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# Textiles — Determination of short-chain chlorinated paraffins (SCCP) and middle-chain chlorinated paraffins (MCCP) in textile products out of different matrices by use of gas chromatography negative ion chemical ionization mass spectrometry (GC-NCI-MS)

*Textiles — Détermination de paraffines chlorées à chaîne courte (PCCC) et de paraffines chlorées à chaîne moyenne (PCCM) dans des produits textiles sur différentes matrices par chromatographie en phase gazeuse couplée à la spectrométrie de masse avec ionisation chimique négative (GC-NCI-MS)*

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# Foreword

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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).

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

Short-chain chlorinated paraffins (SCCPs) ($C_{10}$-$C_{13}$; chlorine content > 48 %) are listed by the Stockholm Convention on Persistent Organic Pollutants.

In Europe, according to REGULATION (EU) 2019/1021[1] of the European Parliament and of the Council of 20 June 2019 on persistent organic pollutants alkanes $C_{10}$-$C_{13}$, chloro [short-chain chlorinated paraffins (SCCPs)] (CAS no. 85535-84-8) as constituents of articles are prohibited. Articles containing SCCPs in concentrations lower than 0,15 % by weight are allowed.

Furthermore, it became industrial practice to restrict alkanes $C_{14}$-$C_{17}$, known as medium-chain chlorinated paraffins (MCCPs) as well.

SCCPs and MCCPs are used as flame retardants in textiles, as plasticizers in polymers and as finishing agents in leather. SCCPs and MCCPs are an issue for textile manufacturers and retailers due to their use within fabrics, coated fabrics, plastisol prints, buttons, leather patches, etc.

The analysis of chlorinated paraffins is a great challenge. The technical compounds are always complex mixtures of substances with different chain lengths and different chlorination degrees. Gas chromatography (GC) separation of these mixtures show an overlapping part of chain length (between short and middle chained) and of chlorination degrees, too. The responses of the different chlorination degrees vary in a big range. This document describes a procedure to get comparable results for SCCPs and MCCPs with a defined calibration standard of the most typical used mixtures (59 % chlorination degree for SCCPs and 55 % chlorination degree for MCCPs) and using four ion traces for SCCPs and four ion traces for MCCPs with gas chromatography negative ion chemical ionization mass spectrometry (GC-NCI-MS).

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# Textiles — Determination of short-chain chlorinated paraffins (SCCP) and middle-chain chlorinated paraffins (MCCP) in textile products out of different matrices by use of gas chromatography negative ion chemical ionization mass spectrometry (GC-NCI-MS)

**WARNING — This document calls for the use of substances/procedures that may be injurious to the health/environment if appropriate conditions are not observed. It refers only to technical suitability and does not absolve the user from legal obligations relating to health and safety/ environment at any stage.**

## 1 Scope

This document specifies a chromatographic method to determine the amount of short-chain chlorinated paraffins (SCCPs: $C_{10}$-$C_{13}$) and middle-chain chlorinated paraffins (MCCPs: $C_{14}$-$C_{17}$) in textile articles, especially in polymer of the coated fabrics, prints made of polymer and buttons made of polymer (e.g. polyvinylchloride) by means of solvent extraction and gas chromatography negative ion chemical ionization mass spectrometry (GC-NCI-MS).

## 2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 4787, *Laboratory glassware — Volumetric instruments — Methods for testing of capacity and for use*

## 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:

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

## 4 Principle

The test specimens are extracted with toluene, followed by a sulfuric acid clean-up. The analysis is carried out using GC-NCI-MS with a defined calibration standard and eight typical ion traces.

It shall be emphasized that this method is a method of convention. All steps shall be performed as described. Variations in procedure induce deviant results.

## 5 Reagents

Unless otherwise specified, analytical grade chemicals shall be used.

**5.1** ***n*-Hexane**, CAS no. 110-54-3.

**5.2 Toluene,** CAS no. 108-88-3.

**5.3 Internal standard (IS) Solution A:** Lindane, CAS no. 58-89-9 as internal standard in solution (IS), about $\rho$ = 100 µg of IS/ml in *n*-hexane.

**5.4 IS Solution B:** Dilute IS Solution A (5.3) 1 to 50. Lindane, CAS no. 58-89-9 as internal standard in solution (IS), about $\rho$ = 2 µg of IS/ml in *n*-hexane.

**5.5 Concentrated sulfuric acid** ($\rho$ = 1,84 g/ml at 20 °C), CAS no. 7664-93-9.

### 5.6 Standard solutions

**5.6.1 SCCPs 55,5 % chlorination degree** (Cl), CAS no. 85535-84-8, technical grade, $\rho$ = 100 µg/ml cyclohexane.

**5.6.2 SCCPs 63 % Cl**, CAS no. 85535-84-8, technical grade, $\rho$ = 100 µg/ml cyclohexane.

**5.6.3 MCCPs 52 % Cl**, CAS no. 85535-85-9, technical grade, $\rho$ = 100 µg/ml cyclohexane.

**5.6.4 MCCPs 57 % Cl**, CAS no. 85535-85-9, technical grade, $\rho$ = 100 µg/ml cyclohexane.

NOTE Commercial solutions are available on the market.

## 6 Apparatus

The usual laboratory equipment and laboratory glassware, according to ISO 4787, shall be used, in addition to the following.

**6.1 Pipettes**, in required sizes and variable pipettes.

**6.2 Analytical balance**, with a precision of at least 1 mg.

**6.3 Glass vials**, tightly sealable with lids suitable for solvent extraction, e.g. 20 ml.

**6.4 Glass GC-vials**, tightly sealable with lids suitable for sulfuric acid clean-up, e.g. 2 ml.

**6.5 Ultrasonic bath**, with controllable heating capable of maintaining a temperature of about 60 °C.

**6.6 Evaporation apparatus**, such as heating block with a controlled flow of gas over the liquid or vacuum rotary evaporator with vacuum control.

**6.7 Membrane filter**, pore width 0,45 µm.

**6.8 Vortex agitator**.

**6.9 Shaker**, ensuring an efficient mixing of the phases.

NOTE Horizontal shaker with minimum frequency of 5 $s^{-1}$, path length 2 cm to 5 cm has been found suitable.

**6.10 Gas chromatograph coupled to a negative chemical ionization mass selective detector** (GC-NCI-MS) system.

NOTE A description of the chromatographic equipment is given in Annex B.

## 7 Preparation of test specimens

The test specimen shall consist of a single material type (e.g. textile, polymer, etc.), which is tested separately.

Cut the homogenous material samples into pieces of about 0,3 cm to 0,5 cm edge length.

NOTE Up to 3 test specimens (of equal mass) of the same material type can be tested together taking into consideration the limits of detection and quantification.

## 8 Procedure

### 8.1 Extraction of test specimen

About (0,50 ± 0,01) g test specimen is weighed with the analytical balance (6.2) into a sealable vessel (6.3). Add 5 ml toluene (5.2). If the test specimen is not sufficiently immersed in the extraction solvent, add more solvent (5.2) and report the final volume for calculation of SCCPs and MCCPs amount. Close the vessel tightly and extract the test specimen at about 60 °C for (60 ± 5) min in an ultrasonic bath (6.5). Cool down to room temperature (less than 27 °C).

### 8.2 Sulfuric acid clean-up

Evaporate 2 ml of the toluene extract (8.1) to dryness, add 2 ml IS solution B (5.4). Redissolve the residue by agitating for 30 s in the vortex agitator (6.8) or for 5 min in the horizontal shaker (6.9), filtrate the solution through a membrane filter (6.7). IS solution shall be added after extraction because its concentration can be affected by the extraction in different ways than SCCPs/MCCPs (due to their different chemical properties). Take 1 ml of the filtrate and add 0,5 ml sulfuric acid (5.5) in a glass vial (6.4), shake for 30 min with horizontal shaker. An efficient mixing of the phases shall be ensured. After separation of the phases (optional centrifugation) put 0,5 ml of the upper phase (*n*-hexane) into another vial, seal the vial and analyse the extract.

### 8.3 Preparation of the calibration solutions

#### 8.3.1 Preparation of SCCPs calibration solution (5 μg/ml) with 59 % Cl

Transfer 53,3 μl of SCCPs 55,5 % Cl standard solution (5.6.1) and 46,7 μl SCCPs 63 % Cl standard solution (5.6.2) into a 2 ml volumetric flask. 40 μl IS solution A (5.3) is added and the flask is filled to mark with *n*-hexane (5.1).

#### 8.3.2 Preparation of SCCPs calibration solution (50 μg/ml) with 59 % Cl

Transfer 533 μl of SCCPs 55,5 % Cl standard solution (5.6.1) and 467 μl SCCPs 63 % Cl standard solution (5.6.2) into a 2 ml volumetric flask. 40 μl IS solution A (5.3) is added and the flask is filled to mark with *n*-hexane (5.1).

#### 8.3.3 Preparation of SCCPs calibration solution (75 μg/ml) with 59 % Cl

Transfer 800 μl of SCCPs 55,5 % Cl standard solution (5.6.1) and 700 μl SCCPs 63 % Cl standard solution (5.6.2) into a 2 ml volumetric flask. 40 μl IS solution A (5.3) is added and the flask is filled to mark with *n*-hexane (5.1).

#### 8.3.4 Preparation of MCCPs calibration solution (5 μg/ml) with 55 % Cl

40 μl of MCCPs 52 % Cl standard solution (5.6.3) and 60 μl MCCPs 57 % Cl standard solution (5.6.4) put into a 2 ml volumetric flask. 40 μl IS solution A (5.3) is added and the flask is filled to mark with *n*-hexane (5.1).

### 8.3.5 Preparation of MCCPs calibration solution (50 µg/ml) with 55 % Cl

400 µl of MCCPs 52 % Cl standard solution (5.6.3) and 600 µl MCCPs 57 % Cl standard solution (5.6.4) put into a 2 ml volumetric flask. 40 µl IS solution A (5.3) is added and the flask is filled to mark with *n*-hexane (5.1).

### 8.3.6 Preparation of MCCPs calibration solution (75 µg/ml) with 55 % Cl

600 µl of MCCPs 52 % Cl standard solution (5.6.3) and 900 µl MCCPs 57 % Cl standard solution (5.6.4) put into a 2 ml volumetric flask. 40 µl IS solution A (5.3) is added and the flask is filled to mark with *n*-hexane (5.1).

### 8.3.7 Daily calibration

It is necessary to use at least a three-point-calibration, see 8.3.1 to 8.3.6, each of these calibration solutions shall be analysed separately. Calibrate SCCPs and MCCPs separately.

Perform quantification with internal standard correction.

For long sequences it can be necessary to calibrate more than once. Check the necessity of calibration by using quality control samples.

## 8.4 GC-MS determination

The extract (see 8.2) shall be analysed using GC-NCI-MS (6.10). An example of a suitable GC-NCI-MS method is given in B.1.

Inlet system shall be in a clean state and optimized, see Figures in B.2.

In Table 1, the ions are listed which should be used for quantification of SCCPs and MCCPs. In Table 2, the ions are mentioned, which can be used for the IS Lindane (5.3).

For calculation of the results, the following steps should be performed.

a) Sum up the quantifier peak areas of the different ions from the three calibration standards (*m/z* 347, *m/z* 361, *m/z* 375 and *m/z* 389 for SCCP and *m/z* 403, *m/z* 417, *m/z* 431 and *m/z* 445 for MCCP).

b) Calculate a response factor for each of the three calibration standards under consideration of the area of the internal standard.

c) Sum up the quantifier peak areas of the different ions from the sample and form a response factor in the same way.

d) Plot a calibration curve with the response factor on the *y*-axis and the concentration of the calibration standards on the *x*-axis.

e) Calculate the response factor for the sample in the same way as for the calibration standards and calculate the concentration of the sample in µg/ml using the calibration curve.

f) Determine the amount of the SCCP and MCCP in mg/kg under consideration of the dilution factor and the sample amount.

Even if one or more chain length peaks are missing, assume the test specimen as positive for SCCPs or MCCPs.

To get a quantitative result, each peak area of the extract chromatogram shall be below the highest calibration point, if not dilute the extract with IS solution B (5.4) in this range or specify the result is bigger than the calculated result. $C_{12}Cl_7$ qualifier and quantifier ions could and should be switched due to interferences of *m/z* 375. $C_{17}Cl_7$ can be critical due to interferences and low response.

**Table 1 — Masses for quantification and qualification of SCCPs and MCCPs**

| CP-group | Substance | Quantifier<br>*m/z* | Qualifier<br>*m/z* |
|---|---|---|---|
| SCCPs | $C_{10}Cl_7$ | 347 | 349 |
| | $C_{11}Cl_7$ | 361 | 363 |
| | $C_{12}Cl_7$ | 375 | 377 |
| | $C_{13}Cl_7$ | 389 | 391 |
| MCCPs | $C_{14}Cl_7$ | 403 | 405 |
| | $C_{15}Cl_7$ | 417 | 419 |
| | $C_{16}Cl_7$ | 431 | 433 |
| | $C_{17}Cl_7$ | 445 | 447 |

**Table 2 — Masses for quantification and qualification of the internal standard Lindane (5.3)**

| Lindane IS | Quantifier<br>*m/z* | Qualifier<br>*m/z* |
|---|---|---|
| possible ions | 325 | 327 |
| possible ions | 255 | 253 |
| possible ions | 255 | 257 |

## 9 Expression of results

### 9.1 Evaluation

The peak shape evaluation (PSE) have been successfully tested and used. The integration shall be done with PSE, in accordance with Annex A. Results of an interlaboratory trial and the reliability of the method are shown in Annex C.

After assessing the peak shape of the sample ion by taking the peak shape of the referring ion of the standard into account, the peak is integrated in the retention time range of the standard peak. Overlays by interfering ions can thereby be avoided. Peaks with not matching peak shape are rejected and will not be integrated.

### 9.2 Determination of the recovery rate of the IS

The recovery of the internal standard in the extracts should be >60 % regarding to the area of the peak of the internal standard of the calibration. If the recovery is not sufficient, the step 8.2 of the procedure should be repeated and the extract shall be analysed using GC-NCI-MS. If the recovery is less than 60 % the second time, this should be noted in the test report.

### 9.3 Interferences

#### 9.3.1 Interferences of MCCPs masses

Quantifier masses 431 and 445 shall be quantified only if their area is above 10 % of the quantifier masses 403 or 417 and the masses are not disturbed (peak shape control). See A.2.

$C_{17}Cl_7$ quantifier (*m/z* 445) shows very low response and show overlay with SCCPs ions, therefore areas should be rejected, if interferences by SCCPs are noticed.

Masses used for MCCPs determination can be interfered by higher concentrations of SCCPs (> 1 %). In this case, the MCCPs result should be set to "n.t." with the comment: "*Cannot be determined due to interferences with SCCP in concentrations above 1 %*".