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Safety of toys —

Part 6:
Toys and children's products — Determination of phthalate plasticizers in polyvinyl chloride plastics

Sécurité des jouets —

Partie 6: Jouets et produits pour enfants — Dosage des plastifiants à base de phtalate dans les plastiques en chlorure de polyvinyl

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 8124-6 was prepared by Technical Committee ISO/TC 181, Safety of toys.

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

— *Part 1: Safety aspects related to mechanical and physical properties*

— *Part 2: Flammability*

— *Part 3: Migration of certain elements*

— *Part 4: Swings, slides and similar activity toys for indoor and outdoor family domestic use*

— *Part 5: Total concentration of certain elements of toys* (in preparation)

— *Part 6: Determination of certain phthalate esters in toys and children's products*

— *Part 7: Finger paints* (in preparation)

— *Part 8: Age determination guidelines* (in preparation)

Safety of toys – Part 6: Determination of certain phthalate esters in toys and children's products

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

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

1 Scope

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

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

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this part of ISO 8124, the following terms and definitions apply.

3.1
laboratory sample
toys or children's products in the form in which it is marketed or intended to be marketed.

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

3.3
coating
all layers of material formed or deposited on the base material of a toy, 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, and which can be removed by scraping with a sharp blade

3.4
scraping
mechanical removal of coatings down to the base material without damaging the substrate material

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

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

NOTE This term precludes the compositing of dissimilar materials e.g. compositing textiles and paint coatings is not permitted.

3.7
composite test
test performed on the composite test portions

3.8
limit of quantification (LOQ)
the lowest amount of the analyte in the sample that can be quantitatively determined with defined precision under the stated experimental conditions

3.9
method blank
an 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. Method blank data are used to assess contamination from the laboratory environment.

4 Principle

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

5 Standards and reagents

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

5.2 Phthalate reference substances, DBP, BBP, DEHP, DNOP, DINP and DIDP, minimum 95 % purity, see Annex A.

5.3 Stock solution, 0,1 g/l of DBP, BBP, DEHP, DNOP each and 0,5 g/l of DINP, DIDP each in dichloromethane (5.1).

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

5.4 External standard (ES) calibration solutions

A series of calibration standard solutions (of at least five equidistant calibrations in the range 0.4 mg/l to 10 mg/l for DBP, BBP, DEHP and DNOP, 2 mg/l to 50 mg/l for DINP and DIDP) are prepared by transferring 0.2 ml to 5 ml of the stock solution (5.3) to a 50 ml volumetric flask and making up to the mark with dichloromethane.

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

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 95 % purity.

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

5.5.2 Internal stock solution, 0,25 g/l of BB or DAP or others, in dichloromethane.

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

5.5.3 Internal standard calibration solutions

A series of calibration standard solutions (of at least five equidistant calibrations in the range 0.4 mg/l to 10 mg/l for DBP, BBP, DEHP and DNOP, 2 mg/l to 50 mg/l for DINP and DIDP) are prepared by transferring 0.2 ml to 5 ml of the stock solution (5.3) to a 50 ml volumetric flask and adding 2 ml of the IS stock solution (5.5.2) before making up to the mark with dichloromethane, each of the calibration standards containing 10 mg/l IS.

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

6 Apparatus

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

6.1 Normal laboratory glassware

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

6.3 Soxhlet extractor, see figure B.1.

6.4 Solvent extractor, see figure B.2.

6.5 Extraction thimble, cellulose.

6.6 Cotton wool, for extraction thimble.

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

6.8 Concentration apparatus, for example a rotary evaporator.

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

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

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

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

7 Selection of test portions

Use a scalpel or other appropriate cutting utensils to cut a representative portion from the laboratory sample into small pieces. For coatings, remove each different coating of the laboratory sample by scraping from the base material. Extra care shall be taken to minimize the inclusion of the base material. Each piece shall, in the

uncompressed condition, have no dimension greater than 5 mm and be mixed uniformly.

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

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

Composite test may be used for a screen test. (see Annex E).

8 Procedure

8.1 Sample weighing

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

8.2 Extraction

Two alternative extraction method A (8.2.1) and method B (8.2.2) are described in the following.

8.2.1 Method A

Place the thimble with test portion into 150ml soxhlet extractor (6.3). In order to prevent the sample from floating, add cotton wool (6.6) to the top of the thimble.

Add 120 ml of dichloromethane (5.1) into the 150 ml flask. Reflux for 6 h with no less than four reflux cycles per hour.

After cooling, reduce the volume of the dichloromethane to about 10 ml using a suitable concentration apparatus (6.8), take care to avoid reduction to dryness.

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

NOTE Care should be taken to condensate temperature on refluxing or concentrating procedures to preventing lose of phthalate esters.

8.2.2 Method B

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

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

NOTE Care should be taken to condensate temperature on refluxing or concentrating procedures to preventing lose of phthalate esters.

8.3 Sample solution for analysis

Filter the solution (8.2.1 or 8.2.2), which is obtained after the dichloromethane extract has been treated according to the following procedure as specified in clause 8.3.1 or 8.3.2 where appropriate, with PTFE membrane filter (6.12) for GC-MS (6.2) analysis.

If necessary, e.g. when the concentrated extract exhibits turbidity, before the filtering above, purify the solution (8.2.1 or 8.2.2) with a pretreated SPE (6.9), Rinse the cartridge with 3 × 3 ml of dichloromethane and collect the eluate.

NOTE Pretreated the SPE cartridge with approximate 10 ml of dichloromethane before purification, discard the effluent.

8.3.1 For quantification by external standard calibration

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

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

8.3.2 For quantification by internal standard calibration

Transfer the extract or the eluate and 1 ml of the IS stock solution (5.5.2) into a 25 ml volumetric flask and make up to the mark by dichloromethane. The final solution contains 10 mg/l of IS.

NOTE The volume of both IS solution and the final solution can be adjusted according to the test specimen mass and concentration, but the concentration of IS in the final solution should be the same with that of standard calibration solutions (5.5.3).

8.4 Determination

8.4.1 GC-MS conditions

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

a) Column: capillary column, non-polar (phenyl-arylene-polymer equivalent to 5 % phenyl-methylpolysiloxane), or equivalent.

b) Oven temperature program.

c) Carrier gas: helium or hydrogen, constant flow.

d) Injector system: split or splitless.

e) Ionization method: electron ionization (EI), 70 eV.

f) Determination: Identification by full scan mode, quantification by Selected Ion Monitoring (SIM) mode simultaneously.

8.4.2 Identification

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

The target compound is identified in the test portion if:

1) The ratio of the retention time of the analyte to that of the IS, i.e. the relative retention time of the analyte, corresponds to that of the calibration solution at a tolerance of ± 0,5 %.

2) The diagnostic ions (see Table C.1) are present at the substance-specific retention time.

3) The relative intensities of the diagnostic ions (refer to table C.1) in full scan correspond to those of the calibration standard. (Relative intensity > 50 %, the maximum permitted tolerance being 10 %; relative intensity within 20 % to 50 %, the maximum permitted tolerance being 15 %; relative intensity within 10 % to 20 %, the maximum permitted tolerance being 20 %; relative intensity ≤ 10 %, the maximum permitted tolerance being 50 %)