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Safety of toys —

Part 6: Certain phthalate esters

Sécurité des jouets —

Partie 6: Certains esters de phtalates

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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 document should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

ISO draws attention to the possibility that the implementation of this document may involve the use of (a) patent(s). ISO takes no position concerning the evidence, validity or applicability of any claimed patent rights in respect thereof. As of the date of publication of this document, ISO had received notice of (a) patent(s) which may be required to implement this document. However, implementers are cautioned that this may not represent the latest information, which may be obtained from the patent database available at www.iso.org/patents. ISO shall not be held responsible for identifying any or all such patent rights.

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

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

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

This third edition cancels and replaces the second edition (ISO 8124-6:2018), which has been technically revised.

The main changes are as follows:

— removal of "children's products" from the title, scope and other parts of this document;

— addition of new definitions for instrument detection limit (3.9) and action limit in (3.11);

— replacement of "4 °C" with "0 °C to 8 °C" in 5.3, 5.4, 5.5.2 and 5.5.3;

— addition of the composite test in 7.3 and 9.2;

— addition of the maximum total mass of composite test portions for the composite test in 8.2.2;

— addition of a clean-up procedure in 8.4.1;

— the volume of the final solution adjusted from 1 ml to 50 ml in 8.4.2.1, 8.4.2.2.1 and 8.4.2.2.2;

— addition of the composite test mathematic model in Annex D;

— addition of a list including other phthalate esters in G.2.

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 does not determine the limits for certain 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 other product categories with materials similar to those of toys. The scope of this document covers various materials used in toys and other product categories.

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 correctly interpreting this document.

Safety of toys —

Part 6:
Certain phthalate esters

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 should be carried out by suitably trained staff.

1 Scope

This document specifies a method standard for the determination of di-*iso*-butyl phthalate (DIBP), 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) in toys. It can also be applied to other phthalate esters (see G.2) if adequate validation is demonstrated.

This document applies to toys made of plastics, textiles, coatings and liquids. This document has been validated for polyvinylchloride (PVC) and polyurethane (PU) plastics and some representative paint coatings (see Annex B).

This document can also be applied to other product categories.

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 8124-1:2022, *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 terminology databases for use in standardization at the following addresses:

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

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

3.1
laboratory sample
toy in the form in which it is marketed or intended to be marketed

3.2
base material
material upon which *coatings* (3.3) may be formed or deposited

[SOURCE: ISO 8124-3:2020, 3.1]

3.3
coating
layers of material formed or deposited on the *base material* (3.2) of toys, 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 8124-3:2020, 3.2]

3.4
scraping
mechanical process for removal of *coatings* (3.3) down to the *base material* (3.2)

[SOURCE: ISO 8124-3:2020, 3.7]

3.5
test portion
portion of homogeneous material taken from a corresponding part of the *laboratory sample* (3.1) for analysis

3.6
composite test portion
mixed *test portion* (3.5) 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* (3.3) are not permitted.

3.7
composite test
test performed on the *composite test portion* (3.6)

3.8
limit of quantification
LOQ
lowest concentration of target in a test sample that can be quantitatively determined with an acceptable level of precision and accuracy under the experimental conditions specified in the method

Note 1 to entry: The LOQ is related to the mass of the *test portion* (3.5) and the final volume of the solvent.

[SOURCE: ISO 15216-1:2017, 3.18, modified — Note 1 to entry revised.]

3.9
instrument detection limit
IDL
lowest concentration at which an instrument can distinguish the presence of analyte from the background generated by a matrix, such as a reagent blank, having a minimal amount of analyte

[SOURCE: ISO 18158:2016, 2.3.5, modified — Definition revised.]

3.10
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.

3.11
action limit
acceptable *limit of quantification* (3.8) that, if exceeded, requires further individual tests

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 Registry Number®[1] (CAS No.) 75-09-2, analytical grade or higher, free of phthalate esters.

5.2 Phthalate esters 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 each of DIBP, DBP, BBP, DEHP and DNOP and 500 mg/l each of DINP and DIDP in dichloromethane (5.1).

Stock solution should be properly stored at 0 °C to 8 °C to prevent change of concentration. It is recommended that these solutions be prepared at least every three months.

5.4 External standard (ES) calibration solutions

A series of calibration standard solutions (of at least five equidistant calibrations in the range of 0,2 mg/l to 10 mg/l for DIBP, DBP, BBP, DEHP and DNOP, 1 mg/l to 50 mg/l for DINP and DIDP) are prepared by transferring 0,1 ml to 5 ml of the stock solution (5.3) to a series of 50 ml volumetric flasks and making up to the mark with dichloromethane.

Calibration standard solutions should be properly stored at 0 °C to 8 °C to prevent change of concentration. It is recommended that these solutions 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 phthalate esters, can be used as alternative internal reference substances.

5.5.2 Internal standard stock solution

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

IS solutions should be properly stored at 0 °C to 8 °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 0,2 mg/l to 10 mg/l for DIBP, DBP, BBP, DEHP and DNOP, 1 mg/l to 50 mg/l for DINP and DIDP) are prepared by transferring 0,1 ml to 5 ml of the stock solution (5.3) to a series of 50 ml volumetric flasks

1) Chemical Abstracts Service (CAS) Registry Number® is a trademark of the American Chemical Society (ACS). This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

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 0 °C to 8 °C to prevent change of concentration. It is recommended that these solutions be prepared at least monthly.

6 Apparatus

6.1 General

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.

6.2 Normal laboratory apparatus

6.2.1 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.

6.2.2 Soxhlet extractor, see Figure C.1.

6.2.3 Solvent extractor, see Figure C.2.

6.2.4 Extraction thimble, made of cellulose.

6.2.5 Cotton wool, for extraction thimble.

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

6.2.7 Concentration apparatus, for example a rotary evaporator.

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

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

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

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

6.2.12 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 shall be 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 provide an effective ultrasonic power intensity of 0,50 W/cm^2 (=200 W/400 cm^2).

6.2.13 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.

6.2.14 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.

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

7 Selection of test portions

7.1 General

Individual test for one test portion and composite test for multiple test portions are used in this document.

7.2 Individual test

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

For liquid materials, use an 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.

Analysis of toy materials present in amounts less than 0,010 g is not required.

NOTE The requirement does not preclude the taking of test portions from materials used to manufacture the toy, provided they are representative of the final toy.

7.3 Composite test

When used properly, the composite test can reduce costs and improve efficiency without affecting the accuracy of the test. A composite test used for quantitative assessment shall meet all the following conditions:

a) 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).

b) Similar masses shall be weighed for each constituent test portion. The mass between any two constituent test portions should not differ by more than 10 %.

c) The limit of quantification (LOQ) of target phthalate esters is lower than 50 mg/kg.

When a composite test is used for the quantitative assessment, the number of the constituent test portions (K) shall be less than or equal to 3 (i.e. $K \leq 3$). Composite tests with K more than 3 can be performed with reference to Annex D.

A composite test is used for judging conformity with requirements. If the result of the composite test is above the action limits, further individual tests are needed.

NOTE Composite testing cannot be used to solve the problem of insufficient mass of a test portion. If the mass of a constituent test portion is not enough to perform an individual test, it is impossible to get a representative result via composite testing.

8 Procedure

8.1 General

Except for 8.2, the following procedures are applicable to both the individual test and the composite test.

8.2 Sample weighing

8.2.1 Individual test

In general, weigh to the nearest 1 mg approximately 1 g of a single test portion into an extraction thimble (6.2.4) or airtight glass reaction vessel (6.2.14). If 1 g test portion cannot be obtained from a single laboratory sample, then as many test portions as possible shall be taken from multiple laboratory samples; 0,05 g is recommended as a minimum test portion.

8.2.2 Composite test

The total amount of all composite test portions shall not exceed 2 g. The mass deviation of each constituent test portion should not exceed 10 %. The mass of constituent test portions shall be recorded and used for subsequent calculation.

8.3 Extraction

8.3.1 General

Three options of extraction procedures, Method A (8.3.2), Method B (8.3.3) and Method C (8.3.4), are described. Laboratories can select the most suitable one at their discretion.

8.3.2 Method A

Place the thimble with the test portion into a 250-ml Soxhlet extractor (6.2.2). In order to prevent the sample from floating, add cotton wool (6.2.5) 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 (6.2.7), 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 the loss of phthalate esters.

8.3.3 Method B

Place the thimble with the test portion into the solvent extractor (6.2.3). In order to prevent the sample from floating, add cotton wool (6.2.5) 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 the loss of phthalate esters.

8.3.4 Method C

8.3.4.1 For solid materials

Add 25 ml of dichloromethane to the sample in the airtight glass reaction vessel (6.2.14). 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 (8.3.2) or Method B (8.3.3) could be preferable.

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

8.3.4.2 For liquid materials

Add 15 ml of dichloromethane to the sample in the airtight glass reaction vessel (6.2.14). Place the vessel in an ultrasonic bath with an initial temperature of 60 °C for 60 min.

8.4 Sample solution for analysis

8.4.1 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 8.3.2, 8.3.3 or 8.3.4, where appropriate, with PTFE membrane filter (6.2.11) for GC-MS (6.2) analysis. Two options of quantification procedures, ES calibration (8.4.2) and IS calibration (8.4.3), are described in this subclause. Laboratories can select the most suitable one at their discretion.

When the extract exhibits turbidity before filtration and a sufficient volume for GC-MS analysis is difficult to obtain, three options of additional treatment are described. Laboratories can select one or more suitable option(s) at their discretion:

a) Precipitate any polymer with acetonitrile or hexane and shake vigorously, then allow at least 5 min for the polymer to settle.

b) Centrifuge at up to 5 000 g (6.2.15).

c) Purify the solution with a pretreated SPE cartridge (6.2.8), which is pretreated with approximately 10 ml of dichloromethane before purification, discard the effluent, rinse the cartridge with 3 ml of dichloromethane three times and collect the eluate.

8.4.2 Quantification by external standard (ES) calibration

8.4.2.1 Method A and Method B

Transfer the extract or the eluate into an appropriately sized volumetric flask and make up to the mark with dichloromethane for GC-MS analysis.

The final solution may be adjusted to obtain a volume between 1 ml and 50 ml according to the mass of the tested specimen. Care should be taken not to affect the LOQ (10.1) and operability.

8.4.2.2 Method C

8.4.2.2.1 For solid materials

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

The final solution may be adjusted to obtain a volume between 1 ml and 50 ml, according to the mass of the tested specimen. Care should be taken not to affect the LOQ (10.1) and operability.

8.4.2.2.2 For liquid materials

Transfer the extract or the eluate into an appropriately sized volumetric flask and make up to the mark with dichloromethane for GC-MS analysis.

The final solution may be adjusted to obtain a volume between 1 ml and 50 ml, according to the mass of the tested specimen. Care should be taken not to affect the LOQ (10.1) and operability.

8.4.3 Quantification by IS calibration

For Method A or Method B, transfer the extract or the eluate and a certain volume of the IS stock solution (5.5.2) into an appropriately sized 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).

8.5 Determination

8.5.1 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 programme.

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.

8.5.2 Identification

Identify the compound by matching both retention times and relative intensities of the diagnostic ions of the test solution and the 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 ± 0,1 minute.

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, di-propyl-heptyl 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 %

8.5.3 Calibration

8.5.3.1 General

Two optional calibration methods, ES (8.5.3.2) and IS (8.5.3.3), are described in this subclause. Either ES or IS can be used for calibration. Laboratories can choose the most suitable calibration method according to their best practice (see Annex C).

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 to the isomeric ratio to the phthalate esters 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.

8.5.3.2 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):

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

where

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

a_1 is the slope of the calibration curve;

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

b_1 is the ordinate intercept of the calibration curve.

8.5.3.3 Internal standard (IS) calibration

Integrate the peak areas of the target quantification ions (see Table F.1) in the chromatogram 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 ester 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 ester 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 10 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 Individual test

9.1.1 External standard (ES) calculation

Calculate the concentration of the individual phthalate ester in the test portion by using Formula (3) based on 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 ester found in the test portion, in %;

A is the peak area or sum of peak areas of the individual phthalate ester 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 should be expressed as a mass percentage (%) and reported with three significant figures or three decimal places.

The response values of phthalate ester in the calibration solutions and test solution should be within the linear range of instrument detection. If the response value is out of the range, further dilution or pre-concentration is needed with dichloromethane.

9.1.2 Internal standard (IS) calculation

Calculate the concentration of the individual phthalate ester in the test portion by using Formula (4) based on 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 ester found in the test portion, in %;

A is the peak area or sum of peak areas of the individual phthalate ester 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 as a mass percentage (%) and reported with three significant figures or with three decimal places.

The response values of phthalate ester in the calibration solutions and test solution should be within the linear range of instrument detection. If the response value is out of the range, further dilution or pre-concentration is needed.

9.2 Composite test

9.2.1 Maximum concentration calculation

For both ES and IS calculations, the maximum concentration (w_{max}) of the target phthalate ester in the composite test portions can be calculated using Formula (5). The maximum concentration (w_{max}) is used to determine whether a further individual test is needed.

$$w_{max} = C \times \frac{V}{m_{min}} \times D \times \frac{1}{10\,000} \quad (5)$$

where

w_{max} is the maximum concentration of the target phthalate esters in the composite test portions in %;

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

V is the volume of the final solution in ml;

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

D is the dilution factor.

NOTE The w_{max} calculation assumes that all determined phthalate esters come from the constituent test portion with minimum mass in the worst case.

9.2.2 Conformity assessment of the composite test result

When the maximum concentration (w_{max}) of the target phthalate ester(s) in the composite test has been calculated, a safety factor (F) shall be introduced to account for the uncertainty of the composite test to ensure all the non-conforming materials can be correctly identified, and the action limit is generated using Formula (6):

$$L_{act} = L \times F \quad (6)$$

where

L_{act} is the action limit in %;

L is the limit for the phthalate ester(s) in %;

F is the safety factor of the limit.

When K ≤ 3, F = 0,8 is recommended.

NOTE The safety factor of 0,8 for phthalate esters is based on practical experience considering multiple uncertainty factors such as mass deviation and possible mutual influence. When K > 3, the laboratory can determine the safety factor based on the uncertainty from the composite test.

When $w_{max} < L_{act}$, each test portion in the composite sample can be considered conforming and no further test is required. When $w_{max} \geq L_{act}$, the result is inconclusive and all test portions in the composite sample should be tested individually.

9.2.3 Examples of composite testing

9.2.3.1 Scenario A: Composite of three test portions for single phthalate requirement (Pass case)

When the masses of three PVC plastic test portions (A, B and C) are 0,305 4, 0,312 5 and 0,325 0 g, and the final volume for the extraction solution of the composite test portion is 25 ml, the concentration of DEHP in the extracted solution of the composite test is 5,90 mg/l by GC-MS.

The maximum concentration of DEHP in one test portion (w_{max}) can be calculated by Formula (5), which is 0,048 %.

If the regulation limit for DEHP is 0,1 % and the safety factor is set at 0,8, the maximum DEHP concentration in one test portion (0,048 %) is lower than the action limit (0,1 % × 0,8 = 0,08 %), indicating that further individual test is not needed and the comforming conclusion can be drawn directly. The test results can be reported as shown in Table 2.

Table 2 — Reference data for scenario A

Composite test portion no.	Test item	Limit %	Action limit %	w_{max} %	Conclusion
PVC A/PVC B/PVC C	DEHP	0,1	0,08	0,048	Pass

9.2.3.2 Scenario B: composite of three test portions for single phthalate requirement (inconclusive; further individual test required)

When the masses of three PVC plastic test portions (A, B and C) are 0,305 4, 0,312 5 and 0,325 0 g, and the final volume for the extraction solution of the composite test portion is 25 ml, the concentration of DEHP in the extracted solution of the composite test is 5,90 mg/l by GC-MS.

The maximum concentration of DEHP in one test portion (w_{max}) can be calculated by Formula (5), which is 0,048 %.

If the limit for DEHP is 0,05 % and the safety factor is set at 0,8, the maximum DEHP concentration in one test portion (0,048 %) is higher than the action limit (0,05 % × 0,8 = 0,04 %), indicating that further individual test is required. The test results can be reported as shown in Table 3.

Table 3 — Reference data for scenario B

Composite test portion no.	Test item	Limit %	Action limit %	w_{max} %	Conclusion
PVC A/PVC B/PVC C	DEHP	0,05	0,04	0,048	Inconclusive; further individual test needed

9.2.3.3 Scenario C: composite of three test portions for sum of three phthalates requirement (pass case)

When the masses of three PVC plastic test portions (A, B and C) are 0,305 4, 0,312 5 and 0,325 0 g, and the final volume for the extraction solutions of the composite test portion is 25 ml, the sum of DINP, DIDP and DNOP concentrations in the extracted solution of the composite test is 4,4 mg/l by GC-MS.

The maximum concentration of the sum of DINP, DIDP and DNOP in one test portion (w_{max}) can be calculated by Formula (5), which is 0,036 %.

If the limit for the sum of DINP, DIDP and DNOP is 0,1 % and the safety factor is set at 0,8, the maximum concentration in one test portion (0,036 %) is lower than the action limit (0,1 % × 0,8 = 0,08 %),

indicating that further individual test is not needed and the conclusion can be drawn directly. The test results can be reported as shown in Table 4.

Table 4 — Reference data for scenario C

Composite test portion no.	Test item	Regulation limit %	Action limit %	w_{max} %	Conclusion
PVC A/PVC B/ PVC C	Sum of DINP, DIDP and DNOP	0,1	0,08	0,036	Pass

10 Quality control

10.1 Limit of quantification (LOQ)

LOQs of the individual phthalate ester are listed as follows for reference, derived from a 1 g test portion in 25 ml dichloromethane.

For DIBP, DBP, BBP, DEHP, DNOP: 5 mg/kg.

For DINP, DIDP: 25 mg/kg.

NOTE The value of LOQ is related to mass and volume and these LOQs are derived from the specified mass and volume. Adjustments in mass and volume can generate different LOQs.

10.2 Method blank

A method blank (3.10) 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 ester 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 batch to demonstrate the stability of the GC-MS. The deviation of each phthalate ester should be within 15 % of the expected value.

11 Precision

The precision of this method 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 8124-6:2023);

b) a complete identification of the product and material tested, and the composite group size (K) used if the composite test was done;

c) a reference to the grouping scenario used if the composite test was done;

d) a reference to the extraction procedure used;

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

f) the individual phthalate ester test result with unit or the maximum possible phthalate ester test result with unit, if the composite test was done, and the measurement uncertainty (if required to assist in the interpretation of the results);

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

h) any deviations from the procedure specified;

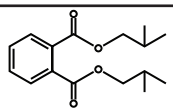
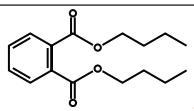
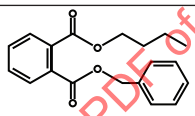
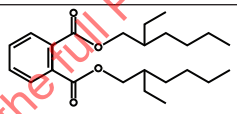
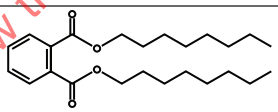
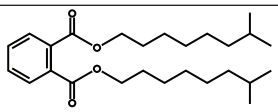
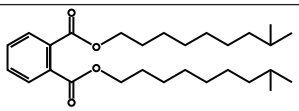
i) any unusual features observed during the test;

j) the date of the test.

Annex A
(normative)

Phthalate esters

Table A.1 — Phthalate esters

No.	Phthalate esters (initialism)	CAS No.	Structure formulae[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] Only one of the isomeric structural formulae of DINP and DIDP is listed.

[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 interlaboratory 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 containing 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 interlaboratory trial test on samples 1 and 2

Phthalate esters	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	15	0	2 441	2,1	146	7,3	499	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	15	0	2 005	3,1	174	8,9	501	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	15	0	3 694	2,5	255	8,2	846	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	9	0	2 103	2,4	139	9,4	552	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	8	0	3 297	6,1	567	15,4	1 424	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	8	0	2 445	4,9	333	14,0	961	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 interlaboratory trial test on samples 3 and 4

Phthalate esters	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 interlaboratory trial test on samples 5 and 6

Phthalate esters	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 interlaboratory trial test on samples 7 and 8

Phthalate esters	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	–	–	–	–	–
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 interlaboratory trial test on samples 9 and 10

Phthalate esters	Method	Coating containing PVC (sample 9)							Coating containing PVC (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 interlaboratory trial test on samples 11 and 12

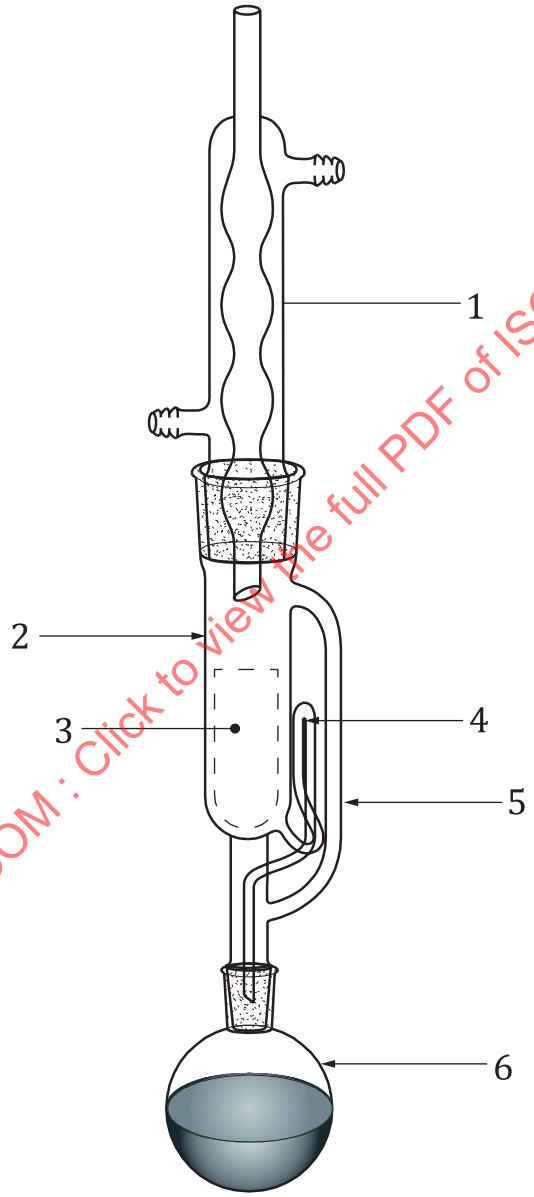
Phthalate esters	Method	Coating containing PAA (sample 11)							Coating containing PAA (sample 12)						
		l	o	M	CV_r	r	CV_R	R	l	o	M	CV_r	r	CV_R	R
			%	mg/kg	%	mg/kg	%	mg/kg		%	mg/kg	%	mg/kg	%	mg/kg
DBP	A	11	8,3	1 022	3,9	112	8,5	243	12	0	9 476	3,7	969	9,0	2 382
BBP	A	11	8,3	1 069	5,3	159	11,3	339	12	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 interlaboratory trial test on samples 13 and 14

Phthalate esters	Method	Coating containing NC (sample 13)							Coating containing NC (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)

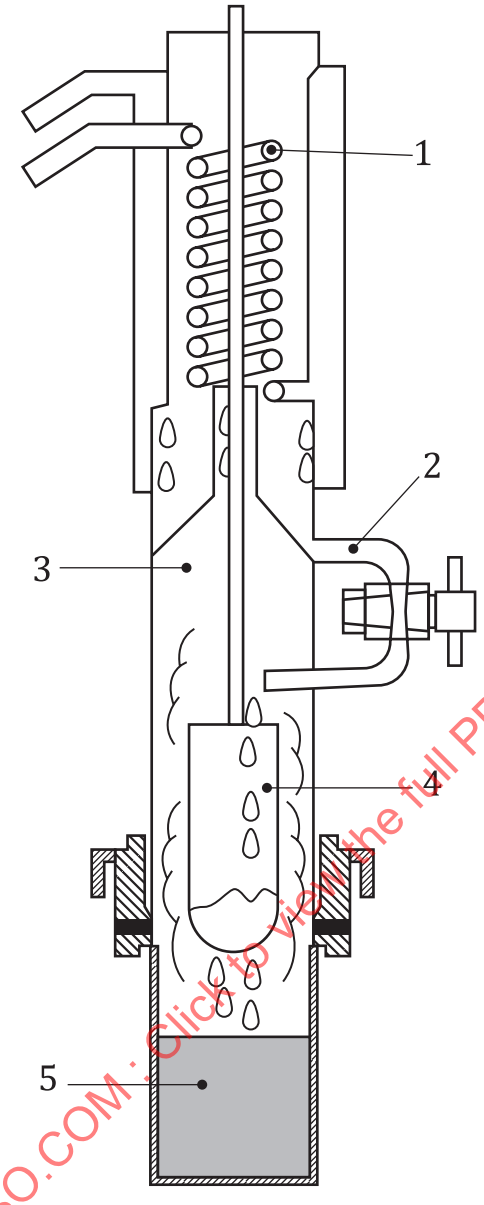
Soxhlet extractor and solvent extractor



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

A large number of test results obtained from the toys and children's products industry show that the unqualified rate is low. Furthermore, the LOQ of the phthalate esters test is relatively low compared with the limit, ensuring the feasibility of composite tests.

The composite test method includes mixing different test portions into a group and testing them. If the result of the composite group passes, all test portions pass and only one test is performed. Otherwise, the test portions of the composite group need to be individually tested. Thus, a total of K+1 tests are performed (K is the number of test portions in the composite group). Composite testing is designed to reduce testing costs and increase efficiency without reducing test accuracy.

The theoretical basis and rules of composite tests are introduced in this annex.

D.2 Assumption

The composite test in this annex is based on the following assumptions:

a) The interference among test portions in one composite group is not considered.

b) The rare case where detectable levels of phthalate esters are present in multiple composite test portions in one composite group is not considered.

c) A test portion will not contain more than four phthalate esters.

It is important to note that composite testing cannot solve the problem of insufficient mass of a test portion. If the mass of a test portion is not enough for an individual test, it cannot be used for a composite test either.

When there are detectable levels of phthalate esters in most test portions of a composite group, it is recommended that the number of test portions in the group is reduced or individual tests are performed.

D.3 Determination of K_a of the composite group

D.3.1 General

Two aspects should be considered to determine the appropriate number of test portions (K_a) in a composite group:

a) The maximum composite group number (K_{max}) based on the limit, LOQ and measurement uncertainty. The calculation method of K_{max} is described in D.3.2.

b) The optimal composite group number (K_{opt}) to minimize the total tests based on the qualified rate. The calculation method of K_{opt} is described in D.3.3.

The final appropriate number(K_a) of test portions in a composite group should be the smaller of K_{max} and $K_{opt.}$

D.3.2 Determination of K_{max}

The maximum number of composite test portions (K_{max}) is affected by measurement errors in the composite test. The calculation of K_{max} should comprehensively analyse the factors that affect the precision of the composite test results. These factors involve L (limits), I (the number of related phthalate esters in the limit), LOQ and instrument detection limit (IDL). Compared with the individual test, composite tests can lead to more errors. The procedures to determine the maximum number of tests (K_{max}) are elaborated in Formula (D.1).

$$K_{max} = \frac{L \times (1 - U_{rel})}{Q_{M,max} \times I} \times F \quad \text{(D.1)}$$

$$Q_{M,max} = \frac{Q_{I,max} \times V}{m_{min}} \quad \text{(D.2)}$$

where

K_{max} is the maximum number of composite test portions, rounding down;

L is the limit for tested phthalate ester(s) in %;

U_{rel} is the relative expanded uncertainty near the regulated limit in %;

$Q_{M,max}$ is the maximum LOQ value among all LOQs of tested phthalate ester(s) and can be estimated using Formula (D.2);

NOTE 1 If L is the sum of three test items (e.g. DINP, DNOP and DIDP), $Q_{M,max}$ is the maximum LOQ of DINP, DNOP and DIDP.

$Q_{I,max}$ is the maximum IDL among all IDLs of tested phthalate esters;

V is the final volume of the composite test solution;

m_{min} is the minimum mass of test portions in the composite test;

F is the safety factor of the limit;

I is the number of test items (phthalate esters) corresponding to the limit.

NOTE 2 If L is the limit of the sum of three phthalate esters of DINP, DNOP and DIDP, then $I = 3$.

If the information on the limit, LOQ, and measurement uncertainty is available, K_{max} can be calculated using Formula (D.1).

For convenience, K_{max} can be obtained according to $Q_{M,max}$, I and U_{rel} listed in Table D.1.

Table D.1 — Determination of the maximum number of test portions in the composite group (K_{max})

$Q_{M,max}$ mg/kg		$Q_{M,max} \leq 10$				$10 < Q_{M,max} \leq 30$				$30 < Q_{M,max} \leq 50$			
I		1	2	3	≥ 4	1	2	3	≥ 4	1	2	3	≥ 4
U_{rel} %	$U_{rel} \leq 15$	10 (59)	10 (29)	10 (19)	10 (14)	10 (19)	9	6	4	10 (11)	5	3	–
	$15 < U_{rel} \leq 20$	10 (56)	10 (28)	10 (18)	10 (14)	10 (18)	9	6	4	10 (11)	5	3	–
	$20 < U_{rel} \leq 25$	10 (52)	10 (26)	10 (17)	10 (13)	10 (17)	8	5	4	10	5	3	–
	$25 < U_{rel} \leq 30$	10 (49)	10 (24)	10 (16)	10 (12)	10 (16)	8	5	4	9	4	3	–

NOTE 1 The K_{max} in Table D.1 is calculated based on the general limit (L) = 0,1 % and safety factor (F) = 0,7.

NOTE 2 The number of phthalate esters in one test portion is limited to no more than 4.

NOTE 3 "–" is not applicable for composite tests under this condition.

NOTE 4 If $Q_{M,max}$ > 50 mg/kg, an individual test is recommended.

NOTE 5 The numbers in parentheses are the K_{max} values calculated by Formula (D.1). However, considering practical constraints, the K_{max} is limited to 10.

D.3.3 Determination of the K_{opt}

It is supposed that the qualified rate of a batch of test portions is q, the number of test portions in a batch is n and the number of test portions in each composite group is K. The "pass" probability of the composite group is q^K–Z(see Table D.2), and the "inconclusive" probability is (1–q^K+Z). If the test result of the composite group passes, only one test is performed. Otherwise, each test portion in the composite group needs to be individually tested and the total number of tests is K+1. These procedures for determining the number of tests are summarized in Table D.2 and Formula (D.4).

Table D.2 — Probability distribution of composite test

Test result	Number of testing for one composite group	Probability	Total number of testing
"Pass"; without individual test needed	1	q^K–Z	$1\times\left(q^K - Z\right)\times\frac{n}{K}$
"Inconclusive"; with individual test needed	1+K	1–q^K+Z	$(K+1)\times\left(1-q^K+Z\right)\times\frac{n}{K}$

Key

q qualified rate

Z probability that a composite group consists of all qualified test portions, but its test result is higher than the action limit

K number of composite test portions in each group, which is an integer ≥ 2

n total number of test portions in one batch

Since phthalate ester is an intentional additive in high concentration (%), targeted phthalate ester with detectable concentrations in a batch is rare, which means that Z is far smaller than q^K. In this case, the probability of Z can be ignored, and the calculation of the total number of tests (N) in one batch can be simplified as shown in Formula (D.3):

$$N = 1\times q^K \times\frac{n}{K} + (K+1)\times\left(1-q^K\right)\times\frac{n}{K} \tag{D.3}$$

where N is the total number of tests in a batch.

The testing workload (S) is reduced when $N < n$, as shown in Formula (D.4).

$$S = 1 - \frac{N}{n} = 1 - \frac{n\left(1 - q^K + \frac{1}{K}\right)}{n} = q^K - \frac{1}{K} \tag{D.4}$$

where S is the saved testing workload: 1 minus the total number of tests in composite testing (N) divided by the number of single tests in the batch (n).

Table D.3 and Figure D.1 show the relationship between S, q and K. The K corresponding to the maximum S is the K_{opt} that can minimize the total number of tests.

Table D.3 — Saved workload of the composite test in different qualified rates

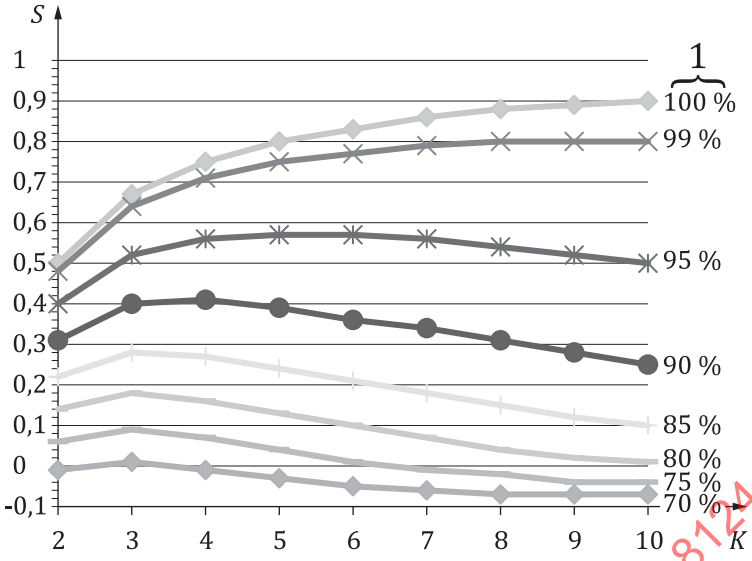
Qualified rate q	Number of composite test portions in each group K								
	2	3	4	5	6	7	8	9	10
100 %	0,50[a]	0,67	0,75	0,80	0,83	0,86	0,88	0,89	0,90
99,9 %	0,50	0,66	0,75	0,80	0,83	0,85	0,87	0,88	0,89
99,5 %	0,49	0,65	0,73	0,78	0,80	0,82	0,84	0,84	0,85
99 %	0,48	0,64	0,71	0,75	0,77	0,79	0,80	0,80	0,80
95 %	0,40	0,52	0,56	0,57	0,57	0,56	0,54	0,52	0,50
90 %	0,31	0,40	0,41[b]	0,39	0,36	0,34	0,31	0,28	0,25
85 %	0,22	0,28	0,27	0,24	0,21	0,18	0,15	0,12	0,10
80 %	0,14	0,18	0,16	0,13	0,10	0,07	0,04	0,02	0,01
75 %	0,06	0,09	0,07	0,04	0,01	−0,01	−0,02	−0,04	−0,04
70 %	−0,01	0,01[c]	−0,01	−0,03	−0,05	−0,06	−0,07	−0,07	−0,07[c]
69 %[d]	−0,02	0,00	−0,02	−0,04	−0,06	−0,07	−0,07	−0,08	−0,08

[a] When q is 100 % and K is 2, S is 0,5 and saves half of the workload.

[b] When q is 90 % and K is 4, S is 0,41 and reaches its maximum.

[c] When q is 70 %, the highest efficiency can be achieved only when the composite number is three ($K = 3$), but only 1 % of the workloads can be saved. With the same time, if K is 10, the workload will increase by 7 %.

[d] When q is less than 70 %, no matter what the composite number is, it cannot reduce the workload.



Key

S saved testing workload

K number of composite test portions in a group

1 qualified rate

Figure D.1 — Saved workload of the composite test in different qualified rates

For convenience, the K_{opt} and its saved workload in the typical qualified rates calculated by Formula (D.4) are shown in Table D.4.

Table D.4 — S_{max} and K_{opt} in different qualified rates

Qualified rate q	S_{max}	K_{opt}	Qualified rate q	S_{max}	K_{opt}
100 %	1,000	∞	85,0 %	0,281	3
99,9 %	0,937	32	80,0 %	0,179	3
99,5 %	0,861	15	75,0 %	0,089	3
99,0 %	0,804	11	70,0 %	0,010	3
95,0 %	0,574	5	69,0 %	0,000	single test
90,0 %	0,406	4			

Considering practical conditions, there are no benefits to performing composite tests for samples with q lower than 80 %. The corresponding optimal group size is shown in Table D.5 for the most common q ranging from 80 % to 100 %.

Table D.5 — Determination of the composite group size (K_{opt}) with the common qualified rates range

q	99,0 % ≤ q	95,0 % ≤ q < 99,0 %	90,0 % ≤ q < 95,0 %	80,0 % ≤ q < 90,0 %
K_{opt}	11	5	4	3

D.3.4 Determination of K_a

The K_a is the appropriate number of test portions in the composite group. The K_a should be the smaller of K_{max} and K_{opt}.

D.3.5 Examples of K_a determination

D.3.5.1 Scenario A

Description: A DEHP is regulated at 0,1 % with U_{rel} = 14 % and $Q_{M,max}$ = 2,4 mg/kg.

— Limit of DEHP < 0,1 %. The number of test items corresponding to the amount I is 1.

— The total mass of the composite test portions is 1 g, the final volume of the composite test is 25 ml and $Q_{M,max}$ of DEHP is 2,4 mg/kg.

— The relative expansion uncertainty of DEHP (U_{rel}), which is close to the limit, is 14 %.

— The qualified rate of the test portions in batch q is 99 %.

The following steps are used to determine K_a:

Step 1: q = 99 %, K_{opt} = 11 is found in Table D.5.

Step 2: I = 1, U_{rel} = 14 % and $Q_{M,max}$ = 2,4 mg/kg, K_{max} = 10 is found in Table D.1.

Step 3: the final composite group size $K_a = \min(K_{max}, K_{opt})$ is 10.

D.3.5.2 Scenario B

Description: Three phthalate esters are regulated at 0,1 %, with U_{rel} = 21 % and $Q_{M,max}$ = 41 mg/kg.

— Limit: sum of DNOP, DINP and DIDP < 0,1 %. The number of test items corresponding to the amount I is 3.

— The total mass of the composite test portions is 1 g, the final volume of the composite test is 25 ml and $Q_{M,max}$ of DNOP, DINP and DIDP is 41 mg/kg.

— The relative expansion uncertainty of DEHP (U_{rel}), which is close to the limit, is 14 %.

— The qualified rate of the test portions in batch q is 95 %.

The following steps are used to determine K_a:

Step 1: q = 95 %, K_{opt} = 5 is found in Table D.5.

Step 2: I = 3, U_{rel} = 21 % and $Q_{M,max}$ = 40 mg/kg, K_{max} = 3 is found in Table D.1.

Step 3: the final composite group size $K_a = \min(K_{max}, K_{opt})$ is 3.

D.3.5.3 Scenario C

Description: Three phthalate esters are regulated at 0,1 % with U_{rel} = 26 % and $Q_{M,max}$ = 68 mg/kg.

— Limit: sum of DNOP, DINP and DIDP < 0,1 %. The number of test items corresponding to the amount I is 3.

— The total mass of the composite test portions is 1 g, the final volume of the composite test is 25 ml and $Q_{M,max}$ of DNOP, DINP and DIDP is 68 mg/kg.

— The relative expansion uncertainty of DEHP (U_{rel}), which is close to the limit, is 26 %.

— The qualified rate of the test portions in batch q is 95 %.

The following steps are used to determine K_a:

Step 1: q = 95 %, K_{opt} = 5 is found in Table D.5.

Step 2: I = 3, U_{rel} = 26 % and $Q_{M,max}$ = 68 mg/kg, K_{max} = "–" is found in Table D.1 and means that the composite test is not applicable.

Step 3: individual tests need to be performed in this case.

D.4 Test procedure

The test procedure specified in Clause 8 can be applied to composite tests.

D.5 Identification of the composite test

The calculation and identification of the composite test result can refer to 9.2.2.

Annex E
(normative)

Ultrasonic bath performance check

E.1 Overview

Not all ultrasonic baths are suitable for the phthalate esters extraction in toys and children's products. Select an appropriate ultrasonic bath as described in 6.2.12 and carry out a performance check on it periodically. This annex describes the performance check procedure.

E.2 Principle

The 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, 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 the thickness in accordance with ISO 8124-1:2022, 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 (6.2.13) 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, and 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 is.

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 effective squares by the number 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.

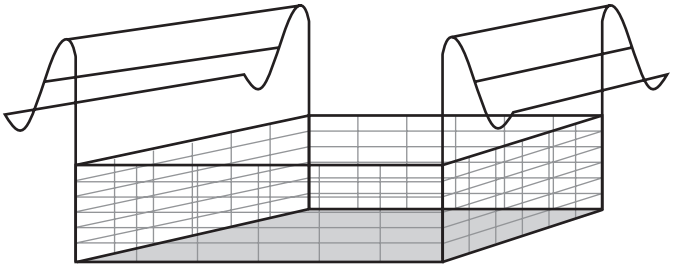


Figure E.1 — Basket covered with aluminium foil

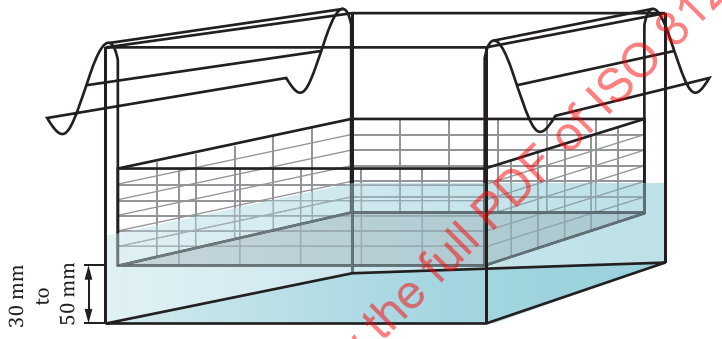
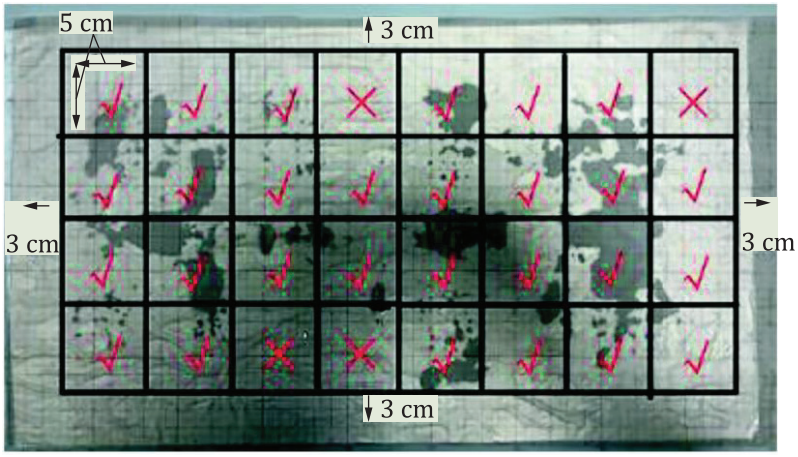


Figure E.2 — Water-filled ultrasonic bath with aluminium foil covering the basket

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 that 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