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Textiles — Determination of the content of phthalates

Textiles — Détermination du contenu des phtalates

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Foreword

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ISO 14389 was prepared by Technical Committee ISO/TC 38.

Introduction

This International Standard covers a test method for determination of some 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.

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.

Textiles — Determination of phthalates — Tetrahydrofuran-acetonitrile method

WARNING — This standard calls for the use of substances and/or procedures that may 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 standard that the execution of its provisions is entrusted to appropriately qualified and experienced operator.

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 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

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

2.3
locally treated textiles
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-acetonitrile. (polyvinylchloride – PVC- is dissolved in tetrahydrofuran and then precipitated with acetonitrile). After dilution of the extract to volume, Gas Chromatography-Mass Spectrometry (GC-MS) is used to determine individually phthalates in the specimen and quantify by using internal standard.

4 Reagents

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

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

4.2 Acetonitrile (ACN), CAS number: 75-05-8.

4.3 Di-isononyl phthalate (DINP), CAS No. 28553-12-0 or 68515-48-0.

4.4 Di-(2-ethylhexyl) phthalate (DEHP), CAS No. 117-81-7.

4.5 Di-n-octyl phthalate (DNOP), CAS No. 117-84-0.

4.6 Di-iso-decyl phthalate (DIDP), CAS No. 26761-40-0 or 68515-49-1.

4.7 Butyl benzyl phthalate (BBP), CAS No. 85-68-7.

4.8 Di-butyl phthalate (DBP), CAS No.84-74-2.

4.9 Di-methyl phthalate (DIBP), CAS No. 84-69-5.

4.10 Di-pentyl phtalate (DPP), CAS number: 131-18-0, Internal Standard (IS).

5 Apparatus

5.1 Gas Chromatography (GC) - Mass Spectrometry (MS) with mass selective detector (MSD).

5.2 Vial, 40 ml.

5.3 Thermostatic ultrasonic bath, with a frequency of 40 kHz.

5.4 Glass stoppered flasks, 100 ml.

5.5 Calibrated volumetric flasks, 50 ml and 100 ml.

5.6 Volumetric graduated pipette, 10 and 20 ml.

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

5.8 Steam bath or rotary evaporator

6 Procedure

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

6.1 Preparation of standard solutions

6.1.1 Internal standard solution

Prepare a 1000 µg/ml stock standard solution of the internal standard in acetonitrile for ultrasonic wave extraction (6.2).

6.1.2 Standard solution

Prepare a series of individual stock standard solutions of the individual phthalate ester in acetonitrile 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 acetonitrile and mix thoroughly to dissolve completely the substance.

Table 1 — Stock solutions

Phthalate ester	DIDP	DINP	DBP	BBP	DNOP	DEHP	DIBP	DPP (IS)
Concentration, µg/ml	1000	1000	1000	1000	1000	1000	1000	1000

6.1.3 Preparation of the calibration solutions

From the individual stock standard solutions, prepare the following five calibration solutions (theoric concentration 1, 3, 15, 30, 90 mg/l) in n-hexane containing all the phthalates. From the stock standard solutions, prepare appropriate phthalate calibration solutions in tetrahydrofuran / acetonitrile 33/66 v/v.

Table 2 — Calibration solutions

Concentrations	**Instructions**
1 mg/l	Add 0,1 ml of each phthalate stock solution in 100 ml volumetric flask plus 0,5 ml of the internal standard (DPP) stock solution then fill up to the mark with tetrahydrofuran /acetonitrile 33/66 v/v.
3 mg/l	Add 0,3 ml of each phthalate stock solution in 100 ml volumetric flask plus 0,5 ml of the internal standard (DPP) stock solution then fill up to the mark with tetrahydrofuran /acetonitrile 33/66 v/v.
15 mg/l	Add 0,75 ml of each phthalate stock solution in 50 ml volumetric flask plus 0,25 ml of the internal standard (DPP) stock solution then fill up to the mark with tetrahydrofuran /acetonitrile 33/66 v/v.
30 mg/l	Add 1,5 ml of each phthalate stock solution in 50 ml volumetric flask plus 0,25 ml of the internal standard (DPP) stock solution then fill up to the mark with tetrahydrofuran / acetonitrile 33/66 v/v.
90 mg/l	Add 4,5 ml of each phthalate stock solution in 50 ml volumetric flask plus 0,25 ml of the internal standard (DPP) stock solution then fill up to the mark with tetrahydrofuran /acetonitrile 33/66 v/v.

6.1.4 Working solution

Prepare an admixture working solution of phthalates in acetonitrile with a suitable concentration depending on test need.

Select (or prepare) at least three appropriate dilutions of the calibration sets to create calibration graphs, add to each an appropriate amount of internal standard and perform GC-MS analysis. Typical quantification ions for phthalates are shown in Annex B.

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

It is necessary to dilute the specimen liquid properly when the concentration is beyond the detection of the response linear range of the equipment.

NOTE The stock standard solution is stocked at 0 C° to 4 C° within twelve months, and the working solution is stocked at 0 C° to 4 C° within six months.

6.2 Ultrasonic wave extraction

Extract every specimen in duplicate and run a blank to control contamination.

The textile specimen shall be cut in the coated part of sample. Cut representative specimen into small pieces, and weigh (0,30 ± 0,01) g of the pieces into a 40 ml vial (5.2) fitted with PTFE stopcock (select stopcock so that it remains tight for the whole dissolution process in the ultrasonic bath). Add, with a volumetric or automatic pipette (5.6), 10 ml of tetrahydrofuran (4.1) containing 5 mg/l of internal standard (DPP).

Place the vial in the ultrasonic bath (5.3) for 1 h ± 5 min at (60 ± 5) °C (dissolution of PVC) and wait until the test specimen is at room temperature. Precipitate the polymer by adding dropwise 20 ml (measured with a volumetric or automatic pipette) of acetonitrile containing 5 mg/l of internal standard (DPP).

Shake vigorously the vial (better with a vortex for at least 30 s) and wait (30 ± 2) min to allow the precipitation of PVC.

Centrifuge at 2500 rpm for (10 ± 2) min and transfer a volume of organic phase into a suitable GC sampling vial and perform GC-MS analysis. If necessary, prepare further diluted solutions using the original solution and repeat the analysis after adding the appropriate volume of tetrahydrofuran / acetonitrile 33/66 v/v containing 5 mg/l of the internal standard.

6.3 Phthalates determination

Determinate the phthalates extracted in 5.2 by GC-MS (5.1). An example of test parameters by GC-MS is given in Annex B.

In some cases when the phthalates level is very low, it is necessary to increase the mass of the pieces and/or concentrate the extract using the rotary evaporator (5.8) in order to reach at least three times the detection limit.

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, 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. Calculate the result according to the formula (1).

$$P_C = \frac{V \times [b - a]}{m_c \times 10\ 000} \qquad (1)$$

where

P_c is the percentage of the individual phthalate, based on the corrected mass of the test specimen;

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

m_c is the corrected mass of specimen (g);

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

