.2.1 Options for extraction method

Three options for extraction procedures, Method A (8.2.2), Method B (8.2.3) and Method C (8.2.4), are described. Laboratories can select the most suitable one at their discretion.

8.2.2 Method A

Place the thimble with test portion into a 250-ml Soxhlet extractor (6.3). In order to prevent the sample from floating, add cotton wool (6.6) to the top of the thimble.

Add 120 ml of dichloromethane (5.1) into the 250-ml flask. Reflux for 6 h with no less than four reflux cycles per hour.

The volume of the dichloromethane may be adjusted according to the Soxhlet extractor.

After cooling, reduce the volume of the dichloromethane to about 10 ml using a suitable concentration apparatus (6.8), taking 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 of between 30 kPa to 45 kPa.

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

8.2.3 Method B

Place the thimble with test portion into the solvent extractor (6.4). In order to prevent the sample from floating, add cotton wool (6.6) to the top of the thimble.

Add 80 ml of dichloromethane (5.1) into the receiver. Immerse for 1,5 h at about 80 °C and reflux for 1,5 h. Finally, concentrate the dichloromethane extract to about 10 ml.

The volume of the dichloromethane may be adjusted according to the solvent extractor.

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

8.2.4 Method C

8.2.4.1 For material in solid form

Add 25 ml of dichloromethane to the airtight glass reaction vessel (6.15). Place the vessel in an ultrasonic bath with an initial temperature of 60 °C for 60 min.

NOTE If the material does not dissolve or swell in dichloromethane, method A (8.2.2) or method B (8.2.3) might be preferable.

The volume of the final solution may be adjusted according to the mass of tested specimen. Care should be taken not to affect the LOQ (10.1).

8.2.4.2 For material in liquid form

Add 15 ml of dichloromethane to an airtight glass reaction vessel (6.15). Place the vessel in an ultrasonic bath with an initial temperature of 60 °C for 60 min.

8.3 Sample solution for analysis

8.3.1 General

After cooling to room temperature, filter the solution, which is obtained after the test portion has been treated according to the procedure as specified in 8.2.2, 8.2.3 or 8.2.4, where appropriate, with PTFE membrane filter (6.12) for GC-MS (6.2) analysis.

Before the filtering procedure, when the extract exhibits turbidity, centrifuge at up to 5 000 g (6.16). If necessary, purify the solution with a pretreated SPE cartridge (6.9), which is pretreated with approximately 10 ml of dichloromethane before purification and discard the effluent, rinse the cartridge with 3 ml of dichloromethane three times and collect the eluate.

Two options for quantification procedures, ES calibration (8.3.2) and IS calibration (8.3.3), are described as follows. Laboratories can select the most suitable one at their discretion.

8.3.2 Quantification by external standard (ES) calibration

8.3.2.1 Method A and Method B

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

The volume of the final solution may be adjusted according to the mass of tested specimen. Care should be taken not to affect the LOQ (10.1).

8.3.2.2 Method C

8.3.2.2.1 Material in solid form

Use the extract or the eluate for GC-MS analysis.

8.3.2.2.2 Material in liquid form

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

The volume of the final solution may be adjusted according to the mass of tested specimen. Care should be taken not to affect the LOQ (10.1).

8.3.3 Quantification by IS calibration

For method A or method B, transfer the extract or the eluate and 1 ml of the IS stock solution (5.5.2) into a 25-ml volumetric flask and make up to the mark with dichloromethane. The final solution contains 10 mg/l of IS.

The volume of both IS solution and the final solution may 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 (5.5.3).

8.4 Determination

8.4.1 GC-MS conditions

Due to the variation of instruments in different laboratories, no universally 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 F.

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.

8.4.2 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 relative retention time of the analyte corresponds to that of the calibration solution at a tolerance of ± 0,5 %;

b) the diagnostic ions (see Table F.1) are present at the substance-specific retention time;

c) the relative intensities of the diagnostic ions (refer to Table F.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.

NOTE Some isomers of DINP or DIDP can interfere with the identification of DINP or DIDP. For example, dipropylheptyl 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.

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 %

8.4.3 Calibration

8.4.3.1 General

Two optional calibration methods, ES (8.4.3.2) and IS (8.4.3.3), are described in the following. Either ES or IS can be used for calibration. Laboratories can choose the most suitable calibration method according to their best practice (see Annex G).

A calibration curve shall be established for either method. A minimum of five equidistant calibration standard solutions (5.4 or 5.5.3) 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.

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 Clause 12 f).

NOTE 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.

8.4.3.2 External standard (ES) calibration

Integrate the peak areas of the target quantification ions (see Table F.1) in the chromatogram by ES calibration.

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

$$A=(a_1\times C)+b_1 \tag{1}$$

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.

8.4.3.3 Internal standard (IS) calibration

Integrate the peak areas of the target quantification ions (see Table F.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):

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

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.

9 Calculation

9.1 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 as a mass percentage (%) 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.

9.2 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 a mass percentage (%) 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.

10 Quality control

10.1 Limit of quantification (LOQ)

LOQ for DIBP, DBP, BBP, DEHP, DNOP: 0,001 %.

LOQ for DINP, DIDP: 0,005 %.

10.2 Method blank

A method blank (3.9) shall be prepared for each batch of samples by following the steps in Clause 8 and Clause 9 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 (10.1).

10.3 Recovery

One spiked blank per batch shall be prepared by adding 1 ml of stock solution (5.3) in the method blank then treating it in the same way as described in Clause 8 and Clause 9. The recovery of each phthalate should be 80 % to 120 % of the expected value.

10.4 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.

11 Precision

The precision of this document is shown in Annex B.

12 Test report

The test report shall contain at least the following information:

a) a reference to this document (i.e. ISO 8124-6);

b) a complete identification of the sample;

c) a reference to the extraction procedure used;

d) a reference to the calculation method used (ES or IS);

e) the results of the individual quantitative phthalate analysis, expressed as a mass percentage (%);

f) the CAS No. of the used DINP or DIDP reference substance given in Table A.1;

g) any deviations from the procedure specified;

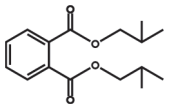
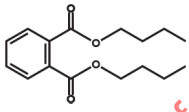
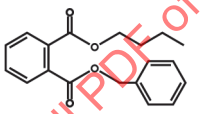
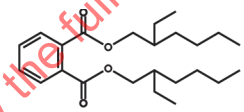
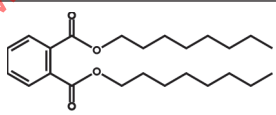
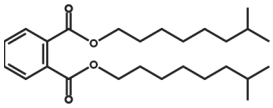
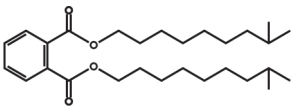
h) any unusual features observed during the test;

i) the date of the test.

Annex A
(normative)

Phthalate esters

Table A.1 — Phthalate esters

No.	Phthalate esters (initialism)	CAS No.	Structure formula[a]	Molecular formula
1	Di-*iso*-butyl phthalate (DIBP)	84–69–5		$C_{16}H_{22}O_4$
2	Di-*n*-butyl phthalate (DBP)	84–74–2		$C_{16}H_{22}O_4$
3	Benzyl butyl phthalate (BBP)	85–68–7		$C_{19}H_{20}O_4$
4	*Bis*-(2-ethylhexyl) phthalate (DEHP)	117–81–7		$C_{24}H_{38}O_4$
5	Di-*n*-octyl phthalate (DNOP)	117–84–0		$C_{24}H_{38}O_4$
6	Di-*iso*-nonyl phthalate (DINP)	28553–12–0[b] 68515–48–0[c]		$C_{26}H_{42}O_4$
7	Di-*iso*-decyl phthalate (DIDP)	26761–40–0[d] 68515–49–1[e]		$C_{28}H_{46}O_4$

[a] The structure formulae of DINP and DIDP are only one of their isomeric compounds.

[b] CAS No. 28553–12–0 is a mixture of esters of *o*-phthalic acid with C9 alkyl alcohols.

[c] CAS No. 68515–48–0 is a mixture of esters of *o*-phthalic acid with C8-C10 (C9 rich) alkyl alcohols.

[d] CAS No. 26761–40–0 is a mixture of esters of *o*-phthalic acid with C10 alkyl alcohols.

[e] CAS No. 68515–49–1 is a mixture of esters of *o*-phthalic acid with C9-C11 (C10 rich) alkyl alcohols.

Annex B
(informative)

Precision of the method

Four inter-laboratory collaborative trial tests were organized with many laboratories participating in the determination of phthalate esters in PVC plastic, polyurethane (PU) plastic, acrylonitrile-butadiene-styrene (ABS) copolymers, polyethylene (PE) plastic and coatings with base resin of PVC, polyacrylic acid (PAA) and nitrocellulose(NC) from 2012 to 2016. Method A, Method B and Method C were used for the tests. The results are shown in Tables B.1 to B.7.

Table B.1 — Summary of the results of the inter-laboratory trial test on samples 1 and 2

Phthalate	Method	PVC plastic (sample 1)							PVC plastic (sample 2)				
		l	o	M	CV_r	r	CV_R	R	l	o	M	CV_R	R
			%	mg/kg	%	mg/kg	%	mg/kg		%	mg/kg	%	mg/kg
DIBP	A	—	—	—	—	—	—	—	7	22,2	2 561	6,5	469
	B	—	—	—	—	—	—	—	4	0	2 319	15,0	975
	C	—	—	—	—	—	—	—	11	21,4	2 333	9,9	648
DBP	A	94	6,0	2 442	2,9	201	8,5	579	8	11,1	1 127	12,7	402
	B	7	0	2 451	2,5	173	3,7	253	4	0	1 135	11,6	369
	C	—	—	—	—	—	—	—	11	21,4	1 045	7,5	219
BBP	A	93	7,0	2 024	3,2	179	8,4	477	8	11,1	1 000	13,6	382
	B	7	0	2 024	4,1	233	7,4	421	4	0	1 059	12,7	377
	C	—	—	—	—	—	—	—	12	14,3	988	13,6	376
DEHP	A	96	4,0	3 737	2,9	301	8,3	867	7	22,2	2 254	5,8	366
	B	7	0	3 888	1,9	203	6,8	744	4	0	2 010	4,4	246
	C	—	—	—	—	—	—	—	14	0	2 100	16,4	966
DNOP	A	57	1,7	2 153	3,9	233	14,5	877	9	0	1 336	16,3	610
	B	5	0	2 286	5,0	317	11,0	704	4	0	1 348	12,8	483
	C	—	—	—	—	—	—	—	14	0	1 411	16,5	650
DINP	A	53	8,6	3 100	2,9	256	20,6	1 784	8	11,1	1 152	18,3	592
	B	5	0	3 126	6,1	536	24,7	2 165	4	0	1 131	14,2	449
	C	—	—	—	—	—	—	—	12	14,3	1 190	19,7	657
DIDP	A	51	12,1	2 244	3,6	224	16,0	1 007	8	11,1	2 245	13,5	850
	B	5	0	2 374	4,9	325	20,1	1 333	4	0	2 065	5,3	305
	C	—	—	—	—	—	—	—	12	14,3	2 207	13,1	807

Key

l: Number of laboratories after outlier rejection

o: Percentage of outliers

M: Median value of the results

CV_r: Coefficient of variation of repeatability

r: Repeatability, $r = 2{,}8 \times S_r$

CV_R: Coefficient of variation of reproducibility

R: Reproducibility, $R = 2{,}8 \times S_R$

Table B.2 — Summary of the results of the inter-laboratory trial test on samples 3 and 4

Phthalate	Method	PU plastic (sample 3)							PU plastic (sample 4)						
		l	o	M	CV_r	r	CV_R	R	l	o	M	CV_r	r	CV_R	R
			%	mg/kg	%	mg/kg	%	mg/kg		%	mg/kg	%	mg/kg	%	mg/kg
DBP	A	11	8,3	724	6,3	129	10,7	216	12	0	2 839	3,7	297	9,8	777
BBP	A	12	0	923	5,2	135	10,8	279	12	0	4 586	4,5	581	7,1	911
DEHP	A	11	8,3	968	6,2	169	9,6	259	12	0	4 023	3,6	408	11,6	1 308
DNOP	A	12	0	869	4,5	109	14,3	348	12	0	3 717	2,4	246	14,1	1 465
DINP	A	11	8,3	1 039	7,5	219	16,0	464	11	8,3	3 760	5,5	578	19,4	2 040
DIDP	A	12	0	1 161	7,4	240	10,5	340	12	0	4 715	5,1	678	21,3	2 813

NOTE For definitions of symbols, see Table B.1.

Table B.3 — Summary of the results of the inter-laboratory trial test on samples 5 and 6

Phthalate	Method	PU plastic (sample 5)							PU plastic (sample 6)				
		l	o	M	CV_r	r	CV_R	R	l	o	M	CV_R	R
			%	mg/kg	%	mg/kg	%	mg/kg		%	mg/kg	%	mg/kg
DBP	A	—	—	—	—	—	—	—	9	0	650	8,4	153
	B	—	—	—	—	—	—	—	4	0	720	12,2	246
	C	—	—	—	—	—	—	—	14	0	745	25,1	524
BBP	A	—	—	—	—	—	—	—	9	0	642	13,1	235
	B	—	—	—	—	—	—	—	4	0	663	9,5	177
	C	—	—	—	—	—	—	—	12	14,3	664	14,0	260
DEHP	A	7	12,5	171	6,5	31	11,8	56	9	0	724	15,0	305
	B	—	—	—	—	—	—	—	4	0	726	12,7	258
	C	—	—	—	—	—	—	—	12	14,3	746	13,3	277
DNOP	A	—	—	—	—	—	—	—	9	0	697	17,4	340
	B	—	—	—	—	—	—	—	4	0	700	12,4	243
	C	—	—	—	—	—	—	—	13	7,1	731	14,6	298
DINP	A	7	12,5	375	6,5	68	14,1	149	9	0	698	19,9	389
	B	—	—	—	—	—	—	—	4	0	720	14,7	296
	C	—	—	—	—	—	—	—	13	7,1	793	18,3	406
DIDP	A	—	—	—	—	—	—	—	9	0	653	23,8	435
	B	—	—	—	—	—	—	—	4	0	712	11,8	236
	C	—	—	—	—	—	—	—	14	0	730	16,9	346

NOTE For definitions of symbols, see Table B.1.

Table B.4 — Summary of the results of the inter-laboratory trial test on samples 7 and 8

Phthalate	Method	ABS plastic (sample 7)					PE plastic (sample 8)				
		l	o	M	CV_R	R	l	o	M	CV_R	R
			%	mg/kg	%	mg/kg		%	mg/kg	%	mg/kg
DIBP	A	9	0	1 191	15,3	511	—	—	—	—	—
	B	4	0	1 432	21,9	880	—	—	—	—	—
	C	12	14,3	1 254	11,9	416	—	—	—	—	—
DBP	A	9	0	1 195	14,1	471	—	—	—	—	—
	B	4	0	1 501	23,0	966	—	—	—	—	—
	C	14	0	1 370	23,1	885	—	—	—	—	—

NOTE For definitions of symbols, see Table B.1.

Table B.4 *(continued)*

Phthalate	Method	ABS plastic (sample 7)					PE plastic (sample 8)				
		l	o	M	CV_R	R	l	o	M	CV_R	R
			%	mg/kg	%	mg/kg		%	mg/kg	%	mg/kg
BBP	A	9	0	1 258	12,9	454	—	—	—	—	—
	B	4	0	1 433	15,2	610	—	—	—	—	—
	C	14	0	1 361	14,0	534	—	—	—	—	—
DEHP	A	9	0	1 454	16,2	660	9	0	640	23,5	422
	B	4	0	1 582	19,2	852	4	0	535	20,4	306
	C	14	0	1 511	14,9	632	14	0	744	29,6	616
DNOP	A	9	0	1 328	16,5	614	—	—	—	—	—
	B	4	0	1 466	10,9	446	—	—	—	—	—
	C	14	0	1 452	17,6	717	—	—	—	—	—
DINP	A	9	0	1 197	21,1	708	—	—	—	—	—
	B	4	0	1 205	10,5	355	—	—	—	—	—
	C	13	7,1	1 291	17,7	640	—	—	—	—	—
DIDP	A	9	0	980	22,6	621	—	—	—	—	—
	B	4	0	1 094	3,0	93	—	—	—	—	—
	C	14	0	1 054	16,6	491	—	—	—	—	—

NOTE For definitions of symbols, see Table B.1.

Table B.5 — Summary of the results of the inter-laboratory trial test on samples 9 and 10

Phthalate	Method	PVC coating (sample 9)							PVC coating (sample 10)						
		l	o	M	CV_r	r	CV_R	R	l	o	M	CV_r	r	CV_R	R
			%	mg/kg	%	mg/kg	%	mg/kg		%	mg/kg	%	mg/kg	%	mg/kg
DBP	A	11	8,3	1 014	5,6	159	10,8	306	12	0	10 084	2,5	703	9,9	2 781
BBP	A	11	8,3	999	4,8	134	6,6	185	12	0	10 822	3,4	1 026	9,9	2 999
DEHP	A	11	8,3	1 012	3,7	105	10,1	286	12	0	10 754	4,2	1 250	9,2	2 778
DNOP	A	11	8,3	897	5,5	137	10,4	261	11	8,3	10 660	6,4	1 925	9,5	2 836
DINP	A	11	8,3	1 306	7,8	286	16,9	617	12	0	10 622	5,2	1 546	14,8	4 391
DIDP	A	12	0	1 242	6,6	231	18,1	628	12	0	11 653	7,6	2 492	14,9	4 852

NOTE For definitions of symbols, see Table B.1.

Table B.6 — Summary of the results of the inter-laboratory trial test on samples 11 and 12

Phthalate	Method	PAA coating (sample 11)							PAA coating (sample 12)						
		l	o	M	CV_r	r	CV_R	R	l	o	M	CV_r	r	CV_R	R
			%	mg/kg	%	mg/kg	%	mg/kg		%	mg/kg	%	mg/kg	%	mg/kg
DBP	A	11	8,3	1 022	3,9	112	8,5	243	12	0	9 476	3,7	969	9,0	2 382
BBP	A	11	8,3	1 069	5,3	159	11,3	339	12	0	10 484	3,5	1 017	8,2	2 419
DEHP	A	11	8,3	1 105	7,8	242	11,7	361	12	0	10 762	4,2	1 266	9,6	2 905
DNOP	A	11	8,3	1 186	3,7	123	11,7	389	12	0	10 727	3,2	960	10,4	3 109
DINP	A	10	16,7	1 456	7,3	297	16,3	666	12	0	10 996	8,7	2 689	11,4	3 507
DIDP	A	10	16,7	1 377	7,2	279	12,8	493	12	0	11 093	7,3	2 252	16,6	5 163

NOTE For definitions of symbols, see Table B.1.

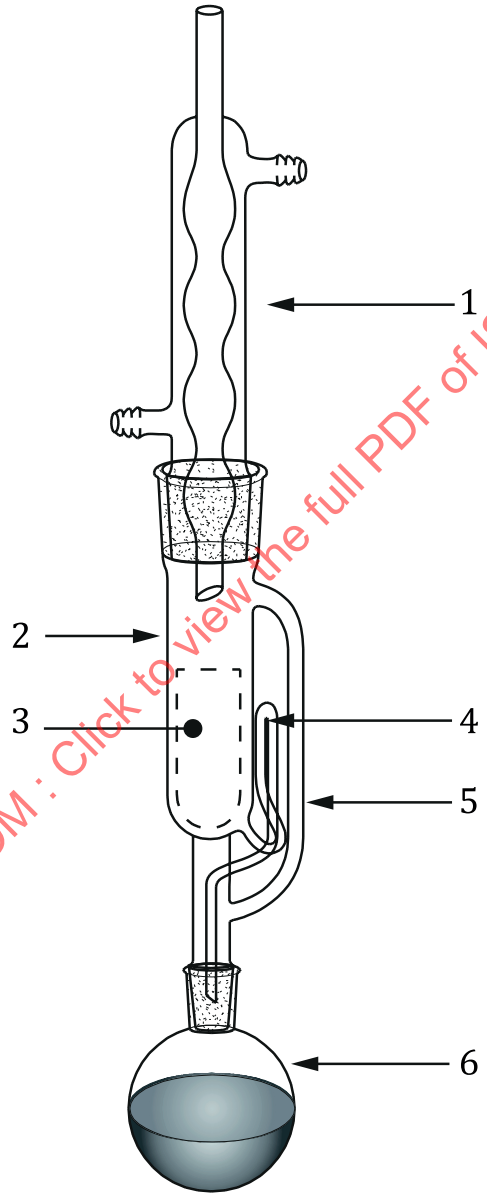
Table B.7 — Summary of the results of the inter-laboratory trial test on samples 13 and 14

Phthalate	Method	NC coating (sample 13)							NC coating (sample 14)						
		l	o	M	CV_r	r	CV_R	R	l	o	M	CV_r	r	CV_R	R
			%	mg/kg	%	mg/kg	%	mg/kg		%	mg/kg	%	mg/kg	%	mg/kg
DBP	A	12	0	985	6,3	174	12,0	332	12	0	9 596	5,3	1 421	9,8	2 640
BBP	A	12	0	1 046	5,1	149	12,3	361	12	0	10 555	4,8	1 433	9,8	2 894
DEHP	A	12	0	1 038	6,2	181	13,3	387	12	0	10 015	4,7	1 313	8,2	2 301
DNOP	A	12	0	1 205	5,9	198	12,0	405	11	8,3	10 948	3,5	1 074	8,2	2 514
DINP	A	12	0	1 501	5,2	218	20,6	867	12	0	11 345	5,3	1 690	9,5	3 031
DIDP	A	11	8,3	1 379	5,7	220	12,7	492	12	0	11 654	8,2	2 676	16,6	5 413

NOTE For definitions of symbols, see Table B.1.

Annex C
(informative)

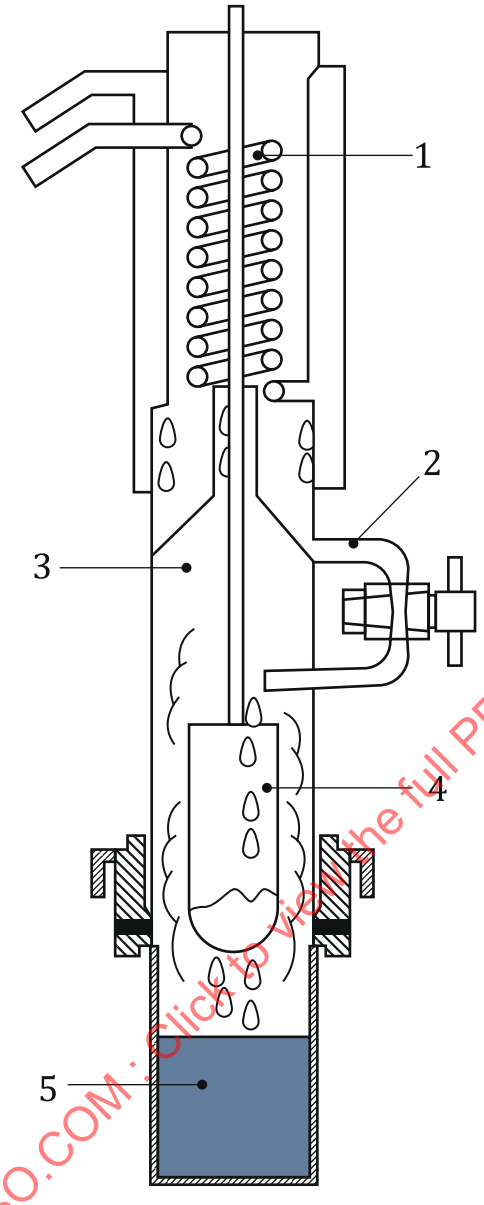
Soxhlet extractor and solvent extractor



Key

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

Figure C.1 — Soxhlet extractor



Key

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

Figure C.2 — Solvent extractor

Annex D
(informative)

Composite test

D.1 Introduction

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

It is important to note that composite testing cannot be used to solve the lack of mass of a test portion. 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.

D.2 Preparation of 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.

D.3 Test procedure

The test procedure specified in Clause 8 of this document can also be applied to composite tests.

D.4 Calculation

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

$$w_{avg} = C \times \frac{V}{m_{tot}} \times D \times \frac{1}{10\,000} \tag{D.1}$$

$$w_{max} = C \times \frac{V}{m_{min}} \times D \times \frac{1}{10\,000} \tag{D.2}$$

where

w_{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_{tot} is the total mass of the composite test portion, in g;

m_{min} is the minimum mass of the individual test portions, in g;

D is the dilution factor.

NOTE The calculation of w_{max} is based on a worst-case assumption that all of the phthalate came from the test portion with the minimum mass.

D.5 Judgement for next action

When the average mass fraction of the target phthalate in the composite test portion (w_{avg}) and the maximum mass fraction of the target phthalate in the individual test portions (w_{max}) have 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 will be judged according to Formula (D.3):

$$L_{act} = L \times F \tag{D.3}$$

where

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

L is the regulated limit, in %;

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

NOTE When $w_{max} < L_{act}$, no further action is needed. When $w_{max} \geq L_{act}$, further action, including individual testing, is needed.

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 historical data accumulated. It is recommended that a safety factor of 60 % is applied based on practical phthalates analysis experience.

D.6 Test report

In addition to the information listed in Clause 12, 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 %.

D.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. The mass of 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. The test result for DEHP in the extracted solution of the composite test portion is 5,90 mg/l.

Formula (D.1) is used to calculate the average mass fraction of the target phthalate in the composite test portion (see Formula (D.4)):

$$w_{avg} = \frac{5,90 \times 25}{0,305\,4 + 0,312\,5 + 0,325\,0} \times \frac{1}{10\,000} = 0,015\,6\ \% \tag{D.4}$$

Formula (D.2) is used to calculate the maximum mass fraction of the target phthalate in the individual test portions (see Formula (D.5)):

$$w_{max} = \frac{5,90 \times 25}{0,305\,4} \times \frac{1}{10\,000} = 0,048\,3\ \% \tag{D.5}$$

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 (0,048 3 %) is below action limit 0,1 % × 0,6 = 0,06 %. No further action is needed, and the test results may be reported as shown in Table D.1.

Table D.1 — Test report of the composite test

Composite test portion no.	Test item	Regulated limit %	Action limit[a] %	w_{avg} %	w_{max} %	Conclusion
1. PVC A/PVC B/PVC C	DEHP	0,1	0,06	0,015 6	0,048 3	Pass
[a] Action limit is calculated with safety factor set at 60 %.						

If the regulated limit for the DEHP is 0,05 % and the safety factor is also set at 60 %, the maximum DEHP content in one of the test portions (0,048 3 %) is above action limit 0,05 × 0,6 = 0,03 %. Each constituent test portion should be tested, and the test results may be reported as shown in Table D.2.

Table D.2 — Test report of the composite test

Composite test portion no.	Test item	Regulated limit %	Action limit[a] %	w_{avg} %	w_{max} %	Conclusion
1. PVC A/PVC B/PVC C	DEHP	0,05	0,03	0,015 6	0,048 3	Individual test
[a] Action limit is calculated with safety factor set at 60 %.						

Annex E
(normative)

Ultrasonic bath performance check

E.1 Overview

Not all ultrasonic baths are suitable for the phthalate extraction in toys and children's products. Select an appropriate one as described in 6.13 and carry out a performance check of the ultrasonic bath periodically. This annex describes the performance check procedure.

E.2 Principle

Ultrasonic transducer creates compression waves in the liquid of the tank, which 'tear' the liquid apart, leaving behind many millions of microscopic 'voids' or 'partial vacuum bubbles' (cavitation). These bubbles collapse with enormous (mechanical) energy which breaks down materials in the liquid into pieces. In this method, ultrasonic waves apply on aluminium foil to force it to form small perforated holes. The intensity of the ultrasonic bath is associated with the perforated rate of the aluminium foil. The performance check of the ultrasonic bath is performed by calculating the perforated rate of the aluminium foil during the ultrasonic process rather than by measuring sound intensity.

E.3 Apparatus

E.3.1 Aluminium foil

Aluminium of minimum 85 % purity, (0,020 ± 0,001) mm in thickness, (185 ± 10) kPa in bursting strength.

Determine the thickness of aluminium foil using a device capable of measuring thickness in accordance with ISO 8124-1:2018, 5.10. Measure the thickness of any sheet at 10 equidistant points across the diagonal.

Determine the bursting strength of aluminium foil using a device capable of measuring bursting strength in accordance with ISO 2758.

E.4 Procedure

1) Spread a piece of aluminium foil on the ultrasonic basket (6.14) and smooth it to avoid wrinkles.

2) Put the basket in the ultrasonic bath, ensuring its underside is about 30 mm to 50 mm above the bath bottom, then fill the ultrasonic bath with water until the aluminium foil is totally immersed. Press the aluminium foil gently to remove the air trapped under the foil if necessary (see Figure E.1 and Figure E.2), then run the ultrasonic bath for 4 min.

3) Keep the aluminium foil smooth and fix it on the basket during the ultrasonic performance check procedure.

4) Take out the aluminium foil and check its perforated holes.

5) Perforated holes can be seen in the aluminium foil, an indicator of the ultrasonic intensity at that position. The larger the hole, the higher the ultrasonic intensity.

6) Calculate the perforated rate of the foil. The fringe area is considered ineffective. The effective area should be at least 25 mm and less than 50 mm away from the four edges of the ultrasonic bath. Divide the effective area into 50 mm × 50 mm squares. Check the squares one by one. A square with one or more holes larger than 5 mm × 5 mm is considered effective. Divide the number of the effective squares by that of the total squares to get the perforated rate. If the perforated rate is greater than 67 %, it can be concluded that the ultrasonic bath has enough ultrasonic intensity and can be used for extraction. See Figure E.4 for an example.

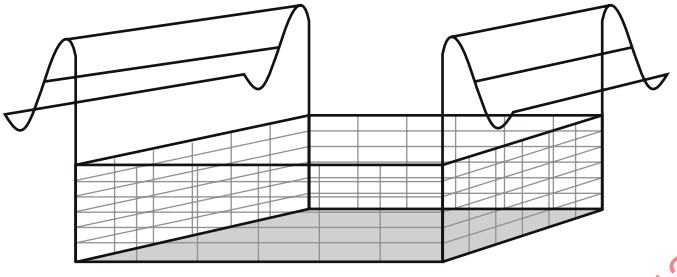


Figure E.1 — Basket covered with aluminium foil

Dimensions in millimetres

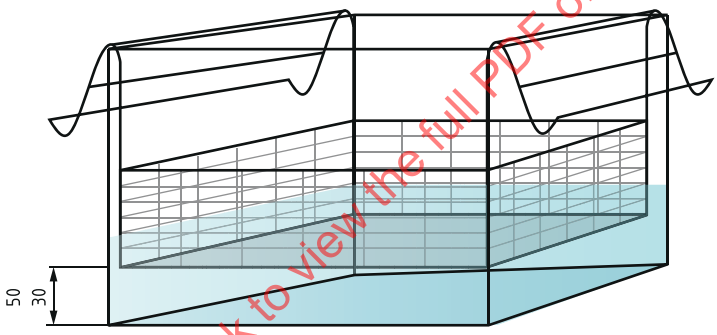
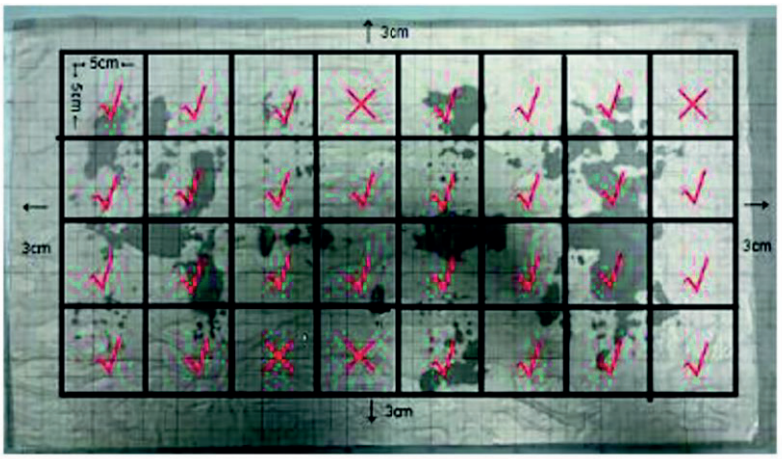


Figure E.2 — Water-filled ultrasonic bath with aluminium foil covering the basket

E.5 Example

The dimensions of the basket for the ultrasonic bath in Figure E.3 are 460 mm × 260 mm. Excluding 30 mm from each side, the effective area for ultrasonic intensity assessment is 400 mm × 200 mm. There are 32 (8 × 4) squares of 50 mm × 50 mm in the foil for hole checking. In Figure E.4, 28 effective squares are found. The perforated rate is therefore calculated as 87,5 % (28/32), which indicates the ultrasonic bath can be used for extraction.

Figure E.3 — Aluminium foil after ultrasonic performance check



Key

✓ effective square

× non-effective square

Figure E.4 — Check the aluminium foil for effective squares

Annex F
(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 F.1 and the chromatograms are shown in Figures F.1 to F.4.

a) Column: DB-5MS capillary column 30 m × 0,25 mm (ID) × 0,25 µm (film thickness).

b) Oven program: $80°C\ (0\,\text{min}) \xrightarrow{30°C/\text{min}} 290°C\ (1\,\text{min}) \xrightarrow{5°C/\text{min}} 300°C\ (3\,\text{min})$

c) Carrier gas: helium, 1 ml/min, constant flow.

d) Injector temperature: 280 °C.

e) Injection: 1,0 µl, split ratio 10:1.

f) Transfer line temperature: 300 °C.

g) Ionization mode: electron ionization (EI), 70 eV; ion source temperature: 230 °C.

h) Mass filter: quadrupole mass filter.

i) Determination: identification by full scan mode (m/z = 50 to 500), quantification by selected ion monitoring (SIM) mode simultaneously, refer to Table F.1 and Figure F.1, Figure F.2, Figure F.3, and Figure F.4.

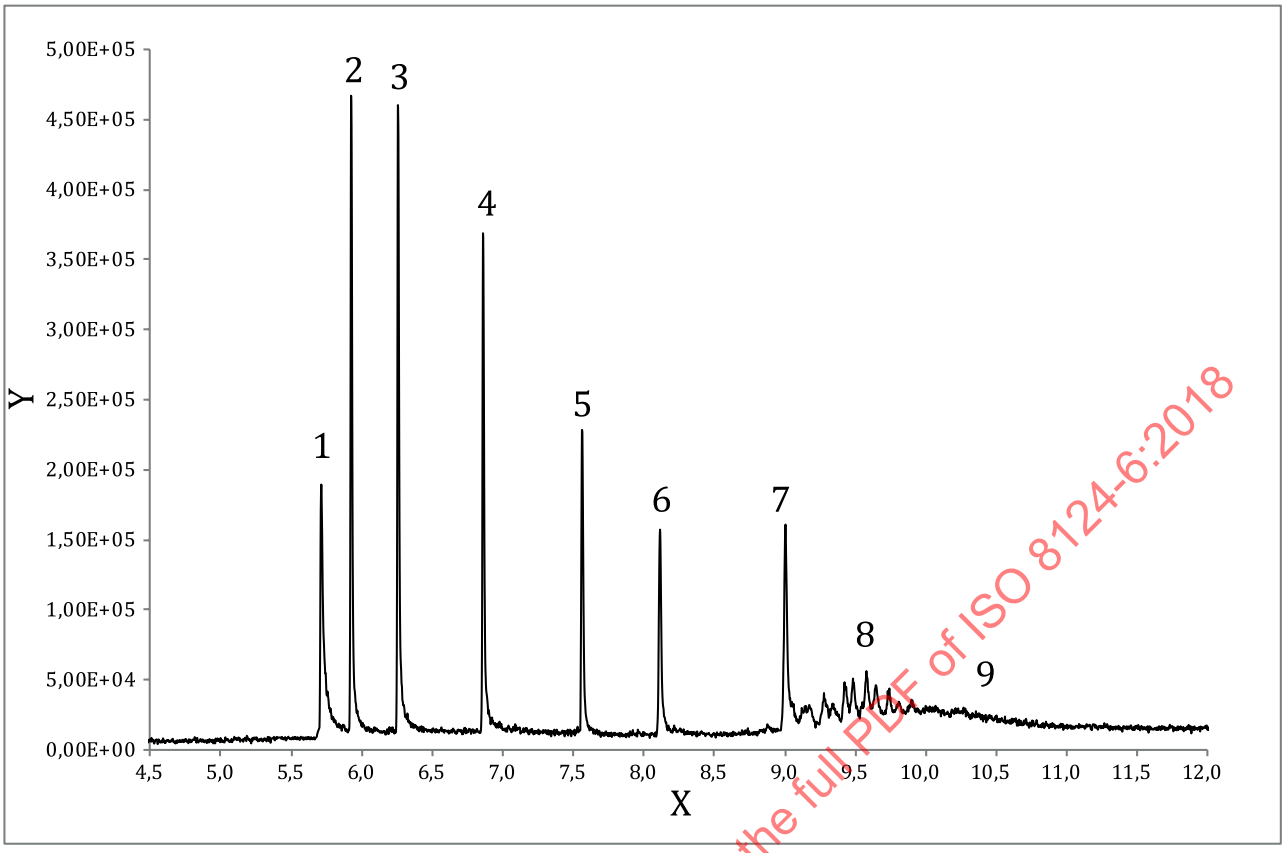
Table F.1 — Retention time and diagnostic ions for chemicals

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

Key

Underlined: the first quantification ions

Italic: the second quantification ions



Key

1 BB
2 DIBP
3 DBP
4 DAP
5 BBP
6 DEHP
7 DNOP
8 DINP
9 DIDP
X abundance
Y time/min

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