

Textiles — Test method for phthalates

ICS 59.080.01

National foreword

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Contents

Page

Foreword.....	3
Introduction	4
1 Scope	5
2 Terms and definitions	5
3 Preparation of the test specimens	5
4 Apparatus and reagents.....	5
4.1 Apparatus	5
4.2 Reagents (analytical grade)	6
5 Test procedure	6
5.1 Principle.....	6
5.2 Reagent (standard solutions).....	6
5.3 Extraction of phthalates	7
5.4 Calculation of results	7
6 Test report	8
Annex A (normative) Calculations.....	9
A.1 Overall treated.....	9
A.2 Locally treated.....	10
Annex B (informative) Suitable Gas Chromatography - Mass Spectrometry (GC-MS) apparatus, method and precision data for determination of phthalate plasticizers [3].....	11
Bibliography	13

Foreword

This document (EN 15777:2009) has been prepared by Technical Committee CEN/TC 248 “Textile and textile products”, the secretariat of which is held by BSI.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by February 2010, and conflicting national standards shall be withdrawn at the latest by February 2010.

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Introduction

This European Standard covers a test method for determination of phthalates in textile articles.

Phthalates are commonly used as plasticizers in polymers. Toxicological concern has arisen due to their potential effect as endocrine disruptors and some of the listed phthalates are toxic in reproduction. The level of media publicity will ensure that their use will continue to be of concern to consumers.

Phthalates are an issue for textile manufacturers and retailers due to their use within motifs, coated fabrics, plastisol prints, buttons, etc. There are textile articles that have to comply with the Directive 2005/84/EC [1] and also articles that fall outside the scope of this legislation, that could be covered by the General Products Safety Directive (2001/95/EC) [2].

WARNING — Persons using this European Standard should be familiar with normal laboratory practice. This European Standard does not claim 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.

This European Standard calls for the use substances and/or procedures that may be injurious to health if appropriate precautions are not observed. It refers only to technical suitability and does not absolve the user from legal obligations relating to health and safety at any stage.

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.

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

1 Scope

This standard specifies a test method for taking representative specimens, extraction of phthalates from the material and determination of phthalates by gas chromatography – mass spectrometry.

This standard applies to textiles articles, where there is a possibility of the presence of some phthalates.

2 Terms and definitions

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

2.1

blank

application of the method without test specimen

2.2

plasticized or softened materials

plastic material (coating, pigment print binder, etc) that is treated with chemicals (for this specific standard they are phthalates) to make it more flexible

2.3

overall treated textiles

textiles with a continuous finish, coating or print

2.4

locally treated textiles

textile with a discontinuous finish, coating or print

2.5

representative specimen

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

3 Preparation of the test specimens

Remove the untreated mass of the specimen if possible (see Annex A). If the untreated mass cannot be removed, see 5.4.

Use a scalpel or other appropriate cutting tool to cut two representative specimens into small pieces.

4 Apparatus and reagents

4.1 Apparatus

4.1.1 Balance (resolution of 1 mg).

4.1.2 150 ml flask.

4.1.3 Soxhlet extractor with siphon cup of approximately 20 ml.

4.1.4 Soxhlet cellulose thimble, approximately 15 mm in diameter and 50 mm height.

4.1.5 Water-cooled condenser.

- 4.1.6 Spark proof heating mantle/water bath.
- 4.1.7 Steam bath or rotary evaporator.
- 4.1.8 Calibrated volumetric flasks of suitable volume.

NOTE Avoid direct contact between the samples and glassware and/or equipment to be used to minimize cross-contamination. Glassware, after washing, should have an extra rinse with 0,1 N nitric acid and finally with acetone, acetone/methanol and/or cyclohexane. Dry at 110 °C (1 h). Beware, the vapour of the organic solvents are highly flammable, especially at high temperature! Allow glassware to cool down before use.

- 4.1.9 Gas chromatography with mass selective detector (GC-MS).

4.2 Reagents (analytical grade)

- 4.2.1 *n*-Hexane, CAS No. 110-54-3.
- 4.2.2 Di-isononyl phthalate (DINP), CAS No. 28553-12-0 or 68515-48-0.
- 4.2.3 Di-(2-ethylhexyl) phthalate (DEHP), CAS No. 117-81-7.
- 4.2.4 Di-*n*-octyl phthalate (DNOP), CAS No. 117-84-0.
- 4.2.5 Di-iso-decyl phthalate (DIDP), CAS No. 26761-40-0 or 68515-49-1.
- 4.2.6 Butyl benzyl phthalate (BBP), CAS No. 85-68-7.
- 4.2.7 Di-butyl phthalate (DBP), CAS No.84-74-2.
- 4.2.8 Dicyclohexyl phthalate (DCHP), CAS no.84-61-7 – Internal Standard.

5 Test procedure

5.1 Principle

The aim of the method is to extract phthalates in textiles and related accessories. This method uses Soxhlet extraction apparatus with *n*-hexane as solvent. However, any apparatus giving equivalent extraction as with Soxhlet can be used.

The total *n*-hexane extractable phthalate plasticizer content is calculated by weight with Gas Chromatography-Mass-Spectrometry (GC-MS) detection to identify and quantify individual phthalates.

5.2 Reagent (standard solutions)

- 5.2.1 Preparation of the internal standard solution.

Prepare a 500 µg/ml stock solution of the internal standard in *n*-hexane.

- 5.2.2 Standard solution.

Prepare a series of individual stock standard solutions of the individual phthalate in *n*-hexane as shown in Table 1.

Table 1 — Stock solutions

Phthalate	DIDP	DINP	DBP	BBP	DNOP	DEHP
Concentration, µg/ml	1000	1000	200	200	200	200

From the stock standard solutions prepare appropriate phthalate calibration solutions in *n*-hexane.

Use at least five appropriate dilutions of the calibration sets to create calibration graphs and add to each an appropriate amount of internal standard and perform GC-MS analysis.

NOTE DIDP and DINP overlap in the chromatogram, choose target ions indicated in Annex B.

5.3 Extraction of phthalates

Prepare the appropriate amount of internal standard solution.

Weigh accurately ($2,0 \pm 0,1$) g of the pieces of a representative specimen into a Soxhlet thimble and add a filter paper disc to the top of the thimble. Extract every sample in duplicate and run a blank to control contamination.

Add approximately 50 ml of *n*-hexane into the flask. Reflux gently for 4 h. Allow sufficient time for the *n*-hexane to cool.

Transfer the extract to a 100 ml volumetric flask. Rinse the flask with 2 aliquots of 20 ml *n*-hexane. Make up to the mark. Transfer a known volume into a suitable GC sampling vial and add appropriate volume of internal standard solution and perform GC-MS analysis. Prepare if necessary further diluted solutions using the original solution and repeat the analysis after added the appropriate volume of internal standard solution.

NOTE In some cases where the corrected mass of the specimen is very low, it will be necessary to increase the weight and/or concentrate the extract in order to reach at least 3 times the detection limit.

5.4 Calculation of results

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 µg/ml correcting for any dilutions. Subtract the blank concentration from the specimen concentration.

$$P = \frac{V \times [b - a]}{m \times 10000} \quad (1)$$

where

P is the percentage of the individual phthalate;

V is the volume of the volumetric flask (ml);

m is the corrected mass of specimen (g);

a is the concentration of the individual phthalate of blank solution (µg/ml);

b is the concentration of the individual phthalate the specimen solution corrected for any dilutions (µg/ml).

If the corrected mass of test specimen cannot be obtained (see Annex A), give a remark in the test report.

An example of the calculation is given in Annex A.

Overall treated material is illustrated in Figure A.1 and locally treated material in Figure A.2.

6 Test report

The test report shall include the following information:

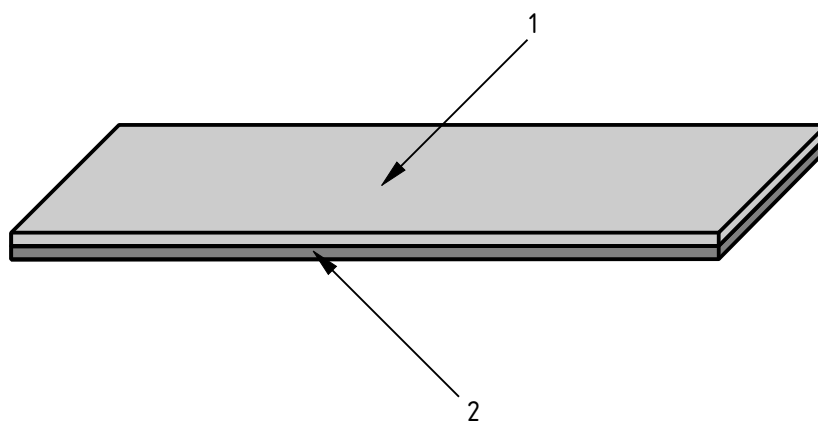
- a) reference to this standard;
- b) all details necessary for complete identification of the sample tested;
- c) description of the apparatus if Soxhlet is not used;
- d) preparation of the specimens and correction of the mass due to the untreated textile components;
- e) percent by mass of each listed phthalate in the plasticized material or textile product;
- f) any deviation by agreement or otherwise from the procedure specified.

Annex A (normative)

Calculations

A.1 Overall treated

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 = total mass of overall treated specimen (g);

m_2 = mass of textile component (g);

m = mass of coating (g)

NOTE Mass of coating is the corrected mass of the specimen as described in the formula in 5.4.

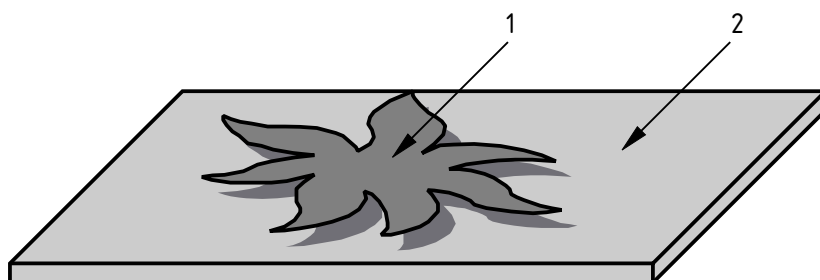
From a test specimen, where (m_1) is measured (g), the plastic component (coating) is removed by a mechanical, thermal or chemical procedure (or combination of these). The plastic component (m) shall be determined by comparison with the textile component (m_2).

The part of the coating can be defined according to the following formula:

$$m = m_1 - m_2 \quad (\text{A.1})$$

A.2 Locally treated

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 = mass per unit area of treated area of specimen (gm^{-2});

m_2 = mass per unit area of textile material (gm^{-2});

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

NOTE Mass of the plastic component is the corrected mass of the specimen as described in the formula in 5.4.

S = surface area of the treated area of the specimen (m^2);

Firstly, determine the mass per unit area from an untreated part (only textile material is involved) w_2

From a test specimen:

- measure the treated mass per unit area w_1 ;
- measure the treated area, S .

The mass of the plastic component can be calculated according to the following formula:

$$m = (m_1 - m_2) \times S \text{ , expressed in g} \quad (\text{A.2})$$

Annex B (informative)

Suitable Gas Chromatography - Mass Spectrometry (GC-MS) apparatus, method and precision data for determination of phthalate plasticizers [3]

The following equipment, column and operating conditions have been found suitable:

Equipment: 6890 Gas Chromatograph (GC) with a Hewlett Packard 5973N Mass Selective Device (MSD), quadrupole.

Column: 5 % phenyl methyl siloxane for MS; length 30 m; 0,32 mm I.D. & 0,25 µm film thickness.

Carrier gas:	Helium.
Flow rate:	2,0 ml/min.
Injector temperature:	250 °C.
Injection volume:	1 µl.
Injection:	splitless or split.
Transfer line temperature:	280 °C.
MSD mode:	Electron impact.
Temperature programme:	150 °C for 1 min to 250 °C at 8 °C/min to 290 °C at 3 °C/min Isothermal 5,00 min.

Total run time is 34 min.

Typical quantification ions for phthalate plasticizers are shown in Table B.1.

Table B.1 — Typical quantification ions for phthalate plasticizers

Phthalate plasticizers	Target ion	Q1	Q2
Dibutyl phthalate (DBP)	149	223	205
Butyl benzyl phthalate (BBP)	149	206	238
Bis-(2-ethylhexyl) phthalate (DEHP)	149	167	279
Di-n-octyl phthalate (DNOP)	149	279	261
Di-iso-nonyl phthalate (DINP)	293	149	127
Di-iso-decyl phthalate (DIDP)	307	149	141
Di-Cyclohexylphthalate (DCHP) (Internal standard)	149	167	249

Depending on the type of equipment used, the appropriate operating conditions may need to be established.

Detection limits and precision data

The detection limits for GC-MS analysis for the phthalate esters are shown in Table B.2:

Table B.2 — Detection limits for GC-MS analysis for phthalate esters

Phthalate ester	DIDP	DINP	DBP	BBP	DNOP	DEHP	DCHP
Detection limit, µg/ml	3,0	2,5	0,05	0,05	0,05	0,05	0,05

The repeatability (r) data on 6 analyses of a polyvinylchloride (PVC) reference material is $(38,62 \pm 0,83)$ % relative CVr = ± 2 %.

The repeatability (r) data on 6 analyses of an article gave a mean value of $(20,5 \pm 0,71)$ % relative CVr = ± 3 % for similar articles.

NOTE Coefficient of variation CV is the ratio of the standard deviation to the average [4].

Bibliography

This document incorporates reference to EU Directives. The reference is cited at the appropriate place in the text and the EU Directives are listed hereafter:

- [1] Commission Directive 2005/84/EC Phthalates in toys and child care articles
- [2] Commission Directive 2001/95/EC General Products Safety Directive

Other publications

- [3] EN 14372:2004, *Child use and care articles — Cutlery and feeding utensils — Safety requirements and tests*
- [4] ISO 3534-1:1993, *Statistics — Vocabulary and symbols — Part 1: General statistical terms and terms used in probability*

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