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

*Cuir — Dosage des hydrocarbures chlorés dans le cuir — Méthode
chromatographique pour les paraffines chlorées à chaîne courte (PCCC)*

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ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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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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 (C₁₀-C₁₃) 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).

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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) C₁₀-C₁₃ 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, CAS¹⁾ 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, C₁₀-C₁₃, with different chlorine content, each 100 µg/ml:

5.4.1 SCCP C₁₀-C₁₃ 55,5 % Cl, technical grade.

5.4.2 SCCP C₁₀-C₁₃ 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 C₁₀-C₁₃ 55,5 % Cl standard solution (5.4.1) and 467 µl SCCP C₁₀-C₁₃ 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:

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

with

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

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

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

V final volume [ml];

m_S mass of the sample [g];

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

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

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

$c_{int.Std}$ concentration of internal standard in calibration standard [$\mu\text{g/ml}$].