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Chemicals for the leather tanning industry — Determination of cyclosiloxanes

Produits chimiques pour l'industrie du tannage du cuir — Détermination des cyclosiloxanes

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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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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.

This document 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 Standardization (CEN) Technical Committee CEN/TC 289, Leather, 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

This document includes a procedure for analysing certain cyclosiloxanes using gas chromatography (GC) with mass spectrometer (MS) equipment. With this analytical method octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6) can be determined.

In the leather industry cyclosiloxanes (D4), (D5) and (D6) are used in the manufacture of silicone-based waterproofing fatliquors and can also be used in the production of silicone-based finishing chemicals especially as handle modifiers.

At present, the official classification recognised in the EU is the following.

— Octamethylcyclotetrasiloxane (D4) is classified as persistent, bioaccumulative and toxic.[1]

— Decamethylcyclopentasiloxane (D5) is classified as persistent, bioaccumulative and toxic.[2]

— Dodecamethylcyclohexasiloxane (D6) is classified as persistent, bioaccumulative and toxic.[3]

Chemicals for the leather tanning industry — Determination of cyclosiloxanes

1 Scope

This document specifies a method for determining the total content of the following cyclosiloxanes in chemicals for the leather tanning industry:

— octamethylcyclotetrasiloxane (D4);

— decamethylcyclopentasiloxane (D5);

— dodecamethylcyclohexasiloxane (D6);

This method requires the use of gas chromatography (GC) equipped with a single quadrupole mass spectrometer (MS) to identify and quantify the cyclosiloxanes.

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 3696, *Water for analytical laboratory use — Specification and test methods*

3 Terms and definitions

No terms and definitions are listed in this document.

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

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

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

4 Principle

After solubilizing the chemical specimen in water, a liquid-liquid extraction with a hexane-ethyl acetate mixture is performed and then the cyclosiloxanes are analysed by gas-chromatography with single quadrupole mass spectrometry (GC-MS). Using an external calibration, quantification is performed taking into account the recovery rate of the internal standard.

5 Apparatus

The usual laboratory apparatus and, in particular, the following shall be used:

5.1 Ultrasonic bath, capable of operating at a starting temperature of 40 °C to 45 °C.

5.2 Horizontal shaker, capable of at least 300 cycles per minute.

5.3 Glass container with a screw cap, e.g. volume of 20 ml.

5.4 Suitable syringe membrane filters, e.g. polyamide with pore size 0,2 µm.

5.5 Volumetric flasks, e.g. volume of 10 ml and 100 ml.

5.6 Plastic test tubes, 50 ml, or suitable vessel that allows separation of organic and aqueous phase, that can be sealed for vigorous shaking.

5.7 GC vials, with cap, e.g. volume of 2 ml.

5.8 Analytical balance, with a resolution of 1 mg or better.

5.9 Pipettes, various sizes, e.g. volume of 0,1 ml to 10 ml.

5.10 Centrifuge, capable of at least 4 000 r/min.

5.11 Instrumental equipment, GC-MS.

6 Reagents

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

6.1 n-hexane, CAS Registry Number® (CAS RN)[1)] 110-54-3, suitable for GC-MS analysis.

6.2 Ethyl acetate, CAS RN 141-78-6, suitable for GC-MS analysis.

6.3 Water grade 1, according to ISO 3696.

6.4 Sodium chloride, CAS RN 7647-14-5, purity ≥ 99,0 % (mass fraction).

6.5 Magnesium sulphate anhydrous, CAS RN 7487-88-9, purity ≥ 99,0 % (mass fraction).

6.6 Octamethylcyclotetrasiloxane (D4), CAS RN 556-67-2, purity ≥ 99,0 % (mass fraction).

6.7 Decamethylcyclopentasiloxane (D5), CAS RN 541-02-6, purity ≥ 99,0 % (mass fraction).

6.8 Dodecamethylcyclohexasiloxane (D6), CAS RN 540-97-6, purity ≥ 99,0 % (mass fraction).

6.9 n-hexane-ethyl acetate 50:50 (volume fraction) mixture, prepared by mixing equal amounts by volume of n-hexane and ethyl acetate.

6.10 Stock solutions of a mix of cyclosiloxanes D4, D5 and D6, ρ = 1 mg/l and 20 mg/l.

EXAMPLE 10 mg of each of the respective octamethylcyclotetrasiloxane (D4) (6.6), decamethylcyclopentasiloxane (D5) (6.7), and dodecamethylcyclohexasiloxane (D6) (6.8), are dissolved together in a 100 ml volumetric flask (5.5) and filled up with mixed solution of n-hexane and ethyl acetate (6.9). Mixed stock solutions are prepared to obtain concentrations of 1 mg/l and 20 mg/l.

6.11 Internal standard, ρ = 100 mg/l.

The use of an internal standard is required to avoid matrix effects.

1) Chemical Abstracts Service (CAS) Registry Number® is a trademark of the American Chemical Society (ACS). This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

Examples of suitable internal standards:

Naphthalene-D8, CAS RN® 1146-65-2;

Tetrakis(trimethylsilyloxy)silane, CAS RN® 3555-47-3.

Prepare a 100 mg/l solution of the internal standard by diluting the internal standard with n-hexane-ethyl acetate 50:50 (volume fraction) mixture (6.9).

6.12 Calibration solutions of cyclosiloxanes.

Prepare at least four calibration solutions of ρ = 0,1 mg/l to ρ = 10 mg/l of the mix of cyclosiloxanes using the stock solutions (6.10), see Table 1.

Table 1 — Example of calibration solutions

Concentration mg/l	**Volume of n-hexane-ethyl acetate 50:50 (volume fraction) mixture** (6.9) µl	**Volume of mix of cyclosiloxanes 1 mg/l** (6.10) µl	**Volume of mix of cyclosiloxanes 20 mg/l** (6.10) µl	**Volume of internal standard 100 mg/l** (6.11) µl
0,1	890	100	0	10
0,5	490	500	0	10
1	940	0	50	10
5	740	0	250	10
10	490	0	500	10

7 Sampling and sample preparation

The specimen should be thoroughly mixed to get a representative test portion for analysis.

In the case of very dense chemical, manually or mechanically shake the sample to homogenize the composition of the test specimen.

8 Procedure

8.1 Sample solution preparation

Weigh (0,5 ± 0,05) g of the test specimen with an analytical balance (5.8) in a 100 ml volumetric flask (5.5) and make up to volume with grade 1 water (6.3). Close the flask and place it for (10 ± 2) min in an ultrasonic bath (5.1) at a starting temperature of 40 °C to 45 °C.

This procedure is only applicable to water-soluble chemicals. Otherwise, use the procedure described in Annex C.

8.2 Liquid-liquid extraction

Pipette 10 ml of the sample solution (8.1) into a plastic test tube (5.6) and add 1 g of sodium chloride (6.4) and 4 g of magnesium sulphate anhydrous (6.5). Then pipette 10 ml of n-hexane-ethyl acetate 50:50 (volume fraction) mixture (6.9) and 10 µl of internal standard (6.11) to the sample solution, close the plastic test tube and shake by hand and degas. Shake for (10 ± 2) min on a mechanical horizontal shaker (5.2) at 300 cycles/min.

For complete phase separation after shaking, the mixture shall be centrifuged (5.10) for (5 ± 1) min at (3 000 ± 400) r/min, then an aliquot of the supernatant of extraction solution is filtered (5.4) into a GC sample vial (5.7). The aliquot is then ready for the GC-MS analysis.

8.3 Instrumental analysis

The detection of the cyclosiloxanes is made using GC-MS. Examples of suitable chromatographic conditions are given in Annex A (for GC-MS).

If the concentration of the cyclosiloxanes is out of the range of the calibration, make an appropriate dilution and analyse again.

9 Expression of results

The content of each cyclosiloxane is calculated as the mass fraction, *w*, in milligrams per kilogram (mg/kg) of the chemical specimen according to Formula (1):

$$w = \frac{\left(\frac{A_s}{A_{isample}} - b\right) \cdot C_{isample}}{a} \times \left(\frac{V \cdot d}{m}\right) \quad (1)$$

where

A_s is the peak area of each cyclosiloxane in the extraction solution;

$A_{isample}$ is the peak area of the corresponding internal standard in the extraction solution;

$C_{isample}$ is the concentration of the internal standard in the extraction solution in micrograms per litre (µg/l);

b is the intercept of the calibration graph;

d is the eventual dilution factor;

a is the slope of the calibration graph;

V is the final volume used (0,01 l);

m is the mass of the chemical specimen in grams (g).

10 Precision

With this method it is feasible to reach limits of quantification (LoQ) below 50 mg/kg for each cyclosiloxane.

The results of interlaboratory trials to determine the content of octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6) in chemicals are presented in Annex B.

11 Test report

The test report shall include at least the following information:

a) a reference to this document, i.e. ISO 23649:2025;

b) type, origin and description of the chemical sample, if possible;

c) date of the test;

d) the type of GC equipment used;

e) mass fraction of each quantified cyclosiloxane (see Clause 9), if requested, expressed in milligrams per kilogram (mg/kg);

f) any deviations from the procedure;

g) any unusual features observed.

Annex A
(informative)

Chromatographic analysis operating parameters for GC-MS

A.1 Preliminary comment

As the GC equipment (5.11) of the laboratories can vary, no general valid instructions can be provided for the chromatographic analysis. The following parameters have been successfully tested and used.

A.2 GC-MS operating parameters

A.2.1 GC-MS chromatographic conditions

Column:	5 % phenyl methyl siloxane, length: 30 m; internal diameter: 0,25 mm; film thickness: 0,25 µm
Injection system: Injection temperature:	splitless, time 2 min 250 °C
Injection volume:	1 µl
Carrier gas:	helium, flow rate: 1,5 ml/min
Temperature programme:	50 °C (3 min) then up to 160 °C at 10 °C/min, up to 240 °C at 40 °C/min. Total run time 16 min
MS conditions:	Transfer line: 280 °C; ion source: 230 °C; quadrupole: 150 °C, solvent delay: 4 min
MS detection:	see Table A.1

Table A.1 — Typical ions for GC-MS

Cyclosiloxane compounds	Quantifier ion m/z	Qualifier ions m/z
octamethylcyclotetrasiloxane (D4)	281	281, 282
decamethylcyclopentasiloxane (D5)	267	73, 267, 355
dodecamethylcyclohexasiloxane (D6)	341	73, 341, 429