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BSI Standards Publication

Leather — Determination of chlorinated hydrocarbons in leather — Chromatographic method for short-chain chlorinated paraffins (SCCP)

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National foreword

This British Standard is the UK implementation of EN ISO 18219:2015.

The UK participation in its preparation was entrusted to Technical Committee TCI/69, Footwear, leather and coated fabrics.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Leather - Determination of chlorinated hydrocarbons in leather - Chromatographic method for short-chain chlorinated paraffins (SCCP) (ISO 18219:2015)

Cuir - Dosage des hydrocarbures chlorés dans le cuir - Méthode chromatographique pour les paraffines chlorées à chaîne courte (PCCC) (ISO 18219:2015)

Leder - Bestimmung von chlorierten Kohlenwasserstoffen in Leder - Chromatographische Verfahren für kurzkettige Chlorparaffine (SCCP) (ISO 18219:2015)

This European Standard was approved by CEN on 29 August 2015.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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European foreword

This document (EN ISO 18219:2015) has been prepared by Technical Committee IULTCS “International Union of Leather Technologists and Chemists Societies" in collaboration with the Technical Committee CEN/TC 289 “Leather” the secretariat of which is held by UNI.

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of an identical text or by endorsement, at the latest by April 2016, and conflicting national standards shall be withdrawn at the latest by April 2016.

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Endorsement notice

The text of ISO 18219:2015 has been approved by CEN as EN ISO 18219:2015 without any modification.

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Foreword

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

ISO 18219 was prepared by the Chemical Test Commission of the International Union of Leather Technologists and Chemists Societies (IUC Commission, IULTCS) in collaboration with the European Committee for Standardisation (CEN) Technical Committee CEN/TC 289, *Leather*, the secretariat of which is held by UNI, in accordance with the agreement on technical co-operation between ISO and CEN (Vienna Agreement).

IULTCS, originally formed in 1897, is a world-wide organization of professional leather societies to further the advancement of leather science and technology. IULTCS has three Commissions, which are responsible for establishing international methods for the sampling and testing of leather. ISO recognizes IULTCS as an international standardizing body for the preparation of test methods for leather.

Introduction

Short-chain chlorinated paraffins (SCCP) are classified as dangerous to the environment, since they are very toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment.

In 2002, the European Directive 2002/45/EC restricted the sale and use of short-chain chlorinated paraffins (C_{10}-C_{13}) in product preparations for the fatliquoring of leather. Preparations containing concentrations equal or higher than 1 % of SCCP were forbidden. This Directive is included as part of the EU Regulation 1907/2006 (REACH). Within this EU Regulation, in October 2008, the short-chain chlorinated paraffins were added to the Candidate List of Substances of Very High Concern (SVHC).

INTERNATIONAL STANDARD

ISO 18219:2015(E)
IULTCS/IUC 30:2015(E)

Leather — Determination of chlorinated hydrocarbons in leather — Chromatographic method for short-chain chlorinated paraffins (SCCP)

1 Scope

This International Standard specifies a chromatographic method to determine the amount of short-chain chlorinated paraffins (SCCP) C_{10}-C_{13} in processed and unprocessed leathers.

Annex A is for information only.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 2418, *Leather — Chemical, physical and mechanical and fastness tests — Sampling location*

ISO 4044, *Leather — Chemical tests — Preparation of chemical test samples*

3 Principle

The test sample is extracted using *n*-hexane at 60 °C in an ultrasonic bath for 60 min. After SPE clean up, an aliquot is then analysed using a gas chromatograph fitted to a mass selective detector with chemical ionization (GC-ECNI-MS).

Liquid chromatography system with single quad (LC-MS) or triple quad mass spectrometry (LC-MS/MS) can also be used if the user has demonstrated that the accuracy of measurement is equivalent to that of the GC-ECNI-MS method.

4 Apparatus and materials

Normal laboratory apparatus and, in particular, the following.

4.1 Analytical balance.

4.2 Sealable vessel, with lid, 20 ml, suitable for extraction with *n*-hexane.

4.3 Ultrasonic bath, (temperature controlled).

4.4 Pipette, 1 ml to 10 ml capacity.

4.5 Volumetric flask, 2 ml.

4.6 Solid phase extraction (SPE) system, with vacuum device and normal phase SPE cartridges, for example 500 mg/6 ml, e.g. Chromabond columns, Sorbent: SiOH, 6 ml, 500 mg.

4.7 PTFE membrane filter.

4.8 Gas chromatograph and mass selective detector with chemical ionization (GC-ECNI-MS).

5 Chemicals

If not otherwise defined, analytical reagent grade chemicals shall be used.

5.1 *n*-hexane, CAS[1)] No.: 110-54-3.

5.2 Dichloromethane, CAS No: 75-09-2.

5.3 Internal standard solution, 1,1,1,3,10,11-hexachloroundecane, CAS No: 601523-28-8, 1 000 µg/ml.

NOTE Other suitable internal standard can be used.

5.4 Standard solutions, SCCP, C_{10}-C_{13}, with different chlorine content, each 100 µg/ml:

5.4.1 SCCP C_{10}-C_{13} 55,5 % Cl, technical grade.

5.4.2 SCCP C_{10}-C_{13} 63 % Cl, technical grade.

NOTE These SCCP calibration solutions are available commercially.

5.5 Nitrogen gas.

6 Sampling

The sampling shall be made according to ISO 2418. If a sampling according to ISO 2418 is not possible (e.g. in case of leather from finished products like shoes, clothing, etc.), the details of the sampling must be stated in the test report. Glue residuals must be mechanically removed from leather samples.

The leather samples shall be ground or cut into smaller pieces, not larger than 2 mm to 3 mm, according to ISO 4044.

7 Sample preparation and analysis

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

533 µl of SCCP C_{10}-C_{13} 55,5 % Cl standard solution (5.4.1) and 467 µl SCCP C_{10}-C_{13} 63 % Cl standard solution (5.4.2) are transferred into a 2 ml volumetric flask (4.5). 20 µl of internal standard solution (5.3) is added and the flask filled up to the volume with *n*-hexane (5.1).

The calibration standard with 59 % chlorine content shall be used for the quantification of all samples, independent of their chlorination degree (if known).

7.2 Extraction of leather

0,5 g ± 0,001 g test leather sample is weighed with the analytical balance (4.1) into the sealable vessel (4.2). 9,9 ml *n*-hexane (5.1) and 100 µl internal standard (5.3) are added and the vessel sealed and extracted at 60 °C in an ultrasonic bath (4.3) for 60 min ± 2 min.

1) Chemical Abstracts Service.

7.3 Clean up

The SPE cartridges (4.6) are pre-treated with 2 ml *n*-hexane (5.1) per 100 mg sorbent. The cartridges shall not be dried during or after the pre-treating. The extraction solution (7.2) is decanted through the cartridges and the eluate is collected in a new vessel. The cartridge is flushed into the vessel with 5 ml of a 50:50 (v/v) mixture from *n*-hexane (5.1) and dichloromethane (5.2). This solution is reduced to 1,0 ml under a gentle stream of nitrogen, filtered through a PTFE membrane filter (4.7) and transferred to a GC-MS vial.

7.4 GC-MS Determination

The solution is analysed using GC-ECNI-MS (4.8). An example of a suitable GC-ECNI-MS method is given in Annex A.

8 Evaluation

Peak areas from the four quantification masses of the standard are summed up and equated with standard concentration. Peak areas of the samples are summed up too and the concentration is calculated with response of the standard.

To check the linearity of the analytical system, a calibration standard as reference standard is analysed after each tenth sample and at the end of the sequence. The deviation in reference to the calibration standard should be within ±20 %, otherwise the analytical system has to be checked before retrying the analysis.

Sample extract should always be diluted in the concentration range of the standard.

The integration of the samples has only to be done in the retention time window of the standard.

The content of the short-chain chlorinated paraffins in leather is calculated according to Formula (1) as a mass fraction w in mg/kg:

$$w = \frac{A_{SCCP-S} \cdot c_{SCCP-Std} \cdot V}{A_{SCCP-Std} \cdot m_S} \cdot \frac{A_{\mathrm{int}.Std}}{A_{\mathrm{int}.S}} \cdot \frac{c_{\mathrm{int}.S}}{c_{\mathrm{int}.Std}} \quad (1)$$

with

$A_{SCCP\text{-}S}$ sum of the peak areas of SCCP in the sample;

$A_{SCCP\text{-}Std}$ sum of the peak areas of SCCP in the calibration standard;

$c_{SCCP\text{-}Std}$ concentration of SCCP in the calibration standard [µg/ml];

V final volume [ml];

m_S mass of the sample [g];

$A_{\mathrm{int}.Std}$ peak area of internal standard in calibration standard;

$A_{\mathrm{int}.S}$ peak area of internal standard in the sample;

$c_{\mathrm{int}.S}$ concentration of internal standard in the sample [µg/ml];

$c_{\mathrm{int}.Std}$ concentration of internal standard in calibration standard [µg/ml].

9 Test report

The test report shall include at least the following:

a) a reference to this International Standard, i.e. ISO 18219;

b) all details necessary for complete identification of the sample tested;

c) extraction procedure used (7.2);

d) amount of extracted SCCP (C_{10}-C_{13}) in mg/kg;

e) any deviation by agreement or otherwise from the procedure specified.

Annex A
(informative)

Chromatographic analysis operating parameters

A.1 Suggested gas chromatography mass spectrometry (GC-ECNI-MS) conditions

Column:	5 % phenyl methyl siloxane, e.g. DB-5 or equivalent is suitable length: 25 m, internal diameter: 0,25 mm film thickness: 0,25 µm
Carrier gas:	helium, flow rate: 1,2 ml/min
Injector temperature:	250 °C, mode splitless, splitless time: 1,5 min
Injection volume:	1 µl
Temperature programme:	120 °C, up to 300 °C at 12 °C/min, 300 °C for 5 min solvent delay: 4 min, total run time: 20 min
MS conditions:	Transfer line: 280 °C Ion source: 150 °C Quadrupole: 120 °C
Chemical ionization (CI) conditions:	CI gas: Methane 5.5 (i.e. >99,9995 % CH_4) CI valve: 40 %

A.2 Calibration and calculation

Table A.1 — *m/z* signals for quantification and qualification

No.	Substance	Quantifier/Qualifier
1	1,1,1,3,10,11-hexachloroundecane	364/362
2	SCCP (C_{10}-C_{13})	347/349 361/363 375/377 389/391

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