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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 committee responsible for this document is ISO/TC 38, *Textiles*.

Introduction

This International Standard 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 (e.g. in the European Union).

Textiles — Determination of the phthalate content — Tetrahydrofuran method

WARNING — This International Standard calls for the use of substances and/or procedures that might 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 International Standard that the execution of its provisions is entrusted to appropriately qualified and experienced operators.

1 Scope

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

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

2 Terms and definitions

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

2.1
plasticized or softened material
plastic material that is treated with chemicals to make it more flexible

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

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

2.2
overall treated textile
textile with a continuous finish, coating or print

2.3
locally treated textile
textile with a discontinuous finish, coating or print

2.4
representative specimen
specimen obtained by mixing pieces of all the different treated parts and colours

3 Principle

The phthalates are extracted from textile specimen by ultrasonic generator 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.). After centrifugation and dilution of the extract to volume, gas chromatography–mass spectrometry (GC-MS) is used to identify individual phthalates in the specimen and quantify them by using an internal standard (IS).

4 Reagents

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

4.1 **Tetrahydrofuran (THF)**, CAS number: 109-99-9.

4.2 **Solvents used for the precipitation**. Examples are:

4.2.1 **Acetonitrile**, CAS number: 75-05-8.

4.2.2 ***n*-Hexane**, CAS number: 110-54-3.

4.3 **Di-cyclohexyl phthalate (DCHP)**, CAS number: 84-61-7, internal standard (IS).

4.4 **Di-isononyl phthalate (DINP)**, CAS number 28553-12-0 or 68515-48-0.

4.5 **Di-(2-ethylhexyl) phthalate (DEHP)**, CAS number 117-81-7.

4.6 **Di-*n*-octyl phthalate (DNOP)**, CAS number 117-84-0.

4.7 **Di-iso-decyl phthalate (DIDP)**, CAS number 26761-40-0 or 68515-49-1.

4.8 **Butyl benzyl phthalate (BBP)**, CAS number 85-68-7.

4.9 **Di-butyl phthalate (DBP)**, CAS number 84-74-2.

4.10 **Di-iso-butyl phthalate (DIBP)**, CAS number 84-69-5.

4.11 **Di-pentyl phthalate (DPP)**, CAS number: 131-18-0.

4.12 **Di-iso-heptyl phthalate (DIHP)**, CAS number: 71888-89-6.

4.13 **Di-methoxyethyl phthalate (DMEP)**, CAS number: 117-82-8.

5 Apparatus

5.1 **Gas chromatograph-mass spectrometer (GC-MS)**, with mass selective detector (MSD).

5.2 **Vial**, of capacity 40 ml.

5.3 **Thermostatic ultrasonic bath**, with a frequency of (40 ± 5) kHz.

5.4 **Glass flasks with glass stoppers**, of capacity 100 ml.

5.5 **Calibrated volumetric flasks**, of capacities 50 ml and 100 ml.

5.6 **Volumetric graduated pipette**, of capacities 10 ml and 20 ml.

5.7 **Balance**, with a resolution of 0,1 mg.

5.8 **Water bath**.

5.9 **Rotary evaporator**.

6 Procedure

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

Avoid direct contact between the samples and glassware and/or equipment used in order to minimize cross-contamination. Glassware, after washing, should be given an extra rinse with 0,1 N nitric acid, water and finally with acetone. Glassware should be completely dried before use. To avoid contamination, do not use any plastic container (e.g. for water).

6.1 Preparation of standard solutions

6.1.1 Internal standard solution

Prepare a 1 000 mg/l stock standard solution of the internal standard in the solvent used for the precipitation (4.2) after the ultrasonic extraction (see 6.2).

6.1.2 Preparation of stock standard solutions

Prepare a series of individual stock standard solutions of the individual phthalate ester in the solvent used for the precipitation as shown in Table 1.

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.

Table 1 — Stock standard solutions

Phthalate ester	**DCHP (IS)**	**DINP**	**DEHP**	**DNOP**	**DIDP**	**BBP**	**DBP**	**DIBP**	**DPP**	**DIHP**	**DMEP**
Concentration, mg/l	1 000										

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 (5x) concentrations than for the other phthalates because of their multi-peak nature. Hence, the higher limit of detection in Annex B.

6.1.3 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 (4.4 through 4.13) and an amount of internal standard (4.3) in a mixture of tetrahydrofuran and the solvent used for the precipitation, mixed by volume at a ratio of 1:2 (33 parts tetrahydrofuran to 66 parts 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 with 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

Concentration	Instructions
Blank	In a 50 ml volumetric flask, add 0,25 ml of internal standard (DCHP) stock solution; then, fill up to the mark with a mixture of tetrahydrofuran and the solvent used for the precipitation, mixed by volume at a ratio of 1:2 (33 parts tetrahydrofuran to 66 parts of the other solvent)
1 mg/l	Add 0,1 ml of each stock standard solution in 100 ml volumetric flask plus 0,5 ml of the internal standard (DCHP) stock solution; then, fill up to the mark with a mixture of 33 parts of tetrahydrofuran to 66 parts of the solvent used for the precipitation.
3 mg/l	Add 0,3 ml of each stock standard solution in 100 ml volumetric flask plus 0,5 ml of the internal standard (DCHP) stock solution; then, fill up to the mark with a mixture of 33 parts of tetrahydrofuran to 66 parts of the solvent used for the precipitation.
15 mg/l	Add 0,75 ml of each stock standard solution in 50 ml volumetric flask plus 0,25 ml of the internal standard (DCHP) stock solution; then, fill up to the mark with a mixture of 33 parts of tetrahydrofuran to 66 parts of the solvent used for the precipitation.
30 mg/l	Add 1,5 ml of each stock standard solution in 50 ml volumetric flask plus 0,25 ml of the internal standard (DCHP) stock solution; then, fill up to the mark with a mixture of 33 parts of tetrahydrofuran to 66 parts of the solvent used for the precipitation.
90 mg/l	Add 4,5 ml of each stock standard solution in 50 ml volumetric flask plus 0,25 ml of the internal standard (DCHP) stock solution; then, fill up to the mark with a mixture of 33 parts of tetrahydrofuran to 66 parts 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 33 parts of tetrahydrofuran to 66 parts of the solvent used for the precipitation containing 5 mg/l of the internal standard, so that the sample can be properly quantified.

NOTE The stock standard solutions are stored at 0 °C to 4 °C for up to 12 months, and the working solutions are stored at 0 °C to 4 °C for up to six months, or sooner if ongoing quality control indicates problems.

6.2 Ultrasonic extraction and determination of phthalates

6.2.1 General

Ultrasonic extraction is performed using tetrahydrofuran on test specimens prepared in duplicate 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.

6.2.2 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. 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 each of two 40 ml airtight vials (5.2) sealed with a PTFE septum. Ensure that the vials remain airtight in the ultrasonic bath (5.3) throughout the entire extraction process.

Using a volumetric graduated pipette (5.6), add to each vial 10 ml of tetrahydrofuran (4.1) containing 5 mg/l of internal standard (4.3).

6.2.3 Extraction procedure

Place the vials in the ultrasonic bath (5.3) at (60 ± 5) °C for 1 h ± 5 min to allow the extraction of phthalates (by complete or partial dissolution of the polymer).Then, remove the vials from the bath and let them stand still until the extraction solution cools down to room temperature.

Using a volumetric graduated pipette, add dropwise to each vial 20ml of the solvent used for the precipitation (4.2) containing 5mg/l of internal standard.

Shake the vials 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.

Centrifuge the vials at least 700 *g* (e.g. 2 500 r/min for 10 cm radius) 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 two suitable GC sampling vials 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 (4.1) and the solvent used for the precipitation (4.2) mixed by volume at a ratio of 1:2 (33 parts tetrahydrofuran to 66 parts of the other solvent) containing 5mg/l of the internal standard (4.3) and then repeat the analysis.

6.2.4 Phthalates determination

Determinate the phthalates extracted in 6.2.3 by GC-MS (5.1). An example of a programme and the parameters for GC-MS analysis of target phthalates are given in Annex B.

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

7 Calculation of the results

7.1 Calculation based on the corrected mass (by default)

From the calibration graph, determine the response of each phthalate, taking into account 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):

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

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 is given in Annex A, as well as an example of the calculation. Overall treated material is illustrated in Figure A.1 and locally treated material 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 7.2.

7.2 Calculation based on the total mass (when relevant)

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

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

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.

8 Test report

The test report shall include the following information:

a) a reference to this International Standard, i.e. ISO 14389;

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 7.1); where relevant, the value of the total mass, m_{T}, in grams (see 7.2);

e) the test results of each listed phthalate in the plasticized material or textile product, w_{c} (or, where relevant, w_{T}), expressed in micrograms per gram (µg/g) or per cent (%);

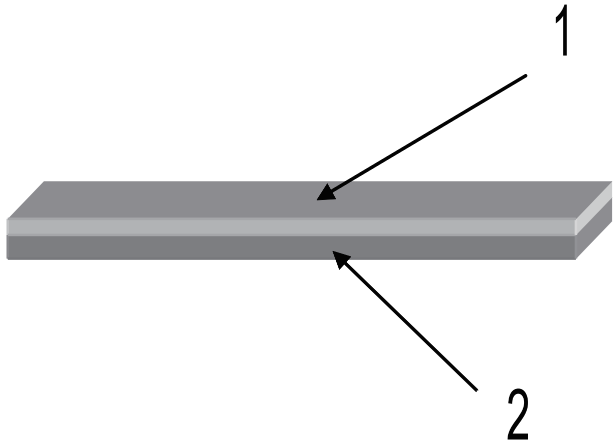
f) any deviation by agreement or otherwise from the procedure specified.

Annex A
(normative)

Calculations

A.1 Overall treated specimens

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



Key

1 plastic component (coating)

2 fabric

Figure A.1 — Overall treated materials

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.

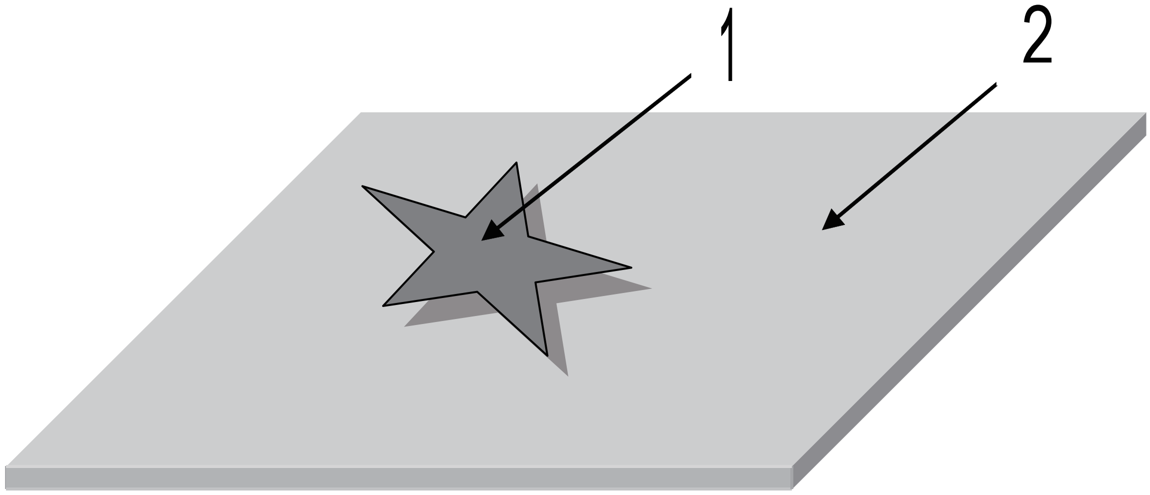
NOTE 2 An example of chemical procedure is given in Annex C.

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

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

A.2 Locally treated specimens

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



Key

1 plastic component (coating)

2 fabric

Figure A.2 — Locally treated specimen

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.

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

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

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 and detection limit

No.	Name	Typical quantification ions/amu			Detection limit µg/g
		Target ion	Quantitative		
			Q1	Q2	
1	Dibutyl phthalate (DBP)	149	150	205	40,0
2	Butyl benzyl phthalate (BBP)	149	206	150	40,0
3	Bis-(2-ethylhexyl) phthalate (DEHP)	149	167	279	40,0
4	Di-*n*-octyl phthalate (DNOP)	279	167	261	40,0
5	Di-iso-nonyl phthalate (DINP)	293	149	127	200,0
6	Di-iso-decyl phthalate (DIDP)	307	149	141	200,0
7	Di-iso-butyl phthalate (DIBP)	149	167	223	40,0
8	Di-pentyl phthalate (DPP)	149	219	237	40,0
9	Di-iso-heptyl phthalate (DIHP)	265	149	99	200,0
10	Di-methoxyethyl phthalate (DMEP)	149	59	207	200,0
11	Di-cyclohexyl phthalate [DCHP (IS)]	149	167	249	200,0

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**, accurate to 0,000 2 g.

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 number: 109-99-9.

C.3.2 **Deionized water**.

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 (5.3) 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 amoutn 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):

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

where

$w_{1\mathrm{A}}$	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, $w_{2\mathrm{A}}$ (%), 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:

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

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

where

i	is the ith component(s) of the fibre mixture;
m_i	is the mass fraction of the ith 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 ith 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$^{\mathrm{th}}$ 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, phthlates 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 could 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 kilgogram 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 could 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 could 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

Table D.1 *(continued)*

Sam-ple	Me thod	DIBP						DBP					
		out-lier	mean mg/kg	r mg/kg	$C_{V,r}$ %	R mg/kg	$C_{V,R}$ %	out-lier	mean mg/kg	r mg/kg	$C_{V,r}$ %	R mg/kg	$C_{V,R}$ %
D	1	0	579,7	76,3	13,2	433,8	74,8	0	3 434,2	369,5	10,8	2 943,9	85,7
	2	0	535,4	61,8	11,5	702,4	131,2	0	2 702,2	251,5	9,3	2 337,6	86,5
	3	0	642,7	70,9	11,0	533,5	83,0	1	3 217,3	332,5	10,3	2 437,6	75,8
	4	5	635,8	19,0	3,0	331,0	52,1	3	3 503,0	290,8	8,3	2 989,1	85,3
E	1	0	3 758,0	424,7	11,3	2 823,0	75,1	0	776,2	74,5	9,6	534,8	68,9
	2	2	2 428,2	155,2	6,4	1 190,5	49,0	0	605,9	56,7	9,4	529,4	87,4
	3	1	3 534,8	430,7	12,2	2 235,2	63,2	0	787,8	78,7	10,0	607,3	77,1
	4	1	4 158,9	382,0	9,2	1 968,6	47,3	2	803,0	54,5	6,8	640,9	79,8

Table D.2 — Results of the collaborative trial for methods 1 to 4 on BBP and DEHP

Sam-ple	Me thod	BBP						DEHP					
		out-lier	mean mg/kg	r mg/kg	$C_{V,r}$ %	R mg/kg	$C_{V,R}$ %	out-lier	mean mg/kg	r mg/kg	$C_{V,r}$ mg/kg	R mg/kg	$C_{V,R}$ %
A	1	0	131,1	19,7	15,0	132,4	101,0	—					
	2	0	73,7	9,2	12,5	75,0	101,7						
	3	0	129,0	12,4	9,6	144,8	112,3						
	4	2	183,4	14,9	8,1	177,1	96,5						
B	1	1	3 788,2	523,3	13,8	1 517,1	40,1	0	848,3	139,6	16,5	680,9	80,3
	2	1	2 590,9	314,5	12,1	3 086,9	119,1	1	795,8	104,4	13,1	762,1	95,8
	3	0	4 088,3	440,9	10,8	2 120,5	51,9	0	888,2	81,5	9,2	846,8	95,3
	4	2	4 620,8	325,7	7,1	1 457,2	31,5	1	982,8	90,1	9,2	907,1	92,3
C	1	—						0	4 028,0	318,4	7,9	3 081,3	76,5
	2							0	3 339,2	670,0	20,1	1 866,6	55,9
	3							1	3 835,8	438,3	11,4	2 178,5	56,8
	4							1	4 560,6	692,6	15,2	2 775,0	60,9
D	1	1	755,1	54,5	7,2	429,6	56,9	1	217,4	15,5	7,1	199,9	1
	2	0	520,9	65,2	12,5	497,9	95,6	2	172,8	9,5	5,5	210,1	2
	3	1	797,0	101,1	12,7	375,4	47,1	0	219,0	39,0	17,8	232,5	3
	4	1	1 113,9	171,9	15,4	1 640,7	147,3	1	242,5	10,5	4,3	273,5	4
E	1	1	147,7	14,5	9,8	156,9	106,2	—					
	2	2	77,8	6,2	7,9	71,0	91,3						
	3	0	15,7	26,3	16,9	203,0	130,4						
	4	1	194,2	17,7	9,1	175,5	90,4						

Table D.3 — Results of the collaborative trial for methods 1 to 4 on DNOP and DIDP

Sample	Method	DNOP						DIDP					
		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	949,3	80,4	8,5	774,2	81,6	2	459,8	53,4	11,6	307,9	67,0
	2	1	743,8	93,6	12,6	608,1	81,8	2	405,8	63,0	15,5	323,0	79,6
	3	0	853,8	79,7	9,3	637,6	74,7	2	440,6	35,7	8,1	307,1	69,7
	4	1	915,6	134,4	14,7	598,1	65,3	2	463,2	75,0	16,2	337,4	72,8
B	1	1	4 370,4	476,8	10,9	2 101,1	48,1	—					
	2	1	3 562,4	312,9	8,8	1 191,9	33,5						
	3	0	4 223,5	418,9	9,9	2 036,5	48,2						
	4	1	4 574,3	620,8	13,6	1 575,1	34,4						
C	1	0	209,3	27,8	13,3	326,9	156,2	3	931,9	95,5	10,3	364,6	39,1
	2	0	166,8	28,1	16,8	279,3	167,4	1	1 135,7	87,0	7,7	2 149,1	189,2
	3	2	201,0	29,6	14,7	309,3	153,9	1	1 174,1	234,7	20,0	1 563,5	133,2
	4	3	218,3	51,3	23,5	362,3	165,9	3	1 385,1	211,7	15,3	1 636,5	118,2
D	1	—						1	4 611,1	647,8	14,1	2 004,9	43,5
	2							1	4 017,5	451,4	11,2	1 596,3	39,7
	3							2	4 685,4	624,2	13,3	2 431,3	51,9
	4							3	4 527,3	497,3	11,0	5 007,4	110,6
E	1	1	1 017,6	89,7	8,8	532,1	52,3	1	535,6	79,2	14,8	385,8	72,0
	2	0	841,2	52,2	6,2	653,0	77,6	1	425,2	90,5	21,3	310,6	73,0
	3	0	960,5	106,0	11,0	606,0	63,1	1	507,8	52,9	10,4	367,1	72,3
	4	1	963,5	185,1	19,2	661,9	68,7	2	501,4	81,2	16,2	400,7	79,9

Table D.4 — Results of the collaborative trial for methods 1 to 4 on DINP

Sample	Method	DINP					
		outlier	mean mg/kg	r mg/kg	$C_{V,r}$ %	R mg/kg	$C_{V,R}$ %
A	1	—					
	2						
	3						
	4						
B	1	0	937,0	197,9	21,1	840,4	89,7
	2	1	704,5	110,2	15,7	478,9	68,0
	3	1	890,1	125,8	14,1	571,5	64,2
	4	1	901,7	125,8	14,0	938,8	104,1
C	1	1	4 797,8	533,9	11,1	1 765,0	36,8
	2	1	3 913,3	427,1	10,9	1 783,3	45,6
	3	3	4 225,4	385,2	9,1	820,7	19,4
	4	1	4 550,1	822,8	18,1	3 919,0	86,1
D	1	1	642,7	110,6	17,2	323,0	50,3
	2	1	480,2	59,6	12,4	349,6	72,8
	3	1	641,3	111,3	17,4	546,3	85,2
	4	2	665,7	124,2	18,7	776,0	116,6
E	1	—					
	2						
	3						
	4						

D.3 Ranges of repeatability and reproducibility coefficients of variation per method

Table D.5 — Repeatability and reproducibility for methods

Method	$C_{V,r}$ %	$C_{V,R}$ %
1	7,1 to 21,1	36,8 to 156,2
2	5,5 to 21,3	33,5 to 189,2
3	8,1 to 20,0	19,4 to 153,9
4	3,0 to 23,5	31,5 to 165,9

D.4 Comparison of results calculated as milligram of phthalate in kilogram of PVC for samples A and E

Table D.6 — Comparison of results among methods

Sample	Method	DIBP mg/kg	DBP mg/kg	BBP mg/kg	DNOP mg/kg	DIDP mg/kg
A	1	3 664,3	802,6	147,5	1 068,2	517,4
	2	2 874,0	637,5	83,0	836,9	456,7
	3	3 802,3	829,0	145,1	960,7	495,7
	4	4 087,3	830,7	206,4	1 030,3	521,3
E	1	3 758,0	776,2	147,7	1 017,6	535,6
	2	2 428,2	605,9	77,8	841,2	425,2
	3	3 534,8	787,8	155,7	960,5	507,8
	4	4 158,9	803,0	194,2	963,5	501,4

D.5 Theoretical recovery of phthalates

Table D.7 — Theoretical recovery of phthalates on DIBP, DBP, BBP and DEHP

Sample	Method	DIBP			DBP			BBP			DEHP		
		expected mg/kg	mean mg/kg	recovery %	expected mg/kg	mean mg/kg	recovery %	expected mg/kg	mean mg/kg	recovery %	expected mg/kg	mean mg/kg	recovery %
A	1	5 018,0	3 664,3	73,0	1 012,0	802,6	79,3	212,0	147,5	69,9	—		
	2	5 018,0	2 874,0	57,3	1 012,0	637,5	63,0	212,0	83,0	39,1			
	3	5 018,0	3 802,3	75,8	1 012,0	829,0	81,9	212,0	145,1	68,4			
	4	5 018,0	4 087,3	81,5	1 012,0	830,7	82,1	212,0	206,4	97,4			
B	1	210,0	135,9	64,7	—			5 042,0	4 264,6	84,6	1 012,0	955,0	94,4
	2	210,0	113,2	53,9				5 042,0	2 916,7	57,8	1 012,0	895,8	88,5
	3	210,0	152,9	72,8				5 042,0	4 602,3	91,3	1 012,0	999,9	98,8
	4	210,0	130,7	62,2				5 042,0	5 201,9	103,2	1 012,0	1 106,3	109,3
C	1	—			230,0	151,8	66,0	—			5 020,0	4 566,9	91,0
	2				230,0	127,9	55,6				5 020,0	3 786,0	75,4
	3				230,0	162,7	70,7				5 020,0	4 349,0	86,6
	4				230,0	154,5	67,2				5 020,0	5 170,8	103,0
D	1	1 015,0	661,5	65,2	5 015,0	3 919,0	78,1	1 010,0	861,7	85,3	211,0	248,1	117,6
	2	1 015,0	611,0	60,2	5 015,0	3 083,6	61,5	1 010,0	594,5	58,9	211,0	197,2	93,4
	3	1 015,0	733,4	72,3	5 015,0	3 671,5	73,2	1 010,0	909,5	90,9	211,0	250,0	118,5
	4	1 015,0	725,6	71,5	5 015,0	3 997,5	79,7	1 010,0	1 271,2	125,9	211,0	275,8	131,2

Table D.7 *(continued)*

Sample	Method	DIBP			DBP			BBP			DEHP		
		expected mg/kg	mean mg/kg	recovery %	expected mg/kg	mean mg/kg	recovery %	expected mg/kg	mean mg/kg	recovery %	expected mg/kg	mean mg/kg	recovery %
E	1	5 018,0	3 758,0	74,9	1 012,0	776,2	76,7	212,0	147,7	69,7	—		
	2	5 018,0	2 428,2	48,4	1 012,0	605,9	59,9	212,0	77,8	36,7			
	3	5 018,0	3 534,8	70,4	1 012,0	787,8	77,8	212,0	155,7	73,4			
	4	5 018,0	4 158,9	82,9	1 012,0	803,0	79,3	212,0	194,2	91,6			

Table D.8 — Theoretical recovery of phthalates on DNOP, DIDP and DINP

Sample	Method	DNOP			DIDP			DINP		
		expected mg/kg	mean mg/kg	recovery %	expected mg/kg	mean mg/kg	recovery %	expected mg/kg	mean mg/kg	recovery %
A	1	1 057,0	1 068,2	101,1	521,0	517,4	99,3	—		
	2	1 057,0	836,9	79,2	521,0	456,7	87,7			
	3	1 057,0	960,7	90,9	521,0	495,7	95,1			
	4	1 057,0	1 030,3	97,5	521,0	521,3	100,1			
B	1	5 005,0	4 920,0	98,3	—			1 012,0	1 054,9	103,4
	2	5 005,0	4 010,4	80,1				1 012,0	793,0	77,7
	3	5 005,0	4 754,6	95,0				1 012,0	1 002,1	98,2
	4	5 005,0	5 149,5	102,9				1 012,0	1 015,1	99,5
C	1	212,0	237,3	111,9	1 018,0	1 056,6	103,8	5 005,0	5 439,7	108,7
	2	212,0	189,1	89,2	1 018,0	1 287,6	126,5	5 005,0	4 436,9	88,6
	3	212,0	227,9	107,5	1 018,0	1 331,2	130,8	5 005,0	4 790,7	95,7
	4	212,0	247,5	116,8	1 018,0	1 570,4	154,3	5 005,0	5 158,9	103,1
D	1	—			5 005,0	5 262,0	105,1	515,0	733,4	142,4
	2				5 005,0	4 584,6	91,6	515,0	548,0	106,4
	3				5 005,0	5 346,8	106,8	515,0	731,9	142,1
	4				5 005,0	5 166,4	103,2	515,0	759,7	147,5
E	1	1 057,0	1 017,6	96,3	521,0	535,6	102,8	—		
	2	1 057,0	841,2	79,6	521,0	425,2	81,6			
	3	1 057,0	960,5	90,9	521,0	507,8	97,5			
	4	1 057,0	963,5	91,2	521,0	501,4	96,2			

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