INTERNATIONAL
STANDARD

ISO
8124-6

First edition
2014-08-15

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

Reference number
ISO 8124-6:2014(E)

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Published in Switzerland

Contents

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 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

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*:

- *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*

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.

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.

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

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

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).

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.

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

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.

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.

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.

7.2 Extraction

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

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.

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).

7.4 Determination

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 %;

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, Dipropylheptyl 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

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).

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.

To establish the calibration curve, the response A is plotted against the concentration C in accordance with Formula (1):

$$A = (a_1 \times C) + b_1 \tag{1}$$

where

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

a_1 is the slope of the calibration curve;

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

b_1 is the ordinate intercept of the calibration curve.

7.4.3.3 Internal Standard (IS) calibration

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

$$\frac{A}{A_{IS}} = \left(a_2 \times \frac{C}{C_{IS}} \right) + b_2 \tag{2}$$

where

A is the peak area or sum of peak areas of the individual phthalate 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 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 1 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.

8 Calculation

8.1 External Standard (ES) calculation

Calculate the mass fraction of the individual phthalate in the test portion by using Formula (3) after solving Formula (1):

$$w_S = \frac{(A - b_1)}{a_1} \times \frac{V}{m} \times D \times \frac{1}{10\,000} \qquad (3)$$

where

w_S is the concentration of the individual phthalate found in the test portion, in %;

A is the peak area or sum of peak areas of the individual phthalate 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 shall be expressed in percentage by weight (%) and reported to three significant figures.

The response value of the tested phthalate in the calibration solution and test solution should be within the instrument detection linear range. If necessary, further diluted solution with dichloromethane should be prepared.

8.2 Internal Standard (IS) calculation

Calculate the mass fraction of the individual phthalate in the test portion by using Formula (4) after solving Formula (2):

$$w_S = \left(\frac{A}{A_{IS}} - b_2\right) \times \frac{C_{IS}}{a_2} \times \frac{V}{m} \times D \times \frac{1}{10000} \qquad (4)$$

where

w_S is the concentration of the individual phthalate found in the test portion, in %;

A is the peak area or sum of peak areas of the individual phthalate 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 in percentage by weight (%) and reported to three significant figures.

The response value of the tested phthalate in the calibration solution and test solution should be within the instrument detection linear range. If necessary, further diluted solution with dichloromethane should be prepared.

9 Quality control

9.1 Limit of quantification (LOQ)

LOQ for DBP, BBP, DEHP, DNOP: 0,001 %;

LOQ for DINP, DIDP: 0,005 %.

9.2 Method blank

A method blank (2.9) shall be prepared for each batch of samples by following the steps in Clause 7 and 8 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 (9.1).

9.3 Recovery

One spiked blank per batch shall be prepared by adding 1 ml of stock solution (4.3) in the method blank; then treat it in the same way as described in Clause 7 and 8. The recovery of each phthalate should be 80 % to 120 % of the expected value.

9.4 Calibration check

A mid-point calibration check solution without extraction should be re-injected after every 20 samples and at the end of the run to demonstrate the stability of the GC-MS. The deviation of each phthalate should be within 15 % of the expected value.

10 Precision

The precision of this part of ISO 8124 is shown in Annex D.

11 Test report

The test report shall contain at least the following information:

a) a reference to this part of ISO 8124 (i.e. ISO 8124-6:2014);

b) a complete identification of the sample;

c) a reference to the extraction procedure used (method A or method B);

d) a reference to the calculation method used (External Standard or Internal Standard);

e) the results of the individual quantitative phthalate analysis, expressed as percentage by weight (%);

f) the CAS No. of the used DINP or DIDP reference substance;

g) any deviations from the procedure specified;

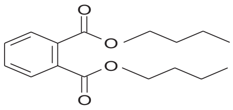
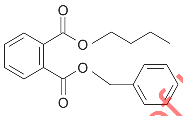
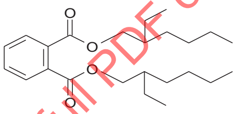
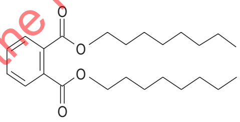
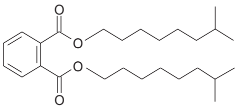
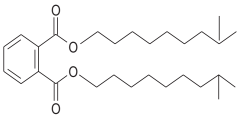
h) any unusual features observed during the test;

i) date of the test.

Annex A
(normative)

Phthalate esters

Table A.1 — Phthalate esters

No.	Phthalate esters (Initialism)	CAS No.	Structure formula[a]	Molecular formula
1	Di-*n*-butyl phthalate (DBP)	84–74–2		$C_{16}H_{22}O_4$
2	Benzyl butyl phthalate (BBP)	85–68–7		$C_{19}H_{20}O_4$
3	*Bis*-(2-ethylhexyl) phthalate (DEHP)	117–81–7		$C_{24}H_{38}O_4$
4	Di-*n*-octyl phthalate (DNOP)	117–84–0		$C_{24}H_{38}O_4$
5	Di-*iso*-nonyl phthalate (DINP)	28553–12–0[b] 68515–48–0[c]		$C_{26}H_{42}O_4$
6	Di-*iso*-decyl phthalate (DIDP)	26761–40–0[d] 68515–49–1[e]		$C_{28}H_{46}O_4$

[a] The structure formulas of DINP and DIDP are only one of their isomeric compounds.

[b] CAS No. 28553–12–0 is a mixture of esters of o-phthalic acid with C9 alkyl alcohols.

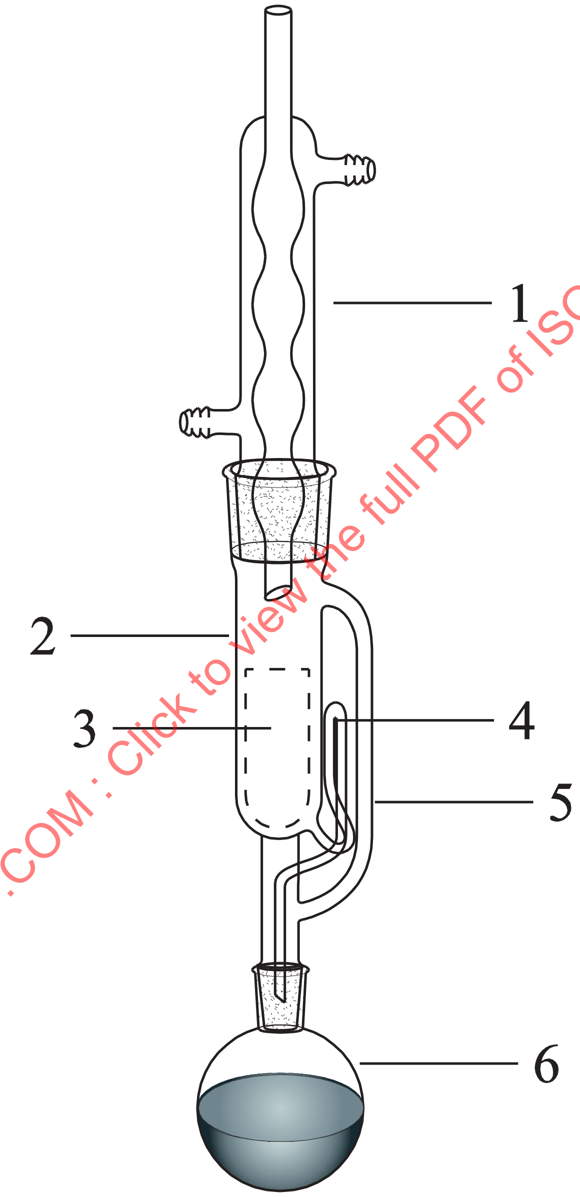
[c] CAS No. 68515–48–0 is a mixture of esters of o-phthalic acid with C8-C10 (C9 rich) alkyl alcohols.

[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)

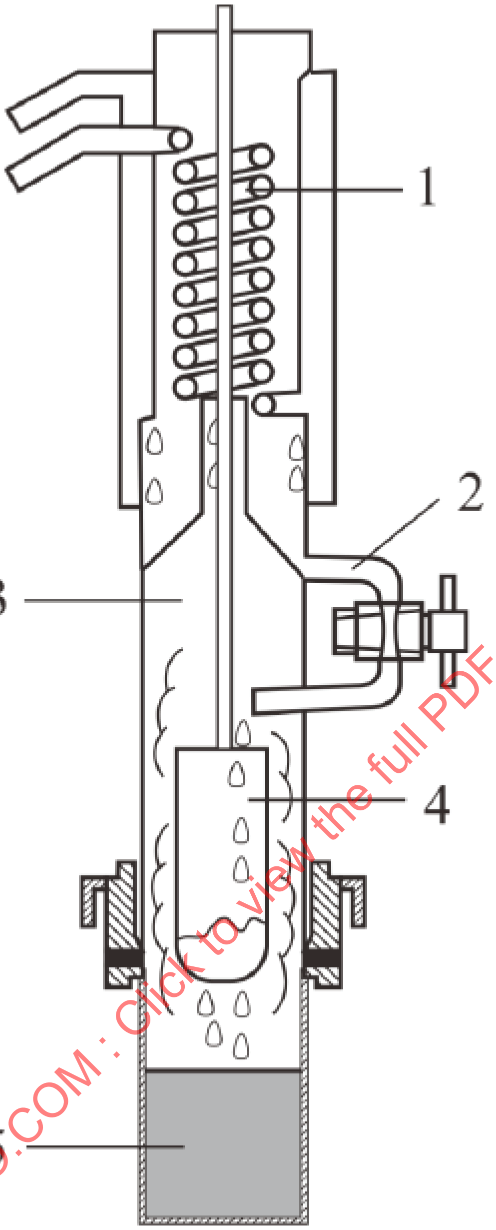
Extraction apparatus



Key

1	condenser
2	extraction chamber
3	thimble
4	siphon tube
5	distillation path
6	boiling flask

Figure B.1 — Soxhlet extractor



Key

1	condenser
2	solvent feed
3	extraction chamber
4	thimble
5	receiver

Figure B.2 — Solvent extractor

Annex C
(informative)

Example of GC-MS conditions

Due to the variation of instruments in different laboratories, no generally applicable instructions can be provided for chromatographic analysis. The following parameters have been tested and used successfully. Retention time and diagnostic ions of the phthalate esters are specified in Table C.1 and the chromatograms are shown in Figure C.1, Figure C.2, Figure C.3, and Figure C.4.

a) Column: DB-5MS capillary column 30 m × 0,25 mm (ID) × 0,25 µm (film thickness)

b) Oven program: $\underset{(0{,}5\ \text{min})}{80\ ^\circ\text{C}} \xrightarrow{25\ ^\circ\text{C/min}} \underset{(4{,}5\ \text{min})}{300\ ^\circ\text{C}}$

c) Carrier gas: helium, 1 ml/min, constant flow

d) Injector temperature: 300 °C

e) Injection: 1,0 µl, 20:1 Split

f) Transfer line temperature: 290 °C

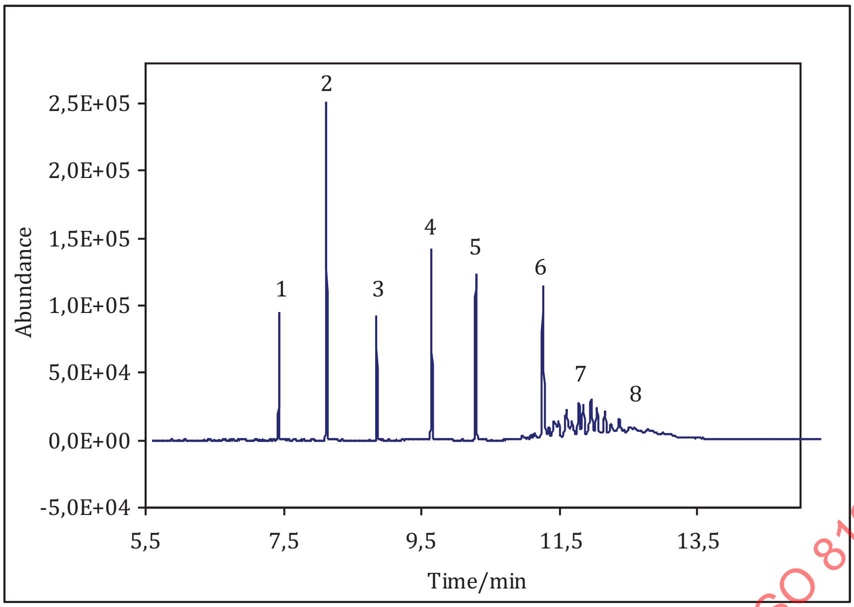
g) Ionization mode: electron ionization (EI), 70 eV; ion source temperature: 230 °C

h) Mass filter: quadruple mass filter

i) Determination: Identification by full scan mode (m/z = 50-500), quantification by selected ion monitoring (SIM) mode simultaneously, refer to Table C.1.and Figure C.1, Figure C.2, Figure C.3, and Figure C.4.

Table C.1 — Retention time and diagnostic ions for chemicals

No.	Chemicals	Retention time min	Diagnostic ions m/z	Relative intensity
–	BB (IS)	7,4	$\underline{105}$, 91, *212*, 194	100:46:17:09
1	DBP	8,1	$\underline{149}$, 150, *223*, 205	100:09:05:04
–	DAP (IS)	8,9	$\underline{149}$, 150, *237*, 219	100:10:06:03
2	BBP	9,6	$\underline{149}$, 091, *206*, 238	100:72:23:03
3	DEHP	10,3	$\underline{149}$, 167, *279*, 150	100:50:32:10
4	DNOP	11,3	149, $\underline{279}$, 150, *261*	100:18:10:03
5	DINP	10,7–13,0	149, *127*, $\underline{293}$, 167	100:14:09:06
6	DIDP	11,0–14,5	149, *141*, $\underline{307}$, 150	100:21:16:10
Underlined: the first quantification ions. Italic: the second quantification ions.				



Key

1 BB
2 DBP
3 DAP
4 BBP
5 DEHP
6 DNOP
7 DINP
8 DIDP

Figure C.1 — Total ion chromatogram (BB, DBP, DAP, BBP, DEHP, DNOP 10 mg/l, DINP, DIDP 50 mg/l)

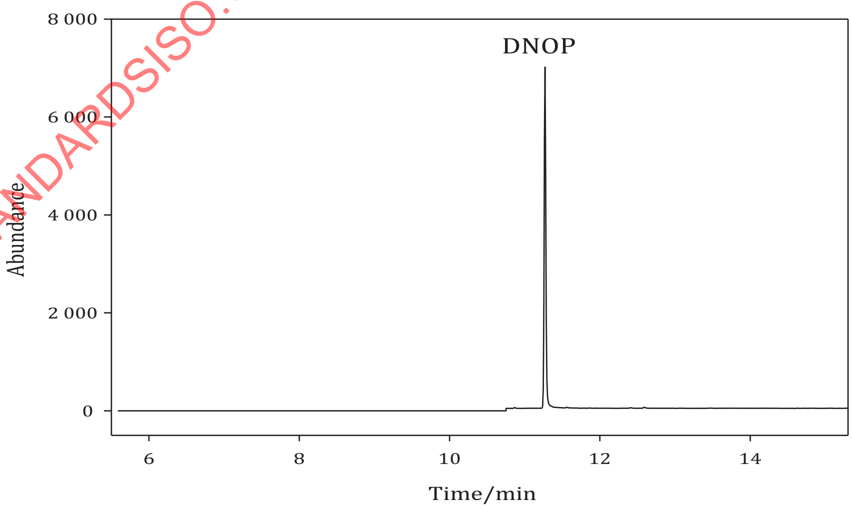


Figure C.2 — Extracted ion chromatogram of DNOP standard (m/z = 279)

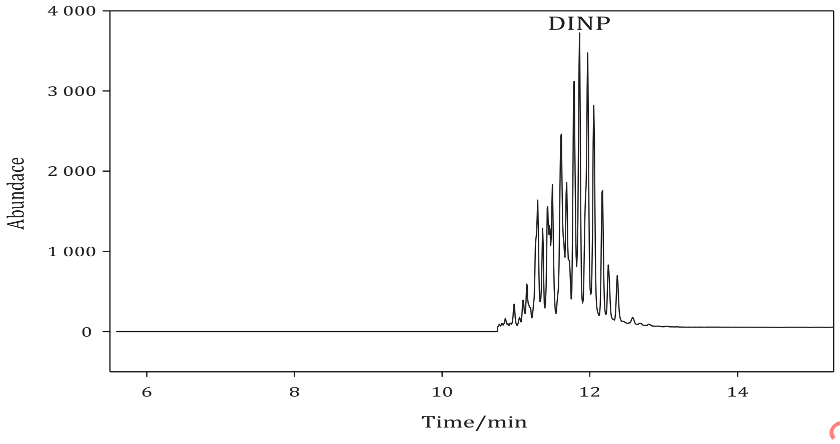


Figure C.3 — Extracted ion chromatogram of DINP standard (m/z = 293)

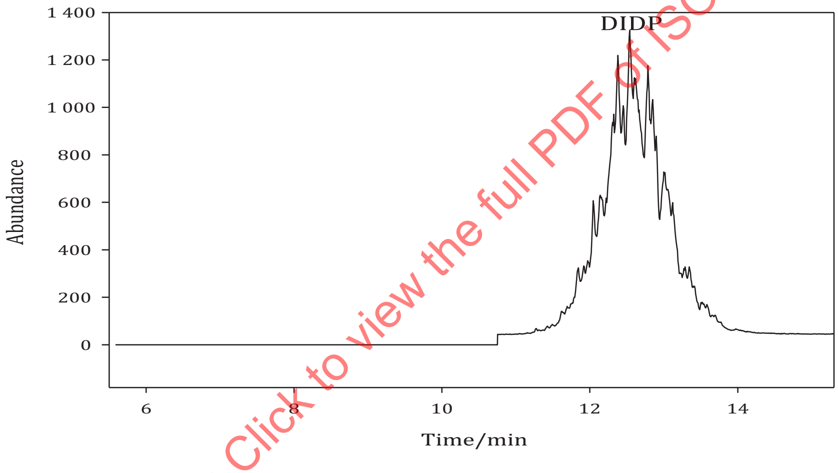


Figure C.4 — Extracted ion chromatogram of DIDP standard (m/z = 307)

Annex D
(informative)

Precision of the method

The first inter-laboratory collaborative trial test was organized in 2010 with 122 laboratories participating in the determination of 6 phthalate esters in PVC toys with one concentration level.

The second inter-laboratory collaborative trial test was organized in 2011 with 12 laboratories participating in the determination of 6 phthalate esters in polyurethane (PU) plastic and coatings with base resin of PVC, polyacrylic acid (PAA), and nitrocellulose(NC) with two concentration levels.

The third inter-laboratory collaborative trial test was organized in 2012 with 8 laboratories participating in the determination of 2 phthalate esters in polyurethane (PU) plastic with low concentration level.

All the precision data are shown in Table D.1 to D.6 for reference.

Table D.1 — Summary of the results of the inter-laboratory trial test on PVC plastic

Phthalate esters	**Method**	***l***	***o***	***M***	s_r	CV_r	***r***	s_R	CV_R	***R***
			%	mg/kg	mg/kg	%	mg/kg	mg/kg	%	mg/kg
DBP	Method A and ES calibration	94	6,0	2 442	72	2,9	201	207	8,5	579
	Method A and IS calibration	15	0	2 441	52	2,1	146	178	7,3	499
	Method B and ES calibration	7	0	2 451	62	2,5	173	90	3,7	253
BBP	Method A and ES calibration	93	7,0	2 024	64	3,2	179	170	8,4	477
	Method A and IS calibration	15	0	2 005	62	3,1	174	179	8,9	501
	Method B and ES calibration	7	0	2 024	83	4,1	233	150	7,4	421
DEHP	Method A and ES calibration	96	4,0	3 737	107	2,9	301	310	8,3	867
	Method A and IS calibration	15	0	3 694	91	2,5	255	302	8,2	846
	Method B and ES calibration	7	0	3 888	72	1,9	203	266	6,8	744

Table D.1 *(continued)*

Phthalate esters	Method	l	o	M	s_r	CV_r	r	s_R	CV_R	R
			%	mg/kg	mg/kg	%	mg/kg	mg/kg	%	mg/kg
DNOP	Method A and ES calibration	57	1,7	2 153	83	3,9	233	313	14,5	877
	Method A and IS calibration	9	0	2 103	50	2,4	139	197	9,4	552
	Method B and ES calibration	5	0	2 286	113	5,0	317	252	11,0	704
DINP	Method A and ES calibration	53	8,6	3 100	91	2,9	256	637	20,6	1 784
	Method A and IS calibration	8	0	3 297	203	6,1	567	509	15,4	1 424
	Method B and ES calibration	5	0	3 126	192	6,1	536	773	24,7	2 165
DIDP	Method A and ES calibration	51	12,1	2 244	80	3,6	224	360	16,0	1 007
	Method A and IS calibration	8	0	2 445	119	4,9	333	343	14,0	961
	Method B and ES calibration	5	0	2 374	116	4,9	325	476	20,1	1 333

Explanation of symbols:

l is the number of laboratories after outlier rejection;

o is the percentage of outliers;

M is the median value of the results;

s_r is the standard deviation of repeatability;

CV_r is the coefficient of variation of repeatability;

r is the repeatability, $r = 2,8 \times S_r$;

s_R is the standard deviation of reproducibility;

CV_R is the coefficient of variation of reproducibility;

R is the reproducibility, $R = 2,8 \times S_R$.

Table D.2 — Summary of the results of the inter-laboratory trial test on PU plastics

Phthalate esters	l	o	M	s_r	CV_r	r	s_R	CV_R	R
		%	mg/kg	mg/kg	%	mg/kg	mg/kg	%	mg/kg
DBP	11	8,3	724	46	6,3	129	77	10,7	216
	12	0	2 839	106	3,7	297	277	9,8	777

For definitions of symbols, see Table D.1.

Table D.2 *(continued)*

Phthalate esters	l	o	M	s_r	CV_r	r	s_R	CV_R	R
		%	mg/kg	mg/kg	%	mg/kg	mg/kg	%	mg/kg
BBP	12	0	923	48	5,2	135	100	10,8	279
	12	0	4 586	208	4,5	581	325	7,1	911
DEHP	11	8,3	968	60	6,2	169	93	9,6	259
	12	0	4 023	146	3,6	408	467	11,6	1 308
DNOP	12	0	869	39	4,5	109	124	14,3	348
	12	0	3 717	88	2,4	246	523	14,1	1 465
DINP	11	8,3	1 039	78	7,5	219	166	16,0	464
	11	8,3	3 760	206	5,5	578	729	19,4	2 040
DIDP	12	0	1 161	86	7,4	240	121	10,5	340
	12	0	4 715	242	5,1	678	1005	21,3	2 813

For definitions of symbols, see Table D.1.

Table D.3 — Summary of the results of the inter-laboratory trial test on PVC coatings

Phthalate esters	l	o	M	s_r	CV_r	r	s_R	CV_R	R
		%	mg/kg	mg/kg	%	mg/kg	mg/kg	%	mg/kg
DBP	11	8,3	1 014	57	5,6	159	109	10,8	306
	12	0	10 084	251	2,5	703	993	9,9	2 781
BBP	11	8,3	999	48	4,8	134	66	6,6	185
	12	0	10 822	366	3,4	1 026	1 071	9,9	2 999
DEHP	11	8,3	1 012	37	3,7	105	102	10,1	286
	12	0	10 754	446	4,2	1 250	992	9,2	2 778
DNOP	11	8,3	897	49	5,5	137	93	10,4	261
	11	8,3	10 660	688	6,4	1 925	1 013	9,5	2 836
DINP	11	8,3	1 306	102	7,8	286	220	16,9	617
	12	0	10 622	552	5,2	1 546	1 568	14,8	4 391
DIDP	12	0	1 242	82	6,6	231	224	18,1	628
	12	0	11 653	890	7,6	2 492	1 733	14,9	4 852

For definitions of symbols, see Table D.1.

Table D.4 — Summary of the results of the inter-laboratory trial test on PAA coatings

Phthalate esters	l	o	M	s_r	CV_r	r	s_R	CV_R	R
		%	mg/kg	mg/kg	%	mg/kg	mg/kg	%	mg/kg
DBP	11	8,3	1 022	40	3,9	112	87	8,5	243
	12	0	9 476	346	3,7	969	851	9,0	2 382
BBP	11	8,3	1 069	57	5,3	159	121	11,3	339
	12	0	10 484	363	3,5	1 017	864	8,2	2 419
DEHP	11	8,3	1 105	86	7,8	242	129	11,7	361
	12	0	10 762	452	4,2	1 266	1 037	9,6	2 905

For definitions of symbols, see Table D.1.

Table D.4 *(continued)*

Phthalate esters	*l*	*o*	*M*	s_r	CV_r	*r*	s_R	CV_R	*R*
		%	mg/kg	mg/kg	%	mg/kg	mg/kg	%	mg/kg
DNOP	11	8,3	1 186	44	3,7	123	139	11,7	389
	12	0	10 727	343	3,2	960	1 110	10,4	3 109
DINP	10	16,7	1 456	106	7,3	297	238	16,3	666
	12	0	10 996	960	8,7	2 689	1 252	11,4	3 507
DIDP	10	16,7	1 377	100	7,2	279	176	12,8	493
	12	0	11 093	804	7,3	2 252	1 844	16,6	5 163
For definitions of symbols, see Table D.1.									

Table D.5 — Summary of the results of the inter-laboratory trial test on NC coatings

Phthalate esters	*l*	*o*	*M*	s_r	CV_r	*r*	s_R	CV_R	*R*
		%	mg/kg	mg/kg	%	mg/kg	Mg/kg	%	mg/kg
DBP	12	0	985	62	6,3	174	119	12,0	332
	12	0	9 596	507	5,3	1 421	943	9,8	2 640
BBP	12	0	1 046	53	5,1	149	129	12,3	361
	12	0	10 555	512	4,8	1 433	1 034	9,8	2 894
DEHP	12	0	1 038	65	6,2	181	138	13,3	387
	12	0	10 015	469	4,7	1 313	822	8,2	2 301
DNOP	12	0	1 205	71	5,9	198	145	12,0	405
	11	8,3	10 948	384	3,5	1 074	898	8,2	2 514
DINP	12	0	1 501	78	5,2	218	310	20,6	867
	12	0	11 345	603	5,3	1 690	1 082	9,5	3 031
DIDP	11	8,3	1 379	79	5,7	220	176	12,7	492
	12	0	11 654	956	8,2	2 676	1 933	16,6	5 413
For definitions of symbols, see Table D.1.									

Table D.6 — Summary of the results of the inter-laboratory trial test on PU plastic in low concentration

Phthalate esters	*l*	*o*	*M*	s_r	CV_r	*r*	s_R	CV_R	*R*
		%	mg/kg	mg/kg	%	mg/kg	Mg/kg	%	mg/kg
DEHP	7	12,5	171	11	6,5	31	20	11,8	56
DINP	7	12,5	375	24	6,5	68	53	14,1	149
For definitions of symbols, see Table D.1.									

Annex E
(informative)

Composite test

E.1 Introduction

Composite testing of similar materials is a general strategy to reduce testing cost but obstacles such as the complexity of the test matrix, interpretation of analytical results, unexpected chemical reactions between different test portions, etc., often lead to inconclusive results. Composite testing is only allowed in the case where a qualitative result is enough for judging the compliance with requirements. The composite test described in this annex is only used for a screening purpose.

It is important to note that composite testing cannot be used for the purpose of solving the lack of test portion's mass. If a test portion's mass is not enough to perform a single test, it is no possible to get a representative result through composite testing either.

E.2 Preparation of a composite test portion

A composite test portion shall meet all of the following conditions:

1) Up to three test portions can be combined to form a composite test portion.

2) 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).

3) Similar mass shall be used for each constituent test portion, i.e. the mass between any two constituent test portions should not differ by over 10 %, and the mass of each constituent test portion in the composite test shall be within 100 mg to 500 mg.

E.3 Test procedure

The test procedure specified in Clause 7 of this part of ISO 8124 can also be applied to composite test.

E.4 Calculation

The average mass fraction of the target phthalate in the composite test portion (w_{avg}) and the maximum mass fraction of the target phthalate in the individual test portions (w_{max}) can be calculated through Formulae (E.1) and (E.2) respectively, regardless of whether ES or IS calibration is used or not.

$$w_{avg} = C \times \frac{V}{m_{tot}} \times D \times \frac{1}{10\,000} \tag{E.1}$$

$$w_{\max} = C \times \frac{V}{m_{\min}} \times D \times \frac{1}{10\ 000} \qquad \text{(E.2)}$$

where

w_{avg} is the average mass fraction of the target phthalate in the composite test portion, in %;

w_{max} is the maximum mass fraction of the target phthalate in the individual test portions, in %;

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

V is the volume of the final solution, in ml;

m_{tot} is the total mass of the composite test portion, in gram;

m_{min} is the minimum mass of the individual test portions, in gram;

D is the dilution factor.

NOTE When calculating w_{max}, it is based on a worst-case assumption that all of the phthalate came from the test portion with the minimum mass.

E.5 Judgment of next action

When the average mass fraction of the target phthalate in the composite test portion (w_{avg}) and the maximum mass fraction of the target phthalate in the individual test portions (w_{max}) has been calculated, the next action should be introduced according to the results obtained. In consideration of the next action from the composite test portion, it is imperative that a sufficient “safety factor” is applied to account for the uncertainty of the composite test to ensure that non-conforming materials are correctly identified.

The next action should be judged according to Formula (E.3)

$$L_{act} = L \times F \qquad \text{(E.3)}$$

where

L_{act} is the action limit, in %;

L is the regulated limit, in %;

F is the safety factor, between 0 % and 100 %.

When $w_{max} < L_{act}$, no further action is needed.

When $w_{max} \geq L_{act}$, further action including individual testing is needed

where

$w_{max}$is the maximum mass fraction of the target phthalate in the individual test portions, in %.

Taking into consideration that the testing capability and uncertainty among different laboratories and the material tested are variables, it is up to the laboratory to decide the best fit safety factor based on their experience and history data accumulated. It is recommended to apply 60 % as a safety factor based on practical phthalates analysis experience.