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Second edition
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Leather — Chemical tests — Determination of free formaldehyde in process auxiliaries

Cuir — Essais chimiques — Dosage du formaldéhyde libre dans les auxiliaires de traitement

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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 27587:2009), which has been technically revised. The main changes to the previous edition are as follows:

— the wording in 5.6, 5.7, 5.12, 7.2, 7.3, 7.4 and Clause 8 has been modified;

— a new Figure 1 has been inserted and the previous Figure 1 changed to Figure 2;

— the recommended HPLC conditions previously in Clause 8 are now given in a new Annex B.

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.

Leather — Chemical tests — Determination of free formaldehyde in process auxiliaries

1 Scope

This document specifies a method for the determination of free formaldehyde, which is released under dynamic conditions when the sample is heated in an inert dry atmosphere, in process auxiliaries for leather. The analytical result obtained according to this procedure is expressed in milligrams per kilogram (mg/kg) sample.

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 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 http://www.electropedia.org/

4 Principle

The sample is heated in an inert atmosphere for a defined period of time. The released formaldehyde is captured and derivatized using a dinitrophenylhydrazine (DNPH) cartridge. The analyte is eluted with acetonitrile and analysed by high-performance liquid chromatography (HPLC) using an ultraviolet (UV) or diode array detector (DAD).

5 Reagents

Use only reagents of recognized analytical grade, unless otherwise stated.

5.1 Sulfuric acid, 3 mol/l.

5.2 Sodium hydroxide, 2 mol/l.

5.3 Sodium thiosulfate, 0,1 mol/l.

5.4 Iodine solution, 0,05 mol/l, i.e. 12,68 g iodine per litre of water.

5.5 Starch solution, 1 g/100 ml water.

5.6 Formaldehyde-2,4-DNPH analytical standard.

5.7 Calibration standards. Prepare solutions by adequate dilution of the formaldehyde-2,4-DNPH analytical standard (5.6).

5.8 Formaldehyde solution, a mass fraction of approximately 37 %.

5.9 Distilled water, quality 2 in accordance with ISO 3696.

5.10 Formaldehyde solution S1, prepare by pipetting 5 ml of formaldehyde solution (5.8) in a 1 000 ml volumetric flask and filling to the mark with distilled water.

5.11 Formaldehyde solution S2 in an adequate dilution for procedure control [e.g. 2,5 ml of the formaldehyde solution S1 (5.10) in a 100 ml volumetric flask, fill up with distilled water. The concentration of this solution should be adapted to ensure that the formaldehyde content is in the middle of the calibrated range.]

5.12 2,4-Dinitrophenylhydrazine cartridges (DNPH cartridges), suitable for fixing a total of 6 400 µg of carbonyls per cartridge.

For lower quantities of free formaldehyde, a smaller capacity cartridge can be used.

For higher quantities of free formaldehyde, increase the number of cartridges to be loaded in series.

It is recommended that the cartridge has an excess capacity of at least 20 % more than the predicted formaldehyde amount.

5.13 Acetonitrile, HPLC grade.

5.14 Water, HPLC grade.

6 Apparatus and materials

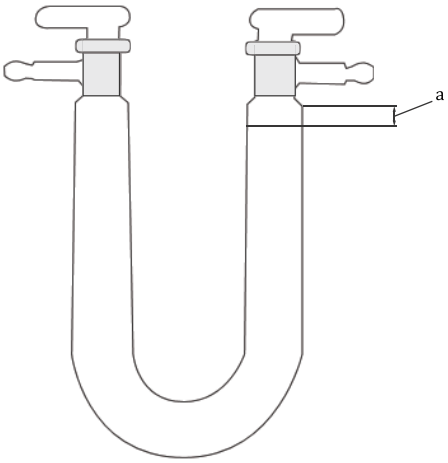
The usual laboratory apparatus is required and, in particular, the following.

6.1 Thermostatic oil bath with stirring facilities, capable of maintaining a constant temperature of (90 ± 3) °C. The oil bath shall be deep enough to allow the U-tube to be dipped in up to the side tubing.

6.2 Silicone oil, suitable for oil bath (6.1).

6.3 Nitrogen, purity 4,6.

6.4 U-tube, calcium chloride tube, U-shaped, with two stopcocks, leg length 150 mm (see Figure 1).



[a] Level A, maximum 1 cm from stopcock.

Figure 1 — U-tube

6.5 Flow meter, suitable to adjust a constant gas flow.

6.6 Silicone tubing.

6.7 Syringe filters, e.g. 0,45 µm, regenerated cellulose.

6.8 Sea sand, purified by acid and calcined; quality grade GR for analysis.

6.9 Polytetrafluoroethylene (PTFE) stopcock grease, free of formaldehyde.

6.10 HPLC equipped with a UV or DAD detector.

6.11 HPLC column, of the RP-C18 type.

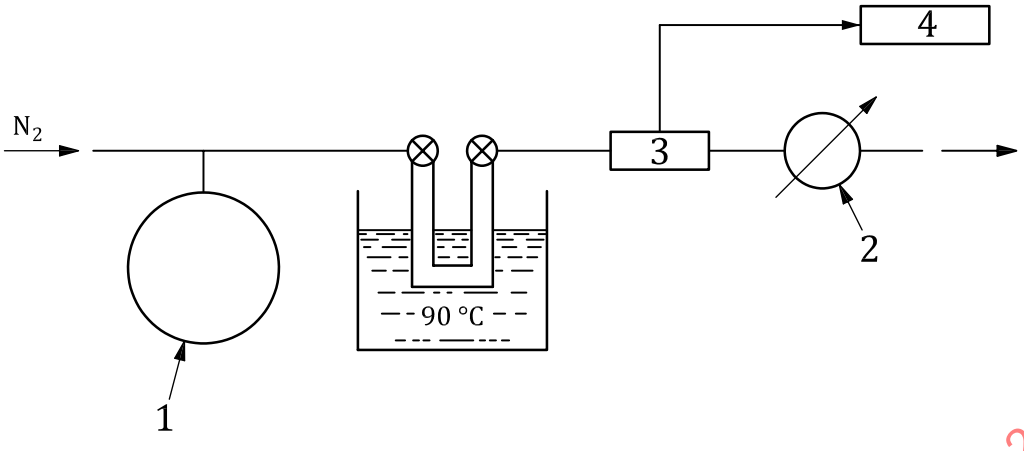
6.12 Hair dryer.

6.13 Volumetric flasks, 10 ml.

7 Methods

7.1 Outline of sample preparation system

See Figure 2.



Key

1 gas tank
2 flow meter
3 DNPH cartridge
4 HPLC

Figure 2 — Schematic outline of sample preparation system

7.2 Setting of initial conditions

Prepare a sample preparation system as described in 7.1. Initially, the U-tube (6.4) and the DNPH cartridge (5.12) are disconnected from the sampling system. All the parts of the sample preparation system shall be dry prior to use. Add 3 g to 4 g of sea sand (6.8) to the U-tube (6.4), ensuring that it is not blocked and that the nitrogen flow can be maintained. Connect the U-tube and purge the system for 15 min with nitrogen (6.3) at a flow rate of 500 ml/min. It is important that the analysis be carried out under an inert atmosphere. The sampling system is slightly pressurized; therefore, all stopcocks should be secured with joint clamps.

7.3 Sample preparation

Accurately weigh 0,1 g to 2 g of sample to the nearest 0,001 g into the U-tube. It may be necessary to reduce the amount of sample if it is in a liquid phase to diminish the likelihood of condensed water giving erroneous results. The sample shall not be diluted. If the sample contains an amount of formaldehyde higher than 80 % of the cartridge capacity, either reduce the sample, increase the number of cartridges to be loaded in series (see 5.12) or do both. Apply a thin layer of stopcock grease (6.9) to the joints of the U-tube.

For each sample, restore the initial conditions (7.2).

In the case of a series of similar samples (different batches from the same production), the procedure of purging with nitrogen may be reduced to 5 min after the first sample.

7.4 Analysis

Introduce the DNPH cartridge (5.12), place the U-tube into the oil bath (6.1) preheated to (90 ± 3) °C and check the flow rate of nitrogen (350 ml/min to 150 ml/min). The U-tube and cartridge shall be covered with aluminium foil to protect them against heat loss.

The U-tube shall be immersed in the oil bath until level A indicated in Figure 1. During sampling, it may be necessary to readjust the flow rate. Check that the temperature is (90 ± 3) °C. After 30 min, remove the U-tube containing the sample from the oil bath. Remove any condensate from the cartridge side of

the tubing and stopcock using a hair dryer (6.12). This step shall be carried out irrespective of whether condensate can be observed.

Remove the DNPH cartridge from the system. Collect the content of all the cartridges in a unique flask and elute it with small portions of acetonitrile (5.13) in a 10-ml volumetric flask or a higher volume, depending on the number of cartridges used. Make up to volume with acetonitrile.

Carefully mix the solution by shaking and filter an aliquot for analysis using a syringe filter (6.7). Analyse the resulting filtrate by HPLC (6.10).

It is recommended that the cartridges be removed from the refrigerator immediately prior to use. Experiments have shown that cartridges should be eluted within 3 days.

8 HPLC conditions

Various types of high-performance liquid chromatographic equipment can be used. Guidelines for suitable HPLC chromatographic conditions for this analysis are given in Annex B.

9 Calibration

Calibration is carried out by means of an external standard in the range of 0,5 µg/10 ml to 100 µg/10 ml.

Prepare adequate dilutions (in acetonitrile) of the formaldehyde-2,4-DNPH analytical standard (5.6). In each of six 10-ml volumetric flasks (6.13), add 2 ml acetonitrile (5.13), then add an adequate quantity of derivatized DNPH-formaldehyde to ensure 0,5 µg; 2,0 µg; 5,0 µg; 20,0 µg; 50,0 µg; and 100,0 µg, respectively, of formaldehyde.

Fill the flasks up to the mark with acetonitrile and mix. After 60 min, analyse the samples using HPLC after filtration through a membrane filter (6.7). Effect the calibration through plotting a graph of the formaldehyde derivative peak area versus the concentration in micrograms per 10 ml.

10 Calculation

Calculate the formaldehyde content (w) expressed in milligrams per kilogram (mg/kg) of sample being tested, as in Formula (1).

$$w = \frac{\rho \cdot F}{m} \tag{1}$$

where

ρ is the concentration of formaldehyde obtained from the calibration graph, expressed in µg/10 ml;

F is the dilution factor;

m is the mass of the sample, expressed in grams (g).

The reliability of the method was determined by an interlaboratory trial, which is reported in Annex A, Table A.1.

11 Checking reagents for absence of formaldehyde

Blank analyses should be carried out on a regular basis and at least for each lot of reagents, mobile phase and cartridges or any other change in the system.

The formaldehyde content detected in the blank solution should be below 75 % of the lowest calibration level (0,5 µg/10 ml).

12 Control of the procedure

Spike the sea sand within the U-tube with 250 µl of formaldehyde solution S2 (5.11). Proceed as described in 7.4. Calculations are carried out as described in Clause 10. A minimum recovery rate of 90 % shall be calculated. In the event of lower levels being detected, possible sources of error shall be detected and eliminated prior to routine analysis of samples.

13 Determination of formaldehyde in solution S1

Pipette 10 ml of formaldehyde solution S1 (5.10) into a 250-ml Erlenmeyer flask and mix with 50 ml of iodine solution (5.4) as well as with sodium hydroxide (5.2) until it turns to yellow. Allow it to settle for 15 min at 18 °C to 30 °C and then add 15 ml sulfuric acid (5.1) while swirling.

After adding 2 ml of starch solution (5.5), titrate the excess iodine with sodium thiosulfate (5.3) until the colour changes. Make three individual determinations. Titrate a blank solution in the same manner, as in Formula (2).

$$\rho_S = \frac{(V_0 - V_1)\cdot c_{Th}\cdot M_{FA}}{2} \quad (2)$$

where

ρ_S is the concentration of the formaldehyde solution S1, in mg/10 ml;

V_0 is the titre volume of the thiosulfate solution for the blank solution, in ml;

V_1 is the titre volume of the thiosulfate solution for the sample solution, in ml;

c_{Th} is the concentration of the thiosulfate solution, in mol/l;

M_{FA} is the relative molecular mass of formaldehyde, 30,02 g/mol.

14 Test report

The test report shall include the following:

a) a reference to this document (ISO 27587:2021);

b) the type, origin and designation of the analysed product and the sampling method used;

c) the analytical result for free formaldehyde content in milligrams per kilogram (mg/kg), rounded to one decimal place;

d) any deviation from the analytical procedure;

e) the date of the test.

Annex A
(informative)

Reliability of the method

The method was tested in an interlaboratory trial in 2007 with two different process auxiliaries (A and B).

Table A.1 — Interlaboratory trial

Values in milligrams per kilogram (mg/kg)

Auxiliary	Free formaldehyde				
	Mean value	s_r	s_R	r	R
A	3,13	0,31	0,87	0,87	2,43
B	8,58	0,62	1,68	1,74	4,69

Key

s_r standard deviation of repeatability

s_R standard deviation of reproducibility

r repeatability

R reproducibility

r, R (probability 95 %; confidence factor 2,8)