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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

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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).

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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.