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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*.

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

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

The main changes compared to ISO 8124-6:2018 are as follows:

— addition of a new definition for instrument detection limit in (3.9);

— replacement of “4 °C” with “0 °C to 8 °C” in (5.3, 5.4, 5.5.2, and 5.5.3);

— addition of a maximum test portion for the composite test in (8.1);

— addition of a clean-up step in (8.3.1);

— addition of the volume of the final solution may be adjusted from 1 ml to 50 ml in (8.3.2.1, 8.3.2.2.1 and 8.3.2.2.2);

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

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

— Clause 7 has been modified significantly. The normative requirements have been moved from Annex D to Clause 7 and Annex D has subsequently been changed into an informative annex.

Introduction

This document is largely based upon the existing Chinese national standard GB/T 22048-2015. 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 should be carried out by suitably trained staff.

1 Scope *(mandatory)*

This document specifies a method 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) (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 (see G.2) and other product materials provided that adequate validation is demonstrated.

2 Normative references *(mandatory)*

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 *(mandatory)*

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 https://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

Note 1 to entry: Text of the note.

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

3.3
coating
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

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

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* (3.6)

3.8
limit of quantification
LOQ
lowest amount of the analyte in the sample that can be quantitatively determined with defined precision and accuracy 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 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 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 0,2 mg/l to 10 mg/l for DIBP, DBP, BBP, DEHP and DNOP, 1 mg/l to 50 mg/l for DINP and DIDP) is prepared by transferring 0,1 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 0 °C to 8 °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 phthalate esters, 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 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) is prepared by transferring 0,1 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 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 glassware

6.3 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.

6.4 Soxhlet extractor, see Figure C.1.

6.5 Solvent extractor, see Figure C.2.

6.6 Extraction thimble, made of cellulose.

6.7 Cotton wool, for extraction thimble.

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

6.9 Concentration apparatus, for example, a rotary evaporator.

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

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

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

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

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

6.15 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.

6.16 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.

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

7 Selection of test portion

7.1 General principle

Individual test and composite test are used in this document.

7.2 Individual test

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.

7.3 Composite test

When used properly, the composite test serves the purpose of reducing test costs and improving efficiency, without affecting the accuracy of the test. A composite test used for quantitative screening shall meet all of 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 mass shall be weighed for each constituent test portion, the mass between any two constituent test portions should not differ by over 10 %;

c) The LOQ_m of target phthalate esters is lower than 50 mg/kg;

When a composite test is used, the number of the constituent test portions shall be less than or equal to 3 (i.e. $K \leq 3$). When the number greater than 3 (i.e. $K>3$) is used in forming the composite test portion in accordance with Annex D.

Composite test is only allowed in cases when it is enough for judging conformance with requirements. And if the conclusion of composite test is failed, further individual tests are needed to find failed samples among composite test portions.

NOTE The composite testing cannot be used to solve the lack of mass of a test portion. If a constituent test portion's mass is not enough to perform an individual test, it is not possible to get a representative result through composite testing either.

8 Procedure

8.1 General

Except for clause 8.2, following procedure are applicable to both individual test and 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 (6.6) or reaction vessel (6.16). 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 0,05 g is recommended as a minimum test portion.

8.2.2 Composite test

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

8.3 Extraction

8.3.1 Options of extraction method

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 (6.4). In order to prevent the sample from floating, add cotton wool (6.7) 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 the loss of phthalate esters.

8.3.3 Method B

Place the thimble with the test portion into the solvent extractor (6.5). In order to prevent the sample from floating, add cotton wool (6.7) 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 material in solid form

Add 25 ml of dichloromethane to the airtight glass reaction vessel (6.16). 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) may be preferable.

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

8.3.4.2 For material in liquid form

Add 15 ml of dichloromethane to an airtight glass reaction vessel (6.16). 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 (6.13) for GC-MS (6.3) analysis. Two options of quantification procedures, External Standard calibration (8.4.2) and IS calibration (8.4.3), are described as follows. 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 minutes for the polymer to settle.

b) Centrifuge at up to 5 000 g (6.17).

c) Purify the solution with a pretreated SPE cartridge (6.10), 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.

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_m (10.1) and operability.

8.4.2.2 Method C

8.4.2.2.1 Material in solid form

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_m (10.1) and operability.

8.4.2.2.2 Material in liquid form

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_m (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).