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Textiles — Determination of the phthalate content — Tetrahydrofuran method

Textiles — Détermination de la teneur en phtalates — Méthode au tétrahydrofurane

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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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 38, *Textiles,* in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 248,*Textiles and textile products,* in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 14389:2014), which has been technically revised.

The main changes are as follows:

- addition of the Clause 2 “Normative references” and renumbering of subsequent clauses;
- replacement of the original internal standard (DCHP) with Benzyl 2-ethyl-hexyl phthalate;
- addition of five detected phthalates (including DCHP);
- replacement of the term “plasticized or soften material” with “plasticized material” in 3.1 (former 2.1);
- revision of the terms and definitions in 3.2 (former 2.2) and 3.3 (former 2.3);
- deletion of the frequency of thermostatic ultrasonic bath in 6.3 (former 5.3);
- deletion of “in duplicate” in 7.3.1 (former 6.2.1);
- revision of extract temperature from “(60 ± 5) °C” to “about 60 °C” in 7.3.3 (former 6.2.3);
- revision of Formula (1) and Formula (2) in Clause 8 (former Clause 7);
- addition of the example of determining the mass of the plastic component (coating) in Annex A.

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 covers a test method for the determination of some phthalates in textile articles.

Phthalates are commonly used as plasticizers in polymers. Phthalates are an issue for textile manufacturers and retailers due to their use within motifs, coated fabrics, plastisol prints, buttons, etc.

Phthalates are controversial because high doses of many phthalates have shown hormonal activity in rodent studies. Studies on rodents involving large amounts of phthalates have shown damage to the liver, the kidneys, the lungs, and the developing testes.

Due to their potential effect as endocrine disruptors, some of the listed phthalates are toxic in reproduction. The listed phthalates are based on those which have been restricted in some regulations (for example, in the European Union).

Textiles — Determination of the phthalate content — Tetrahydrofuran method

WARNING — This document calls for the use of substances and/or procedures that can be injurious to health if adequate precautions are not taken. It refers only to technical suitability and does not absolve the user from legal obligations relating to health and safety at any stage. It has been assumed in the drafting of this document that the execution of its provisions is entrusted to appropriately qualified and experienced operators.

1 Scope

This document specifies a method of determining phthalates in textiles with gas chromatography–mass spectrometry (GC-MS).

This document is applicable to textile products where there is a risk of the presence of some phthalates.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

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

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at https://www.electropedia.org/

3.1
plasticized material
plastic material that is treated with chemicals to make it more flexible

Note 1 to entry: For this specific document, the chemicals are phthalates.

EXAMPLE Examples of plastic material: coating, pigment print binder, etc.

3.2
overall treated
with a continuous finish, coating or print

3.3
locally treated
with a discontinuous finish, coating or print

3.4
representative specimen
specimen obtained by mixing pieces of all the different treated parts and colours

4 Principle

The phthalates are extracted from textile specimen by ultrasonic bath with tetrahydrofuran. As the plastic polymer is partially or completed dissolved, the phthalate extraction is followed by the precipitation of the dissolved polymer using the appropriate solvent (acetonitrile, *n*-hexane, etc.). Centrifugate the extract and then take a suitable volume of the organic solution for analysis. Gas chromatography–mass spectrometry (GC–MS) is used to identify individual phthalates in the specimen and quantify them by using an internal standard (IS).

5 Reagents

Unless otherwise specified, use only reagents of recognized analytical grade.

5.1 Tetrahydrofuran (THF), CAS Registry Number®[1] (CAS RN®): 109-99-9.

5.2 Solvents used for the precipitation. Examples are:

a) **Acetonitrile**, CAS Registry Number® (CAS RN®): 75-05-8; or

b) ***n*-Hexane**, CAS Registry Number® (CAS RN®): 110-54-3.

5.3 The list of **phthalates** determined by this method is given in Table 1. Other phthalates can be analysed by this method if the laboratory performs a validation.

Table 1 — List of phthalates

No.	Substance [a]	Abbreviation	CAS RN®
1	Di-cyclo-hexyl phthalate	DCHP	84-61-7
2	Di-iso-nonyl phthalate	DINP	28553-12-0 or 68515-48-0
3	Bis-(2-ethylhexyl) phthalate	DEHP	117-81-7
4	Di-n-octyl phthalate	DNOP	117-84-0
5	Di-iso-decyl phthalate	DIDP	26761-40-0 or 68515-49-1
6	Butyl benzyl phthalate	BBP	85-68-7
7	Di-butyl phthalate	DBP	84-74-2
8	Di-iso-butyl phthalate	DIBP	84-69-5
9	Di-n-pentyl phthalate	DPP	131-18-0
10	1,2-benzenedicarboxylic acid; Di-C_{6-8} -branched alkyl esters, C_7-rich	DIHP	71888-89-6
11	Bis-(2-methoxyethyl) phthalate	DMEP	117-82-8
12	Di-iso-pentyl phthalate	DIPP	605-50-5
13	Di-n-hexyl phthalate	DNHP	84-75-3
14	N-pentyl-iso-pentyl phthalate	PIPP	776297-69-9
15	Di-iso-hexyl phthalate	DIHxP	71850-09-4

[a] Not all commercially available phthalate standards are of analytical grade.

5.4 Benzyl 2-ethyl-hexyl phthalate, CAS Registry Number® (CAS RN®): 27215-22-1, internal standard (IS). Other internal standards (for example, deuterated phthalates) can be used if the laboratory performs a validation.

6 Apparatus

6.1 Gas chromatography, coupled with mass spectrometer (GC–MS).

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1) CAS Registry Number® is a trademark of CAS corporation. 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.

6.2 Vial, airtight glassware to be sealed with a PTFE septum. 40 ml vials have been found suitable.

6.3 Thermostatic ultrasonic bath, with controllable heating capable of maintaining a temperature of about 60 °C in water bath.

6.4 Glass flasks with glass stoppers. 100 ml glass flasks have been found suitable.

6.5 Calibrated volumetric flasks, of capacities 50 ml and 100 ml.

6.6 Volumetric device, of capacities 10 ml and 20 ml.

6.7 Analytical balance, with a resolution of 0,1 mg.

6.8 Centrifuge.

7 Procedure

WARNING — The vapour of the organic solvents is highly flammable, especially at high temperature. Allow glassware to cool down before use.

7.1 Cross-contamination provisions

Glassware and/or equipment used shall be free from phthalates in order to minimize cross-contamination. For pre-used glassware, after washing, should be given an extra rinse with 0,1 mol/l nitric acid, water and finally with acetone. Glassware should be completely dried before use. To avoid contamination, do not use any plastic container (for example, for water).

7.2 Preparation of standard solutions

7.2.1 Internal standard solution

Prepare a 1 000 mg/l stock standard solution of the internal standard in the solvent used for the precipitation (5.2) after the ultrasonic extraction (see 7.3).

7.2.2 Preparation of stock standard solutions

Separately prepare a series of 1 000 mg/l individual stock standard solutions of the individual phthalate (5.3) in the solvent used for the precipitation.

For example, weigh 50,0 mg of a phthalate in a 50 ml volumetric flask and fill the volumetric flask up to the mark with the solvent used for the precipitation and mix thoroughly to dissolve completely the substance.

Most of the stock standards may be made in a mixed stock. This saves time and effort when preparing calibration solutions. DINP, DIDP and DIHP have overlapping peaks. It is recommended to make up these stock standard solutions separately, as their calibration solutions have to be made in higher (for example, 5 times) concentrations than for the other phthalates because of their multi-peak nature.

7.2.3 Preparation of the calibration solutions

From the stock standard solutions, prepare at least five appropriate phthalate calibration solutions (example of concentrations at 1 mg/l, 3 mg/l, 15 mg/l, 30 mg/l and 90 mg/l as described in the Table 2), each containing an equal amount of the target phthalates (5.3) and an amount of internal standard (5.4) in a mixture of tetrahydrofuran and the solvent used for the precipitation, mixed by volume at a ratio of 1:2 (1/3 of tetrahydrofuran to 2/3 of the other solvent), as shown in Table 2. Each calibration solution should have a final internal standard concentration of 5 mg/l. Prepare one calibration blank. Analyse the calibration solutions and calibration blank by the GC-MS. Qualitatively analyse the result to ensure proper retention times and the absence of contamination and built up the calibration curve.

Table 2 — Examples of calibration solutions

Operation items	Blank	L1	L2	L3	L4	L5
Concentration of phthalate (mg/l)	0	1	3	15	30	90
Volumetric flask (ml)	50	100	100	50	50	50
Volume of phthalate stock solution (ml)	/	0,1	0,3	0,75	1,5	4,5
Volume of internal solution (ml)	0,25	0,5	0,5	0,25	0,25	0,25
Fill up to the mark	with a mixture of 1/3 of tetrahydrofuran to 2/3 of the solvent used for the precipitation					

If target ions other than 149 are used for quantification of DEHP, DNOP, DINP, DIDP and DIHP, all the listed phthalates may be calibrated and quantified together.

Typical quantification ions for phthalates are shown in Annex B.

If DIDP and DINP overlap in the chromatogram; choose target ions indicated in Annex B.

In case the concentration of some phthalate in the extraction solution of a specimen lies outside the limits of the calibration curve, dilute the solution with a mixture of 1/3 of tetrahydrofuran to 2/3 of the solvent used for the precipitation containing 5 mg/l of the internal standard, so that the phthalates in the sample can be properly quantified.

NOTE The stock standard solutions are stored at 0 °C to 4 °C for up to six months, and the working solutions are stored at 0 °C to 4 °C for up to three months, or sooner if ongoing quality control indicates problems.

7.3 Ultrasonic extraction and determination of phthalates

7.3.1 General

Ultrasonic extraction is performed using tetrahydrofuran on test specimens prepared from each textile sample, followed by precipitation of the (partially or completed) dissolved plastic component using an appropriate solvent, centrifugation, and determination of phthalates. A blank is run in parallel to avoid errors caused by contamination from the laboratory environment.

NOTE For example, polyvinylchloride (PVC) is completely dissolved in tetrahydrofuran.

7.3.2 Preparation of test specimen

A representative test specimen shall be prepared by mixing and cutting pieces from every coated area/part of the textile sample (see Annex A for further information on coating types). Cut the representative specimen into small pieces (less than 5 mm in the greatest dimension), homogenize it, and weigh (0,30 ± 0,01) g of these pieces in the vial (6.2).

Using an appropriate volumetric device (6.6), add to vial 10 ml of tetrahydrofuran (5.1) containing 5 mg/l of internal standard (5.4) and seal it tightly.

7.3.3 Extraction procedure

Place the vial in the ultrasonic bath (6.3) at about 60 °C for 1 h ± 5 min to allow the extraction of phthalates (by complete or partial dissolution of the polymer). Then, remove the vial from the bath and let it stand still until the extraction solution cools down to room temperature.

Ensure that the vial remain airtight in the ultrasonic bath (6.3) throughout the entire extraction process.

Using an appropriate volumetric device (6.6), add dropwise to the vial 20 ml of the solvent used for the precipitation (5.2) containing 5 mg/l of internal standard.

Shake the vial vigorously (preferably on a vortex type shaker) for at least 30 s and allow them to stand still for (30 ± 2) min in order to allow the precipitation of polymer.

Centrifugate the vial at least 700 g (for example, 2 500 min^{-1} for 10 cm radius) by the centrifuge (6.8) for at least 10 min to drive and settle any remaining suspended precipitates of polymer in organic phase to the bottom to obtain a transparent organic solution. Then, withdraw and transfer a specimen aliquot of the organic solution into a suitable GC sampling vial for GC-MS analysis.

CAUTION — Direct injection into GC-MS of suspended matter solution or cloudy solution might contaminate the equipment.

If necessary, prepare further diluted solutions using an appropriate volume of a mixture of tetrahydrofuran (5.1) and the solvent used for the precipitation (5.2) mixed by volume at a ratio of 1:2 (1/3 of tetrahydrofuran to 2/3 of the other solvent) containing 5 mg/l of the internal standard (5.4) and then repeat the analysis.

7.3.4 Phthalates determination

Determinate the phthalates extracted in 7.3.3 by GC-MS (6.1).

An example of the parameters for GC-MS analysis of target phthalates is given in Annex B.

The statistical data of interlaboratory trials in the first edition is shown in Annex D.

In some cases when the phthalates level is very low, it may be necessary to increase the mass of the test specimens.

8 Calculation of the results

8.1 Calculation based on the corrected mass (by default)

From the calibration graph, determine the response of each phthalate, corrected for the internal standard peak area, and interpolate the concentration of the phthalate, in milligrams per litre (mg/l), correcting for any dilutions. Subtract the blank concentration from the specimen concentration. Calculate the result using Formula (1):

$$w_c = \frac{V \times (b - a) \times F}{m_c \times 10\,000} \qquad (1)$$

where

w_c is the mass fraction of the individual phthalate, based on the corrected mass of the test specimen (%);

V is 30 ml, that is the total volume of the phthalate solution before any dilution (10 ml of tetrahydrofuran used for the extraction +20 ml of the solvent used in the precipitation step);

m_c is the corrected mass of specimen (g);

a is the concentration of the individual phthalate of the blank solution (mg/l);

b is the concentration of the individual phthalate of the specimen solution (mg/l);

F is the dilution factor.

The determination of the corrected mass of test specimen shall be in accordance with Annex A. Examples of the calculation are also given. Overall treated materials are illustrated in Figure A.1 and locally treated materials in Figure A.2.

If the corrected mass of the test specimen, m_c, cannot be obtained, give a remark in the test report and calculate the result according to 8.2.

8.2 Calculation based on the total mass (when relevant)

If the corrected mass of the test specimen, m_c, in accordance with Annex A, cannot be obtained and used for the calculation of the results, then calculate the result using Formula (2).

$$w_T = \frac{V \times (b - a) \times F}{m_T \times 10\ 000} \tag{2}$$

where

w_T is the mass fraction of the individual phthalate, based on the total mass of the test specimen (%);

V is 30 ml, that is the total volume of the phthalate solution before any dilution (10 ml of tetrahydrofuran used for the extraction + 20 ml of the solvent used in the precipitation step);

m_T is the total mass of specimen (g);

a is the concentration of the individual phthalate of the blank solution (mg/l);

b is the concentration of the individual phthalate of the specimen solution (mg/l);

F is the dilution factor.

9 Test report

The test report shall include at least the following information:

a) a reference to this document, i.e. ISO 14389:2022;

b) all details necessary for complete identification of the sample tested;

c) details on the preparation of the specimens;

d) the value of the corrected mass, m_c, in grams (see 8.1); where relevant, the value of the total mass, m_T, in grams (see 8.2);

e) the test results of each listed phthalate in the plasticized material or textile product, w_c (or, where relevant, w_T), expressed in percentage (%) or milligram per kilogram (mg/kg);

f) any deviation by agreement or otherwise from the procedure specified;

g) any unusual features observed;

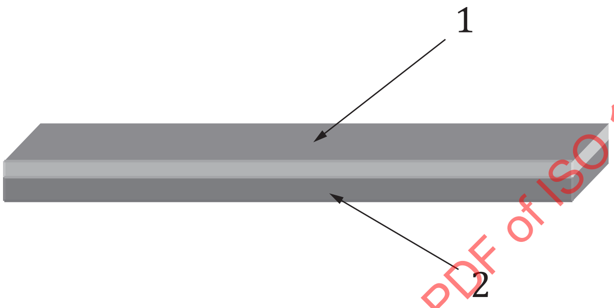
h) the date of the test.

Annex A
(normative)

Calculations

A.1 Overall treated materials

In the case of overall treated specimen, see Figure A.1:



Key

1	plastic component (coating)
2	fabric

Figure A.1 — Overall treated specimen

The part of the coating is obtained by using Formula (A.1):

$$m = m_1 - m_2 \tag{A.1}$$

where

m_1 is the total mass of overall treated specimen (g);

m_2 is the mass of textile component (g);

m is the mass of coating (g).

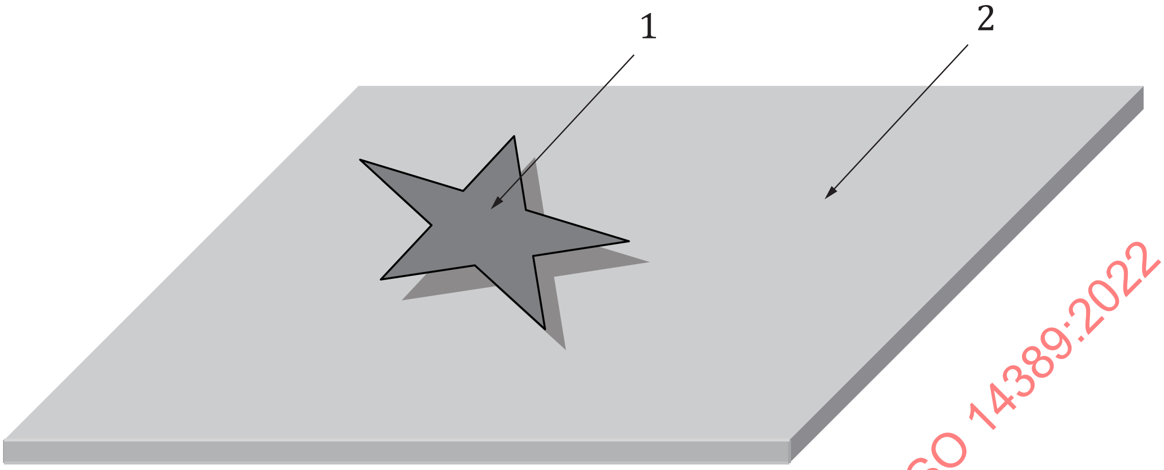
NOTE 1 The mass of coating is the corrected mass of the specimen as described in Formula (1).

From a test specimen, where the total mass of overall treated specimen, m_1, is measured (g), the plastic component (coating) is removed by a mechanical, thermal or chemical procedure (or a combination of these). The plastic component, m, shall be determined by comparison with the textile component m_2.

NOTE 2 An example of chemical procedure is given in Annex C.

A.2 Locally treated materials

A.2.1 In the case of locally treated specimen, see Figure A.2.



Key

1	plastic component (coating)
2	fabric

Figure A.2 — Locally treated specimen

The mass of the plastic component, m, expressed in grams (g), is calculated by using Formula (A.2):

$$m=(m_1-m_2)\times S \tag{A.2}$$

where

m_1 is the surface density (mass divided by area) of treated area of specimen (g/m^2);

m_2 is the surface density (mass divided by area) of textile material (g/m^2);

m is the mass of the plastic component (coating) (g);

NOTE The mass of the plastic component is the corrected mass of the specimen as described in Formula (1).

S is the surface area of the treated area of the specimen (m^2).

Firstly, determine the surface density (mass divided by area) from an untreated part (only textile material is involved) m_2.

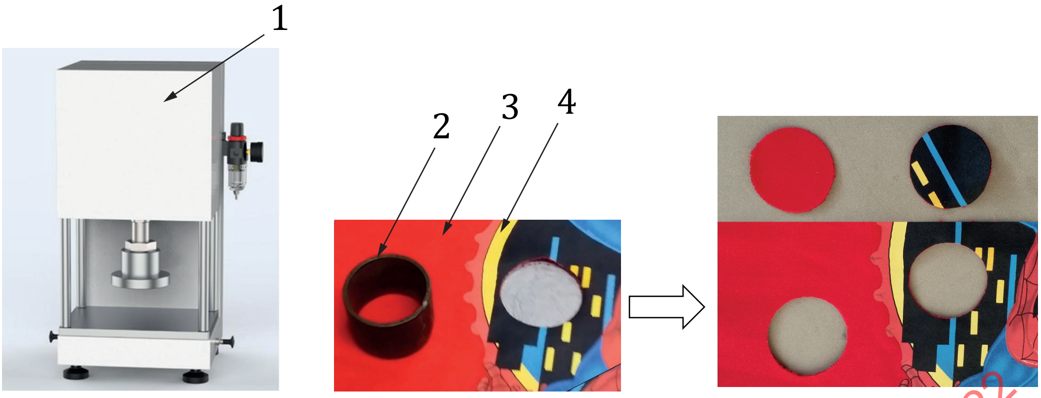
From a test specimen:

— measure the treated surface density (mass divided by area), m_1;

— measure the treated area, S.

A.2.2 An example of determining the mass of the plastic component (coating) is given below.

If the plastic component (coating) is uniform, the cutting sample machine (for example, pneumatic) can be used to obtain specimens with the same area (very important) shown in Figure A.3 and the cutting dice can be available in different size and shape.



Key

1	cutting sample machine
2	cutter/blade
3	textile component (deep red)
4	treated part

Figure A.3 — Example of cutting sample

Firstly, the ratio of plastic component (coating) mass to total mass can be calculated by using Formula (A.3):

$$r = \frac{m_1 - m_2}{m_1} \tag{A.3}$$

where

r is the ratio of coating mass to total mass;

m_1 is the total mass of treated part with the same area (g);

m_2 is the mass of textile component with the same area (g).

Then, the mass of coating can be obtained by using Formula (A.4):

$$m_c = r \times m_T \tag{A.4}$$

where

r is the mass ratio of plastic component (coating) to treated part;

m_T is the total mass of treated part (g). Same as m_T in Formula (2) in 8.2;

m_c is the mass of plastic component (coating) (g). Same as m_c in Formula (1) in 8.1.

Annex B
(informative)

Example of test parameters by GC-MS

As the instrumental equipment of the laboratories can vary, no generally applicable parameters can be provided for chromatographic analyses. The following parameters have been found to be successful.

a) Capillary column: DB-5MS, length 30 m, inside diameter 0,25 mm, film thickness 0,1 µm; or equivalent;

b) Temperature programme:

  — 100 °C (1 min), 100 °C to 180 °C (15 °C/min);

  — 180 °C (1 min), 180 °C to 300 °C (5 °C/min);

  — 300 °C (10 min);

c) Injector temperature: 300 °C;

d) Transfer line temperature: 280 °C;

e) Carrier gas: helium, purity no less than 99,999 %, 1,2 ml/min;

f) Ionization mode: EI;

g) Ionization energy: 70 eV;

h) Detection mode: selected ion monitor detection;

i) Injector system: split/splitless injector, split at 1,5 min;

j) Injector volume: 1 µl.

Typical quantification ions for phthalates are shown in Table B.1.

Table B.1 — Typical quantification ions for phthalates

No.	Name	Typical ions amu		
		Quantitative	Qualitative	
1	Di-butyl phthalate (DBP)	149	223	205
2	Butyl benzyl phthalate (BBP)	149	206	91
3	Bis-(2-ethylhexyl) phthalate (DEHP)	167	149	279
4	Di-*n*-octyl phthalate (DNOP)	279	167	261
5	Di-iso-nonyl phthalate (DINP)	293	149	127
6	Di-iso-decyl phthalate (DIDP)	307	149	141
7	Di-iso-butyl phthalate (DIBP)	149	167	223
8	Di-n-pentyl phthalate (DPP)	149	219	237
9	1,2-benzenedicarboxylic acid; Di-C$_{6-8}$ -branched alkyl esters, C$_7$-rich (DIHP)	265	149	99
10	Bis-(2-methoxyethyl) phthalate (DMEP)	149	59	207

Table B.1 *(continued)*

No.	Name	Typical ions amu		
		Quantitative	Qualitative	
11	Di-cyclo-hexyl phthalate (DCHP)	149	167	249
12	Di-iso-pentyl phthalate (DIPP)	149	237	219
13	Di-n-hexyl phthalate (DNHP)	149	251	104
14	N-pentyl-iso-pentyl phthalate (PIPP)	149	237	219
15	Di-iso-hexyl phthalate (DIHxP)	149	251	85
16	Benzyl 2-ethyl-hexyl phthalate (internal standard)	149	150	262

Annex C
(informative)

Determination of PVC mass fraction by chemical method

C.1 Principle

The PVC layer is dissolved (out) from a known dry mass of the sample, with tetrahydrofuran. The textile residue is collected, washed, dried and weighed; its mass, corrected if necessary, is expressed as a percentage of the dry mass of the sample. The mass fraction of dry PVC is found by difference.

The method has been validated by the European Commission's Joint Research Centre (JRC) in collaboration with 12 laboratories using a cotton sample spread with PVC. No outliers were detected. The repeatability coefficient of variation and reproducibility coefficient of variation obtained were 0,6 % and 1,4 %, respectively. For cotton, the d correction factor was determined to d = 1,00. In case fibres other than cotton, the d correction factor for a pure fibre [needed for calculation of results in Formula (C.1)] should be determined by applying the method to 100 % pure fibre (at least three specimens of 1 g each) and calculating d as the ratio of the dry mass of the specimen after pretreatment (described in ISO 1833-1[1]) to the dry-mass of the residue after the application of the method. The drying step shall be carried out in a ventilated oven (105 °C) for 14 h to 16 h.

C.2 Apparatus

C.2.1 Weighing bottle, or any other apparatus giving identical results.

C.2.2 Filter crucibles.

C.2.3 Desiccator, containing self-indicating silica gel.

C.2.4 Ventilated oven, for drying specimens at (105 ± 3) °C.

C.2.5 Analytical balance, with a resolution of 0,1 mg.

C.2.6 Glass conical flasks, fitted with screw PTFE cap, of at least 100 ml in capacity.

C.2.7 Thermostatic ultrasonic bath.

C.2.8 Graduated cylinder, of capacity 50 ml.

C.3 Reagents

Unless otherwise specified, use only reagents of recognized analytical grade.

C.3.1 Tetrahydrofuran (THF), CAS Registry Number® (CAS RN®): 109-99-9.

C.3.2 Grade 3 water, in accordance with ISO 3696.

C.4 Sampling

Use the specimens as received.

C.5 Test procedure

Dry at least three specimens of 1 g each, each one in a different weighing bottle, in a ventilated oven (105 °C) for 14 h to 16 h.

At the same time, dry three filter crucibles in three weighing bottles in a ventilated oven (105 °C) for 14 h to 16 h.

Cool all the mentioned weighing bottles, containing specimens and filter crucibles, in a desiccator (placed beside the balance) for at least 2 h.

Weigh the weighing bottles containing specimens.

Transfer quantitatively specimens in the glass conical flask fitted with a screw PTFE cap of at least 100 ml capacity, that will be used for the method, and then weigh empty weighing bottles (the difference is the mass of specimens, sample mass).

Weigh filter crucibles.

To each specimen contained in the glass conical flask, add 50 ml of tetrahydrofuran per gram of specimen. Dissolve the PVC in the ultrasonic bath (6.3) for 1 h at 60 °C and then filter immediately the solution through the weighed filter crucible. Transfer the residue to the filter crucible. Wash twice the residue in the filter crucible with 30 ml tetrahydrofuran preheated at 60 °C, and allow draining under gravity. Then, rinse thoroughly with water and allow draining under gravity. Make sure that specimens are washed with a liberal amount of water, sufficient to avoid a tetrahydrofuran smell when residues are dried in the oven. Finally, drain the crucible with suction.

Dry filter crucibles with residues in the weighing bottle in a ventilated oven (105 °C) for 14 h to 16 h.

Cool them in a desiccator (placed beside the balance) for at least 2 h.

Weigh, within 2 min of their removal from the desiccator, the filter crucibles with residues (the difference with empty filter crucibles is the mass of residues, residue mass).

C.6 Calculation of results

Calculate the results as described in Formula (C.1):

$$w_1 = 100 \times \frac{r \times d}{m} \tag{C.1}$$

where

w_1 is the mass fraction of clean, dry insoluble textile component (%);

m is the dry mass of the specimen (g);

r is the dry mass of the textile residue (g);

d is the correction factor for loss of mass of the insoluble textile component in the reagent during analysis.

Then, calculate the mass fraction of the insoluble textile component on a clean, dry mass basis, with adjustment by conventional factors (agreed allowances[4]) using Formula (C.2):

$$w_{1\text{A}} = 100 \times \frac{w_1 \times \left(1 + \frac{a_1}{100}\right)}{w_1 \times \left(1 + \frac{a_1}{100}\right) + (100 - w_1)} \tag{C.2}$$

where

$w_{1\text{A}}$ is the mass fraction of insoluble component, adjusted by agreed allowance (%);

w_1 is the mass fraction of clean, dry insoluble component as calculated from Formula (C.1);

a_1 is the agreed allowance for the insoluble component.

The mass fraction of the soluble component, in this case, PVC, $w_{2\text{A}}$ (%), is obtained by difference.

In case the textile sample coated with PVC is composed of a mixture of fibres, which are insoluble under the conditions of this method, the correction factor, d, and the agreed allowance, a_1, in Formulae (C.1) and (C.2), respectively, will have to be applied to the mixture of fibres. In order to calculate the combined parameters, Formulae (C.3) and (C.4) shall be used:

$$d_{\text{combined}} = \sum_{i=1}^{n} m_i \times d_i \tag{C.3}$$

$$a_{\text{combined}} = \sum_{i=1}^{n} m_i \times a_i \tag{C.4}$$

where

i is the i^{th} component(s) of the fibre mixture;

m_i is the mass fraction of the i^{th} component of the fibre mixture;

d_{combined} is the correction factor for loss of mass of the fibre mixture in the reagent during analysis;

d_i is the correction factor for loss of mass of the i^{th} insoluble fibre component of the fibre mixture in the reagent during analysis;

a_{combined} is the agreed allowance of the fibre mixture;

a_i is the agreed allowance for the i^{th} insoluble fibre component of the fibre mixture.

Annex D
(informative)

Statistical data

D.1 Summary

On behalf of ISO/TC 38/WG 22, as well as CEN/TC 248/WG 26, the European Commission's Joint Research Centre (JRC) organized, in 2011, a collaborative trial for the validation of four methods for the determination of phthalates and one method for the quantification of PVC in textile products. The first four methods investigated had been developed and used in both European and non-European countries, while the fifth method was developed by the JRC.

Methods 1, 2 and 3 were based on ultrasonic extraction of phthalates (with 80 parts *n*-hexane to 20 parts acetone, *n*-hexane and tert-butyl methyl ether, respectively); method 4 was based on the dissolution of PVC with tetrahydrofuran in an ultrasonic generator, followed by the re-precipitation of it with acetonitrile. In all cases, phthalates were then quantified by GC-MS.

Method 5 for the determination of mass fraction of PVC was based on the dissolution of PVC with tetrahydrofuran in an ultrasonic generator, followed by the washing of the residue and its gravimetric determination.

The collaborative exercise was organized, according to ISO 5725-2[2] as a balanced uniform-level experiment, i.e. with the same number of test results in each laboratory, which each laboratory analysing the same levels of test samples. Thirteen laboratories, 8 European and 5 from outside of the EU, provided results.

The homogeneity assessment, carried out by the JRC with method 2, proved that all samples can be considered "sufficiently homogeneous" according to the IUPAC harmonized protocol for proficiency testing.

In total, four cotton samples spread with PVC layer and one sample made of PVC containing 7 phthalates (DEHP, DBP, BBP, DINP, DIDP, DNOP and DIBP) at 3 concentration levels were analysed by 13 laboratories in triplicates. Levels I, II and III refer to samples containing a specific phthalate in concentrations of approximately 200 mg, 1 000 mg and 5 000 mg of phthalate per kilogram of PVC. In the case of DIDP and DINP, level I corresponded to approximately 500 mg/kg. In addition, one sample was measured to determine its PVC mass fraction. In total, 4091 test results were collected. The samples were produced by an Italian company.

Out of the 104 data sets, only 27 can be considered as being part of a normal distribution at 95 % probability level using the Shapiro-Wilk test. The situation improved after the elimination of outliers (47 data sets were normally distributed). The distribution of the mean values was proved to be normal in the majority of cases.

The results were statistically evaluated, according to ISO 5725-2[2] and ISO 5725-5[3], with a specific software. The consensus values and the precisions of the various methods, in terms of repeatability, *r* and reproducibility, *R*, limits as well as repeatability coefficient of variation, $C_{V,r}$, and reproducibility coefficient of variation, $C_{V,R}$, were calculated. Applying ISO 5725-2[2] the statistical outliers identified with Cochran's and Grubbs' tests were rejected, together with the results of LC0004 for method 4 and the ones of LC0005 for DIDP in methods 1 to 4, which were identified as outliers with Mandel's h statistics. According to ISO 5725-5[3], all test results were retained and robust statistics were used. These two alternative approaches gave results that can be considered in good agreement. Generally, the differences were lower than 35 %, except in a few cases.

Considering phthalates, both the minimum and the maximum coefficient of variation of repeatability were obtained in method 4 (3,0 % and 23,5 %, respectively). Concerning the coefficient of variation of reproducibility, the minimum value 19,4 % was shown by method 3 and the highest 189,2 % by method 2. Results indicated that both the four methods for phthalates and the laboratories' performance have to be drastically improved. Poor repeatability was observed in the case of several laboratories and the large spread in the mean values calculated in the 13 laboratories was responsible for the high observed coefficients of variation of reproducibility.

Two samples, one made of PVC (E) and one made of cotton spread with PVC (A), were prepared starting from the same plastisol batch. Results were in good agreement when the concentrations of phthalates were expressed in milligram (mg) of phthalate per kilogram (kg) of PVC.

The best method in terms of phthalates' recovery was number 4, based on tetrahydrofuran; whereas, method 2 was the worst one. The same extraction efficiency was practically shown by methods 1 and 3.

Method 5 for the quantification of PVC showed good precision and may be considered validated for cotton samples spread with PVC. The repeatability and reproducibility coefficients of variation were 0,6 and 1,4, % respectively. These values are in line with the ones obtained in the case of similar dissolution methods validated in the context of quantification of fibre binary mixtures.

Even though the collaborative trial was not a proficiency test, the performances of the participating laboratories were evaluated. Laboratories LC0003 and LC0008 showed the best performance: their z-scores were in almost all cases good (|z| < 1) and in the others at least satisfactory (|z| < 2). On the contrary, laboratories LC0004 and LC0005 obtained the worst performance: they showed, respectively, 25 and 17 z-scores considered questionable or unsatisfactory out of 104.

Regarding the methods, after the elimination of outliers, method 4 showed 6,2 % of questionable and unsatisfactory z-scores. Methods 2, 1 and 3 followed with 5,9 %, 3,7 % and 3,7 %, respectively.

See Tables D.1 to D.8.

D.2 Results of the collaborative trial for methods 1 to 4

IMPORTANT — The trials have been carried out in order to elaborate the ISO test method.

Table D.1 — Results of the collaborative trial for methods 1 to 4 on DIBP and DBP

Sample	Method	DIBP						DBP					
		outlier	mean mg/kg	r mg/kg	$C_{V,r}$ %	R mg/kg	$C_{V,R}$ %	outlier	mean mg/kg	r mg/kg	$C_{V,r}$ %	R mg/kg	$C_{V,R}$ %
A	1	1	3 256,5	353,5	10,9	2 104,0	64,6	0	713,3	71,2	10,0	594,7	83,4
	2	3	2 554,1	199,3	7,8	912,4	35,7	1	566,5	62,5	11,0	615,3	108,6
	3	0	3 379,1	373,1	11,0	1 553,4	46,0	0	736,7	86,1	11,7	565,8	76,8
	4	1	3 632,3	406,4	11,2	1 441,9	39,7	2	738,3	54,6	7,4	551,2	74,7
B	1	1	120,7	17,4	14,4	108,1	89,6	—					
	2	1	100,6	17,1	17,0	92,6	92,1						
	3	2	135,8	22,4	16,5	133,8	98,5						
	4	2	116,1	12,3	10,6	79,5	68,5						
C	1	—						0	133,9	14,9	11,1	146,3	109,3
	2							0	112,8	18,6	16,5	148,5	131,6
	3							0	143,5	18,7	13,0	158,6	110,6
	4							1	136,3	25,7	18,9	170,2	124,9