TECHNICAL REPORT

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Textiles — Determination of certain flame retardants —

Part 3: Chlorinated paraffin flame retardants

Textiles — Détermination de certains retardateurs de flamme —

Partie 3: Retardateurs de flamme à base de paraffines chlorées

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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).

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This document was prepared by Technical Committee ISO/TC 38, *Textiles*.

A list of all parts in the ISO 17881 series can be found on the ISO website.

Textiles — Determination of certain flame retardants —

Part 3: Chlorinated paraffin flame retardants

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1 Scope

This document describes a method for determining short-chain chlorinated paraffins (C_{10}-C_{13}) (SCCPs) in textiles using carbon skeleton reaction gas chromatography with a flame ionization detector (GC-FID).

It is applicable to all kinds of textile products.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

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

— IEC Electropedia: available at https://www.electropedia.org/

— ISO Online browsing platform: available at https://www.iso.org/obp

4 Principle

SCCPs are extracted from textile specimens by an ultrasonic generator with *n*-hexane/acetone. SCCPs are pretested by gas chromatography with an electron capture detector (GC-ECD) and then quantified by GC-FID using an external standard method. SCCPs are dechlorinated by reacting with hydrogen to generate straight-chain alkane (C_{10}-C_{13}) under the action of a $PdCl_2$ catalyst. GC-FID is used to determine the quantity of straight-chain alkane following an external standard method, and then the quantity of SCCPs is calculated.

5 Reagents

Unless otherwise specified, only reagents of recognized analytical grade are used.

5.1 Short-chain chlorinated paraffins (SCCPs) (C_{10}-C_{13}, 51,5 % Cl), 100 µg/ml in cyclohexane.

5.2 Short chain chlorinated paraffins (SCCPs) (C_{10}-C_{13}, 55,5 % Cl), 100 µg/ml in cyclohexane.

5.3 Short-chain chlorinated paraffins (SCCPs) (C_{10}-C_{13}, 63 % Cl), 100 µg/ml in cyclohexane.

5.4 Straight-chain alkane (C_{10}-C_{13}), purity > 99,5 %.

5.5 *n*-hexane/acetone, 1:1 (volume fraction).

5.6 Diethyl ether.

5.7 Acetic acid solution, 5 % (volume fraction).

5.8 Ammonia, 25 % (mass fraction).

5.9 Mixture of *n*-hexane/diethyl ether, 90/10 (volume fraction).

5.10 Cyclopentane.

5.11 Cyclohexane.

5.12 Calcium carbonate ($CaCO_3$).

5.13 Palladium chloride ($PdCl_2$) catalyst.

After dissolving 0,08 g of $PdCl_2$ in 10 ml of 5 % acetic acid (5.7), the solution is transferred to the watch glass filled with 19 g of glass beads (6.11). The watch glass is placed into a boiling water bath, and the solution is constantly stirred to evaporate until dried. Distilled water is added on the watch glass, ammonia (5.8) is used to adjust the pH to 9, and the solution is evaporated until dried again. The glass beads are transferred to a glass filter crucible to be washed with 50 ml of cyclopentane (5.10) and then dried in the air.

6 Apparatus

6.1 Gas chromatograph with an electron capture detector (GC-ECD), used for pretesting SCCPs.

6.2 Gas chromatograph with a flame ionization detector (GC-FID), used for quantifying SCCPs.

The $PdCl_2$ catalyst (5.13) and reaction injection liners (6.9) are prepared and fitted into the GC-FID.

6.3 Ultrasonic generator, with a frequency of 35 kHz to 45 kHz.

6.4 Water bath and rotary evaporator.

6.5 Glass vials, 40 ml with tight closure.

6.6 K-D concentrator tube, 30 ml.

6.7 Round-bottom flask, 100 ml.

6.8 Florisil®[1] solid phase extraction (SPE) column, 1 g, 6 ml.

6.9 Reaction injection liners, successively filled with 0,5 cm rock wool, 0,2 cm $CaCO_3$, 2,0 cm $PdCl_2$ catalyst and 0,5 cm rock wool.

1) Florisil® is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

6.10 Balance, accurate to 0,1 mg.

6.11 Watch glass, filled with 19 g of glass beads (60 to 80 mesh).

7 Procedure

7.1 Preparation of standard solutions

7.1.1 Stock standard solutions

A 100 µg/ml stock standard solution of SCCPs is prepared in cyclohexane (5.11).

A 1 000 µg/ml stock standard solution of straight-chain alkane (5.4) is prepared in *n*-hexane (5.5) only for GC-FID.

7.1.2 Working solutions

For GC-ECD, a working solution of SCCPs is prepared in *n*-hexane (5.5) and dilutions are carried out with a series of suitable concentrations depending on the test needs. At least five appropriate dilutions of the calibration sets are selected to create a calibration curve and an analysis is performed.

For GC-FID, a working solution of straight-chain alkane (5.4) is prepared in *n*-hexane (5.5) and dilutions are carried out with a series of suitable concentrations depending on the test needs. At least five appropriate dilutions of the calibration sets are selected to create a calibration curve and an analysis is performed. The working solution of SCCPs is prepared in *n*-hexane to calculate the transformation efficiency (8.2.2).

The specimen liquid should be diluted properly when its concentration is beyond the detection of the response linear range of the equipment.

7.2 Specimen extraction

7.2.1 Ultrasonic wave extraction

Every specimen is extracted in duplicate and a blank test is run to control contamination.

A representative specimen is cut into small pieces, (1,00 ± 0,01) g of which is weighed with a balance (6.10) and placed into a vial with a tight closure (6.5), where 20 ml of *n*-hexane/acetone (5.5) is added. The vial is placed into an ultrasonic generator (6.3) for 30 min at room temperature. The extract is filtered and transferred into a 100 ml round-bottom flask (6.7), and 20 ml of *n*-hexane/acetone is added to the residue in the vial. The vial is placed into the ultrasonic generator for 15 min at room temperature and the residue is extracted. The extract is filtered and merged into the round-bottom flask (6.7).

The extract obtained is concentrated almost to dryness by the rotary evaporator (6.4) in the water bath at 40 °C, and 1 ml of *n*-hexane is added to dissolve the residue.

7.2.2 Purification

After the SPE column (6.8) is activated with 10 ml of *n*-hexane, the solution obtained at 7.2.1 is added to the SPE column, then 2 ml of *n*-hexane is added to the column and the effluent liquid is removed. The elution is performed with 5 ml of *n*-hexane/diethyl ether (5.9). The eluent is collected into the K-D concentrator tube (6.6) and concentrated almost to dryness by the rotary evaporator in the water bath at 40 °C, and 2 ml of *n*-hexane is added to dissolve the residue. The solution is ready for determination of SCCPs.

7.3 Pretesting by GC-ECD

Pretesting is performed by the GC-ECD (6.1). A set of test parameters is given in Annex A as an example.

If typical peaks of SCCPs are observed, the GC-FID is used to quantify SCCPs as described in 7.4. Otherwise, the result is reported as "not detectable".

7.4 Determination by GC-FID

According to the pretesting result, one kind of SCCP reference material with a suitable degree of chlorination is taken (51,5 %, 55,5 % or 63 %), as provided in 5.1 to 5.3.

SCCPs in the solution (see 7.2) react with hydrogen to generate straight-chain alkane (C_{10}-C_{13}) under the effect of the $PdCl_2$ catalyst (5.13). The GC-FID (6.2) is used to determine the straight-chain alkane following an external standard method. The quantity of SCCPs in the textile specimen is calculated as explained in 8.2.

The working solution of SCCPs is injected in the GC-FID to confirm the transformation efficiency (see 8.2.2) of SCCPs ($r \geq 80$ %). If r is lower than 80 %, the reaction injection liners (6.9) are re-prepared.

A set of test parameters for GC-FID is given in Annex B as an example.

When the SCCP level is very low, the mass of the specimens is increased in order to reach at least three times the detection limit.

8 Calculation

8.1 Pretesting result obtained by GC-ECD

The pretesting concentration of SCCPs is read on the calibration curve. The pretested quantity of SCCPs is calculated by using Formula (1):

$$X = \frac{(C - C_0) \times V}{m} \quad (1)$$

where

X is the mass ratio of SCCPs to test specimen, in µg/g;

C is the concentration of SCCPs in the specimen solution, in µg/ml;

C_0 is the concentration of SCCPs in the blank solution, in µg/ml;

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

m is the mass of the textile specimen, in g.

8.2 Quantity of SCCPs obtained by GC-FID

8.2.1 The transformation factor is calculated by using Formula (2):

$$k = \frac{100 - z + \frac{z}{35,5}}{100} \quad (2)$$

where

k is the transformation factor;

z is the chlorine percentage of SCCPs;

35,5 is the atomic weight of Cl.

EXAMPLE For SCCPs (C_{10}-C_{13}, 55,5 % Cl), k = (100 − 55,5 + 55,5/35,5)/100 = 0,460 6.

8.2.2 The concentration of the straight-chain alkane is read on the calibration curve. The transformation efficiency is calculated by using Formula (3):

$$r = \frac{\sum C_{ci}}{k \times C_s} \times 100 \quad (3)$$

where

r is the transformation efficiency in % ($r \geq 80$ %);

C_{ci} is the concentration of the straight-chain alkane transformed from SCCPs in the calibration solution, in µg/ml (i = C_{10}-C_{13});

k is the transformation factor;

C_s is the concentration of SCCPs in the calibration solution, in µg/ml.

8.2.3 The concentration of the straight-chain alkane is read on the calibration curve. The quantity of SCCPs in the specimen is calculated by using Formula (4):

$$X = \frac{\sum (C_{si} - C_{0i}) \times V}{m \times k} \quad (4)$$

where

X is the quantity of SCCPs in the specimen, in µg/g;

C_{si} is the concentration of the straight-chain alkane transformed from SCCPs in the specimen solution, in µg/ml (i = C_{10}-C_{13});

C_{0i} is the concentration of the straight-chain alkane transformed from SCCPs in the blank solution, in µg/ml (i = C_{10}-C_{13});

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

m is the mass of the textile specimen, in g;

k is the transformation factor.

9 Detection limit

The detection limit of the GC-ECD method or the GC-FID method is 20 mg/kg.

10 Test report

The test report includes the following information:

a) a reference to this document, i.e. ISO/TR 17881-3:2018;