INTERNATIONAL STANDARD

ISO 8124-6

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Safety of toys —

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

Sécurité des jouets —

Partie 6: Jouets et produits pour enfants — Dosage de certains phtalates d'esters dans les jouets et produits pour enfants

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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 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).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

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The committee responsible for this document is Technical Committee ISO/TC 181, *Safety of toys*.

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

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

The following parts are under preparation:

- *Part 5: Determination of total concentration of certain elements in toys*
- *Part 7: Finger paints — Requirements and test methods*
- *Part 8: Age determination guidelines*

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Introduction

This part of ISO 8124 is largely based upon the existing Chinese national standard GB/T 22048-2008. Relevant standards of some countries and regions are referred to as well.

Considering the diversity of laws and regulations in different countries, this International Standard has not set out limits for phthalate esters. It is intended to be used as a method standard in conformity assessment. The user of this part of ISO 8124 is therefore advised to be aware of relevant national requirements.

Whereas in some countries, phthalate ester requirements for toys are also applicable to children products and whereas children product materials are generally similar to those of toys, this part of ISO 8124 whose scope covers various materials can be applicable to both toys and children products.

Annex A is normative and Annex B, Annex C, Annex D, Annex E, and Annex F are for information purposes only, but they are crucial and helpful for the correct interpretation of this part of ISO 8124.

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Safety of toys —

Part 6:
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 with 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, and coatings, etc. This International Standard has been validated for polyvinylchloride (PVC) plastics, polyurethane (PU) plastics, and some representative paint coatings (see Annex D). It might also be applicable to other phthalate esters and other products materials provided that adequate validation is demonstrated.

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2 Terms and definitions

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

2.1
laboratory sample
toy or children's product in the form in which it is marketed or intended to be marketed

2.2
base material
material upon which coatings can be formed or deposited

2.3
coating
all layers of material formed or deposited on the base material of toys or children's products, including paints, varnishes, lacquers, inks, polymers, or other substances of a similar nature, whether they contain metallic particles or not, no matter how they have been applied to the toy or children's product, and which can be removed by scraping with a sharp blade

2.4
scraping
mechanical removal of coatings down to but not including the base material

2.5
test portion
portion of homogeneous material taken from a corresponding part of the laboratory sample for analysis

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2.6
composite test portion
mixed test portion formed by physically mixing several test portions of similar material

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

2.7
composite test
test performed on the composite test portion

2.8
limit of quantification
LOQ
lowest amount of the analyte in the sample that can be quantitatively determined with defined precision under the stated experimental conditions

2.9
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.

3 Principle

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The test portion of a toy or children's product 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).

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4 Reagents

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

4.2 Phthalate reference substances, DBP, BBP, DEHP, DNOP, DINP, and DIDP (see Annex A), minimum of 95 % purity.

4.3 Stock solution, 100 mg/l of DBP, BBP, DEHP, DNOP each, and 500 mg/l of DINP, DIDP each in dichloromethane (4.1).

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.

4.4 External Standard (ES) calibration solutions.

A series of calibration standard solutions (of at least five equidistant calibrations in the range of 0,4 mg/l to 10 mg/l for DBP, BBP, DEHP, and DNOP, 2 mg/l to 50 mg/l for DINP and DIDP) is prepared by transferring 0,2 ml to 5 ml of the stock solution (4.3) 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 4 °C to prevent change of concentration. It is recommended to prepare the solution at least monthly.

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4.5 Internal Standard (IS) calibration solutions.

4.5.1 Internal reference substances, benzyl benzoate (BB, CAS No.120-51-4) or di-*n*-amyl phthalate (DAP, CAS No.131-18-0) [also known as di-*n*-pentyl phthalate (DPP)], minimum of 95 % purity.

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

4.5.2 Internal stock solution, 250 mg/l of BB or DAP or others, in dichloromethane.

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.

4.5.3 Internal Standard calibration solutions.

A series of calibration standard solutions (of at least five equidistant calibrations in the range of 0,4 mg/l to 10 mg/l for DBP, BBP, DEHP and DNOP, 2 mg/l to 50 mg/l for DINP and DIDP) is prepared by transferring 0,2 ml to 5 ml of the stock solution (4.3) to a 50 ml volumetric flask and adding 2 ml of the IS stock solution (4.5.2) before making up to the mark with dichloromethane, each of the calibration standards containing 10 mg/l IS.

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.

5 Apparatus

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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.

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5.1 Normal laboratory glassware.

5.2 Gas chromatography-mass spectrometer (GC-MS), with a capillary column coupled to a mass spectrometric detector (electron ionization, EI) used for the analysis. See 7.4.1.

5.3 Soxhlet extractor, see Figure B.1.

5.4 Solvent extractor, see Figure B.2.

5.5 Extraction thimble, cellulose.

5.6 Cotton wool, for extraction thimble.

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

5.8 Concentration apparatus, for example, a rotary evaporator.

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

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

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

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

6 Selection of test portion

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 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.

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

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

Composite test can be used for screening. See Annex E.

7 Procedure

7.1 Sample weighing

Weigh, to the nearest 1 mg, approximately 1 g of the test portion into an extraction thimble (5.5). If 1 g test portion cannot be obtained from a single laboratory sample, sampling as much as possible from more than one laboratory samples, but 0,1 g should be a minimum test portion.

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7.2 Extraction

Two optional extraction methods are described in the following, and the laboratory can select the most suitable one at its discretion.

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7.2.1 Method A

Place the thimble with test portion into the 150-ml Soxhlet extractor (5.3). In order to prevent the sample from floating, add cotton wool (5.6) to the top of the thimble.

Add 120 ml of dichloromethane (4.1) 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 (5.8). Take 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 between 30 kPa and 45 kPa.

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

7.2.2 Method B

Place the thimble with test portion into the solvent extractor (5.4). In order to prevent the sample from floating, add cotton wool (5.6) to the top of the thimble.

Add 80 ml of dichloromethane (4.1) 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 During the refluxing and concentration steps, careful temperature control is necessary in order to avoid loss of phthalate esters.

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7.3 Sample solution for analysis

Filter the solution (7.2.1 or 7.2.2), which is obtained after the dichloromethane extract has been treated according to the procedure specified in 7.3.1 or 7.3.2 where appropriate, with PTFE membrane filter (5.12) for GC-MS (5.2) analysis.

If necessary, e.g. when the concentrated extract exhibits turbidity, before the filtering above, purify the solution (7.2.1 or 7.2.2) with a pretreated SPE (5.9). Rinse the cartridge with 3 ml of dichloromethane three times and collect the eluate.

NOTE Pretreat the SPE cartridge with approximate 10 ml of dichloromethane before purification. Discard the effluent.

7.3.1 For quantification by External Standard calibration

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

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

7.3.2 For quantification by Internal Standard calibration

Transfer the extract or the eluate and 1 ml of the IS stock solution (4.5.2) into a 25-ml volumetric flask and make up to the mark with dichloromethane. The final solution contains 10 mg/l of IS.

NOTE The volume of both IS solution and the final solution can 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 (4.5.3).

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7.4 Determination

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7.4.1 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 (phenylarylene polymer equivalent to 5 % phenylmethyl polysiloxane), or equivalent.

b) Oven temperature program.

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

d) Injector system: split or splitless.

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

f) Determination: Identification by full scan mode, quantification by selected ion monitoring (SIM) mode simultaneously.

7.4.2 Identification

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

The target compound is considered to be identified in the test solution if the following criteria are fulfilled:

a) the 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 %;

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

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

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 %

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

7.4.3 Calibration

7.4.3.1 General

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Two optional calibration methods, External Standard (ES) (7.4.3.2) and Internal Standard (IS) (7.4.3.3), are described in the following. Either ES or IS can be used for calibration. Laboratories can choose the suitable calibration method according to their best practice (see Annex F).

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A calibration curve shall be established for either method. A minimum of five equidistant calibration standard solutions (4.4 or 4.5.3) 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.

NOTE 1 DINP and DIDP are available as different isomeric mixtures under different CAS numbers. Since the chromatogram of the GC-MS is different for each mixture, the laboratory should choose the reference substance that matches as closely as possible the isomeric ratio to the phthalates in the test portion and report the CAS No. of the reference material used in accordance with 11 f).

NOTE 2 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.

7.4.3.2 External Standard (ES) calibration

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

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