# SLOVENSKI STANDARD
# oSIST prEN ISO 23702-1:2021

**01-november-2021**

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**Usnje - Per- in polifluoroalkil snovi - 1. del: Določevanje nehlapnih spojin z metodo ekstrakcije z uporabo tekoče kromatografije (ISO/DIS 23702-1:2021)**

Leather - Per- and polyfluoroalkyl substances - Part 1: Determination of non-volatile compounds by extraction method using liquid chromatography (ISO/DIS 23702-1:2021)

Leder - Per- und Polyfluoralkylsubstanzen - Teil 1: Bestimmung von nichtflüchtigen Verbindungen durch Extraktion mit Flüssigchromatographie (ISO/DIS 23702 1:2021)



Cuir - Substances perfluoroalkylées et polyfluoroalkylées - Partie 1: Détermination des composés non volatils par une méthode d'extraction utilisant la chromatographie en phase liquide (ISO/DIS 23702-1:2021)



**Ta slovenski standard je istoveten z:** **prEN ISO 23702-1**

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**ICS:**

| | | |
|---|---|---|
| 59.140.30 | Usnje in krzno | Leather and furs |

**oSIST prEN ISO 23702-1:2021** **en,fr,de**

DRAFT INTERNATIONAL STANDARD

# ISO/DIS 23702-1
# IULTCS
# IUC 39-1

IULTCS

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Voting begins on:
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# Leather - Per- and polyfluoroalkyl substances —

## Part 1:
## Determination of non-volatile compounds by extraction method using liquid chromatography

ICS: 59.140.30



IMPORTANT — Please use this updated version dated 2021-07-29, and discard any previous version of this DIS. IULTCS reference missing

This document is circulated as received from the committee secretariat.

**ISO/CEN PARALLEL PROCESSING**



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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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.



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*, the secretariat of which is held by UNI, in accordance with the Agreement on technical cooperation 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.

This second edition cancels and replaces the first edition (ISO 23702-1:2018), which has been technically revised as follows:

— to clarify the relevant organic fluorine compounds the title has been modified to “Leather — Per- and polyfluoroalkyl substances — Part 1: Determination of non-volatile compounds by extraction method using liquid chromatography”;

— the Scope and clauses 3, 4, 5, 6, 7, 8, 9, and 10 have been editorially and technically modified;

— the previous clause 7 has been split into 2 separate clauses, “Sampling” and “Procedure” respectively;

— the previous clause 9 has been included in this edition as part of clause 8;

— a new Annex A listing the category of application of the per- and polyfluoroalkyl substances (PFAS) has been inserted. The following Annexes have been re-lettered accordingly;

— Annexes B and C have been technically modified and in this edition are lists of “PFAS regulated substances” and “PFAS non-regulated substances” respectively.

A list of all parts in the ISO 23702 series can be found on the ISO website.

 

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

The per- and polyfluoroalkyl substances (PFAS) consists of a large group of surface active compounds. The most well-known are perfluorooctanioc sulfonic acid (PFOS) and perfluorooctanooic acid (PFOA). Table A1 presents PFAS substances category and applications.

Perfluorooctanoic sulfonic acid (PFOS) is classified as persistent, bio-accumulative and toxic (PBT). PFOS and its salts are restricted and regulated in many countries regarding its marketing and use (see references [3] and [4]).

Perfluorooctanoic acid (PFOA) and its salts are suspected of having a similar risk profile to PFOS.

A number of long chain per- and polyfluoroalkyl compounds have been included in the EU Candidate List of Substances of Very High Concern (SVHC), which is available at: https://echa.europa.eu/candidate-list-table.

The regulatory thresholds for restricted per- and polyfluoroalkyl compounds limit the use to a level below which they cannot be meaningfully used. The thresholds need to take into consideration the possible presence of unavoidable impurities and unintentional trace contaminants.

The long chain, fully fluorinated anions are non-volatile. They are heat stable and resistant to breaking down in the environment. The per- and polyfluoroalkyl compounds have been widely used in many industries, including in oil-, soil- and water-repellent finishes for textiles, leather products, paper, furniture and carpets.

# Leather - Per- and polyfluoroalkyl substances —

# Part 1:
# Determination of non-volatile compounds by extraction method using liquid chromatography

**WARNING — The use of this document involves hazardous materials. It does not purport to address all of the safety or environmental problems associated with its use. It is the responsibility of users of this document to take appropriate measures to ensure the safety and health of personnel and the environment prior to application of this document, and fulfil the relevant requirements for this purpose.**

## 1 Scope

This document specifies a test method for detection and quantification of extractable non-volatile per- and polyfluoroalkyl substances (PFAS) in leather and coated leather by solvent extraction and liquid chromatography coupled with mass spectrometry.

This document, taking into account the three-dimensional distribution of the fibres within leather, makes the evaluation of the PFAS with respect to the mass.



Classes of regulated compounds listed in Annex B, Table B.1, include acids, telomers, sulfonates and sulphonamide alcohols. Classes of other non-regulated compounds that can be determined by this document are listed in Annex C, Table C.1.



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

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

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

EN 15987, *Leather — Terminology — Key definitions for the leather trade.*

## 3 Terms and definitions

For the purposes of this document, the leather terms and definitions given in EN 15987 apply.

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 https://www.electropedia.org/

## 4 Principle

The PFAS substances listed in Annexes B and C, are extracted in an ultrasonic bath with methanol at 60 °C; the extract is analysed by high-performance liquid chromatograph with a tandem mass spectrometric detector (LC-MS/MS).

## 5 Reagents

Unless otherwise specified, all reagents shall be of a recognised analytical grade.

**5.1 Water**, grade 1 (according to ISO 3696) or LC-MS grade.

**5.2 Methanol,** CAS Registry Number®[1)] 67-56-1, LC-MS grade.

**5.3 Ammonium acetate,** CAS RN® 631-61-8

**5.4 Stock solutions of reference compounds**, purity > 95 % for the pure substance.

Solutions of the reference compounds listed in Annex B and Annex C are available commercially. They should be diluted to the required concentrations. If reference compounds are obtained pure, for example, weigh 100 mg of each standard separately into a 100 ml volumetric flask and fill up to the mark with methanol (5.2). Dilute this solution with methanol (5.2) at a ratio of 1:1 000 to prepare a 1 000 µg/l stock solution.



**5.5 Target compound solutions.**

Prepare a 25 µg/l solution of each target compound by diluting the 1 000 µg/l reference compound stock solutions (5.4) with methanol (5.2)



For the preparation of the target compound solution, certified solutions are commercially available. The purity level and the solvent shall be checked in order to be in accordance with the present standard.

**5.6 Internal standard.**

At least two suitable internal standards for perflurooctane sulfonate (PFOS) and perfluoroactanoic acid (PFOA) shall be used. The impurity level of the internal standard should be determined prior to the use of every new lot.

Examples of suitable mass-labelled internal standards are:

— $^{13}C_x$-PFOA (e.g. perfluoro[1,2,3,4-$^{13}C_4$ ]-octanoic-acid, CAS RN® 960315-48-4);

— $^{13}C_x$-PFOS (e.g. sodium perfluoro-1-[1,2,3,4-$^{13}C_4$ ]-octanesulfonate, CAS RN® 960315-53-1);

— $^{18}O_x$-PFOS (e.g. $[F(CF_2)_8SO_3^-\ H^+]$-, $^{18}O_2$).

When other types of suitable internal standards become available, they may be used.

Prepare a 1 00 µg/l solution of the internal standard by diluting the commercial solution with methanol (5.2).

**5.7 Preparation of calibration solutions.**

Materials and liquids shall be stored at 4 °C and in clean containers.

1) CAS Registry Number® (CAS RN®) is a trademark of CAS corporation. 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.

Prepare suitable calibration solutions using methanol (5.2), target compound solutions (5.5) and the internal standard solution (5.6). At least five calibration solutions shall be prepared with a concentration range to match the limits given. For example, prepare according to the volumes given in Table 1 in a 1 000 µl flask.

**Table 1 — Example of calibration solutions**

| Concentration (µg/l) | 0,25 | 0,5 | 1 | 2,5 | 5 | 10 |
|---|---|---|---|---|---|---|
| Volume methanol (µl) | 940 | 930 | 910 | 850 | 750 | 550 |
| Volume target compound solution at 25 µg/l (µl) | 10 | 20 | 40 | 100 | 200 | 400 |
| Volume internal standard solution at 100 µg/l(µl) | 50 | 50 | 50 | 50 | 50 | 50 |

### 5.8 Eluent for the LC-MS/MS.

10 mM ammonium acetate solution is prepared by dissolving 0,771 g of ammonium acetate (5.3) in 1 000 ml deionized water (5.1).

## 6 Apparatus

### 6.1 General



Equipment or any accessible part of it that may come into contact with the sample or the extract shall be free from interfering compounds, see Annex E.

Use equipment free from all types of fluoropolymer plastics, including polytetrafluoroethene (PTFE) and glassware.



For example, use equipment made of polypropylene (PP) or polyethylene (PE).

Clean all labware and accessible parts of the extraction apparatus by rinsing with methanol (5.2).

Sample containers shall be rinsed thoroughly with water (5.1) and methanol (5.2) and checked for possible background contamination before use.

**6.2** Suitable device with a **sharp blade** to cut leather sample.

**6.3** **Volumetric flasks**, PP or PE, with inert stopper may be used.

**6.4** **Extraction vials**, suitable PP or PE vials, volume at least 20 ml and able to be used in a centrifuge.

**6.5** **Laboratory centrifuge,** suitable for the extraction vials (6.4).

**6.6** **Ultrasonic bath**, equipped with adjustable bath temperature control, up to at least 60 °C.

**6.7** **Analytical balance,** weighing up to 0,001 g.

**6.8** **High-performance liquid chromatograph coupled with a tandem mass spectrometric detector**, (LC-MS/MS), free from all types of fluoropolymer plastics, including polytetrafluoroethene (PTFE).

**6.9** **Membrane filter equipment** and **polyamide or polypropylene membrane filter,** e.g. 0,22 µm pore size.

## 7 Sampling

The chosen leather sample should be representative of the lot it is taken from. Sample in accordance with ISO 2418. If sampling in accordance with ISO 2418 is not possible (e.g. leathers from finished products like shoes or garments), details about sampling shall be given in the report. When sampling leather products that have separate distinct parts, the product shall be taken apart and each part shall be analysed separately.

In the case of coated leather, separate, if possible, the coating from the leather substrate. The leather substrate shall be analysed according to the procedure in this document. If separation of the coating from the leather cannot be carried out, the entire article shall be analysed according to this procedure.

NOTE The coating can be analysed according to CEN/TS 15968:2010[2].

Take a leather sample by mass using ≥ 1 g of leather. The results shall be reported in units of mg/kg.

Cut (6.2) the leather sample into small pieces according to the method specified in ISO 4044.

## 8 Procedure

Accurately weigh 1,0 g ± 0,1 g of the leather pieces with the analytical balance (6.7) into an appropriate extraction vial (6.4). Record the mass of the leather test sample, *m*.

Add 10 ml methanol (5.2) and 50 µl of the internal standard solution (5.6) to the extraction vial containing the leather pieces. Extract the test specimen in an ultrasonic bath (6.6) at a temperature of (60 ± 5) °C for (120 ± 5) min. Let the solution cool down to room temperature and pipette 0,5 ml of the residual extract plus 0,5 ml of water in the HPLC-vial and seal with a cap for LC-MS/MS. If necessary, the extracted solution can be filtrated with a membrane filter (6.9) or centrifuged before taking the 0,5 ml aliquot.



This extract is analysed by LC-MS/MS (6.8). An example of suitable conditions for LC/MS/MS analysis are given in Annex D



As methanol is used for extraction, transesterification is possible and FTOH can be set free from the telomer intermediate/pre-polymer. To avoid it, water should be added (1 to 1 dilution) for LC-MS/MS analysis.

Matrix interferences may be caused by contaminants that are co-extracted from the samples. The extent of matrix interferences varies considerably depending on the nature of the samples, see Annex E.

## 9 Expression of results

### 9.1 Calibration

For each of the target PFAS substances, set up individually the linear regression function, by using the following ratio (Ae/Ais) and (Ce/Cis) with the help of the formula:

$$\frac{A_e}{A_{is}} = a \cdot \left( \frac{C_e}{C_{is}} \right) + b$$

where:

$A_e$ is the peak area for the corresponding target PFAS compound;

$A_{is}$ is the peak area for the internal standard chosen;

$C_e$ is the concentration of the target PFAS in the calibration standard in micrograms per litre;

 