DRAFT INTERNATIONAL STANDARD

# ISO/DIS 22818

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| ISO/TC **38** | Secretariat: **JISC** |
| Voting begins on: **2020-04-10** | Voting terminates on: **2020-07-03** |

# Textiles — Determination of SCCP and MCCP in textile products out of different matrices by use of GC-NCI-MS

ICS: 59.060.01





This document is circulated as received from the committee secretariat.

**ISO/CEN PARALLEL PROCESSING**

Reference number
ISO/DIS 22818:2020(E)

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Published in Switzerland

# Contents

Page

# Foreword

# Introduction

Short-chain chlorinated paraffins (C10-C13; chlorine content > 48 %) are listed by the Stockholm Convention on Persistent Organic Pollutants.

In Europe according to REGULATION (EC) No 850/2004 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 29 April 2004 on persistent organic pollutants amended by Commission Regulation (EU) 2015/2030 of 13th November 2015, Article 3, clause 1 in conjunction with Annex I Alkanes C10-C13, chloro (short-chain chlorinated paraffins) (SCCPs) (CAS No 85535-84-8) as constituents of articles shall be prohibited. Articles containing SCCPs in concentrations lower than 0,15 % by weight shall be allowed.

Furthermore, it has become industrial practice to restrict Alkanes C14-C17, chloro (medium-chain chlorinated paraffins) (MCCPs) as well.

SCCP and MCCP are used as flame retardants in textiles, as plasticizers in polymers and as finishing agents in leather. SCCP and MCCP 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 substances with different chain lengths and different chlorination degrees. 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 standard 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 GC-NCI-MS (gas chromatography negative ion chemical ionization mass spectrometry).

# Textiles — Determination of SCCP and MCCP in textile products out of different matrices by use of 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 and middle-chain chlorinated paraffins (SCCP: C10-C13 and MCCP: C14-C17) 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 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 4787:2010, *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 http://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 cleanup. The analysis is carried out using GC-NCI-MS with a defined calibration standard and 8 typical ion traces.

It has to be emphasized, that this method is a conventional method. All steps have to be performed as described. Variations in procedure induce deviant results.

## 5 Reagents

Unless otherwise specified, analytical grade chemicals have to be used.

### 5.1 n-Hexane

### 5.2 Toluene

### 5.3 IS Solution A: Lindane 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 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)

**Standard solutions**

**5.6 SCCP 55,5 % Cl technical grade, $\rho$ = 100 µg/ml cyclohexane**

**5.7 SCCP 63 % Cl technical grade, $\rho$ = 100 µg/ml cyclohexane**

**5.8 MCCP 52 % Cl technical grade, $\rho$ = 100 µg/ml cyclohexane**

**5.9 MCCP 57 % Cl technical grade, $\rho$ = 100 µg/ml cyclohexane**

NOTE Commercial solutions are available on the market.

## 6 Equipment

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** Tight sealable glass vials with lids in capacities of 20 ml and ca. 2 ml, suitable for solvent extraction, sulfuric acid clean-up and GC-MS analysis.

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

**6.5** Evaporation apparatus, e.g. heating block with a controlled flow of gas over the liquid or vacuum rotary evaporator with vacuum control.

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

**6.7** Vortex agitator.

**6.8** 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.

**6.9** 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 Calibration solutions

### 7.1 Preparation of SCCP calibration solution (5 µg/ml) with 59 % chlorination degree

Transfer 53,3 µl of SCCP 55,5 % Cl standard solution and 46,7 µl SCCP 63 % Cl standard solution 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.



 

### 7.2 Preparation of SCCP calibration solution (50 µg/ml) with 59 % chlorination degree

Transfer 533 µl of SCCP 55,5 % Cl standard solution and 467 µl SCCP 63 % Cl standard solution 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.

### 7.3 Preparation of SCCP calibration solution (75 µg/ml) with 59 % chlorination degree

Transfer 800 µl of SCCP 55,5 % Cl standard solution and 700 µl SCCP 63 % Cl standard solution 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.

### 7.4 Preparation of MCCP calibration solution (5 µg/ml) with 55 % chlorination degree

40 µl of MCCP 52 % Cl standard solution and 60 µl MCCP 57 % Cl standard solution 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.

### 7.5 Preparation of MCCP calibration solution (50 µg/ml) with 55 % chlorination degree

400 µl of MCCP 52 % Cl standard solution and 600 µl MCCP 57 % Cl standard solution 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.

### 7.6 Preparation of MCCP calibration solution (75 µg/ml) with 55 % chlorination degree

600 µl of MCCP 52 % Cl standard solution and 900 µl MCCP 57 % Cl standard solution 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.

NOTE Each laboratory is responsible for validation and has ascertained that the required determination limits are achieved.



## 8 Test specimen sampling

Material should be cut to small pieces of 3 mm to 5 mm.

### 8.1 Extraction of test specimen

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

### 8.2 Sulfuric acid cleanup procedure

Evaporate 2 ml of the toluene extract (8.1) to dryness, add 2 ml IS solution B (5.4) redissolve the residue by vortex agitator 30 second or horizontal shaking (5 min), filtrate the solution through a membrane filter. Take 1 ml of the filtrate and add 0,5 ml sulfuric acid (5.5), 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 analyze the extract.

NOTE Internal standard solution has to be added after extraction because its concentration may be affected by the extraction in different ways than SCCP/MCCP (due to their different chemical properties).

## 9 GC-MS determination

The solution has to be analyzed using GC-NCI-MS. An example of a suitable GC-NCI-MS method is given in Annex B.1.

Inlet system has to be in a clean state and optimized, see pictures in Annex B.2.

## 9.1 Daily calibration

It is necessary to use at least a three-point-calibration, look at 7, each of these calibration solutions has to be analyzed separately. Calibrate SCCP and MCCP 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.

## 9.2 Used Ions

In Table 1 the ions are listed which should be used for quantification of SCCP and MCCP. In Table 2 the ions are mentioned, which can be used for the internal standard Lindane.

Sum up the quantifier peak areas from the standard and equate with the standard concentration. Sum up the quantifier peak areas of the sample, too, and calculate the concentration with responses of the calibration standards.

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

To get a quantitative result, each peak area of the extract chromatogram has to 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.



**Table 1 — Masses for quantification and qualification of SCCP and MCCP**

| CP-group | Substance | Quantifier *m/z* | Qualifier *m/z* |
|---|---|---|---|
| SCCP | C10Cl7 | 347 | 349 |
| | C11Cl7 | 361 | 363 |
| | C12Cl7 | 375 | 377 |
| | C13Cl7 | 389 | 391 |
| MCCP | C14Cl7 | 403 | 405 |
| | C15Cl7 | 417 | 419 |
| | C16Cl7 | 431 | 433 |
| | C17Cl7 | 445 | 447 |
| NOTE C12Cl7 qualifier and quantifier ions could and should be switched due to interferences of *m/z* 375. C17Cl7 could be critical due to interferences and low response. | | | |

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

| Lindane IS | Quantifier *m/z* | Qualifier *m/z* |
|---|---|---|
| possible Ions | 325 | 327 |
| possible Ions | 255 | 253 |
| possible Ions | 255 | 257 |