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Leather — Chemical tests — Determination of the 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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 27587/IUC 26 was prepared by the European Committee for Standardization (CEN) Technical Committee CEN/TC 289, *Leather*, in collaboration with the Chemical Tests Commission of the International Union of Leather Technologists and Chemists Societies (IUC Commission, IULTCS), 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.

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

1 Scope

This International Standard specifies a method for the determination of free formaldehyde in process auxiliaries for leather. The analytical result obtained according to this procedure is expressed in milligrams per kilogram (mg/kg) sample. The upper limit of quantification of the method is given by the capacity of the cartridge (total carbonyls 6 400 µg/cartridge).

2 Normative references

The following referenced documents are indispensable for the application 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

For the purposes of this document, the following terms and definitions apply.

3.1
free formaldehyde
formaldehyde that is released under dynamic conditions when the sample is heated in an inert dry atmosphere

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 a UV detector.

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 hydrazone solution.

5.7 Calibration standards. Prepare solutions by adequate dilution of the formaldehyde hydrazone solution (5.6).

5.8 Formaldehyde solution, approximately 37 % mass fraction.

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

5.10 Formaldehyde solution S2 in an adequate dilution for procedure control [e.g. 2,5 ml of the formaldehyde stock solution S1 (5.9) 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.]

5.11 Distilled water, quality 2 according to ISO 3696.

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. It is recommended that the cartridge have 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

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.

6.5 Flow meter.

6.6 Silicone tubing.

6.7 Syringe filters, 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 detector.

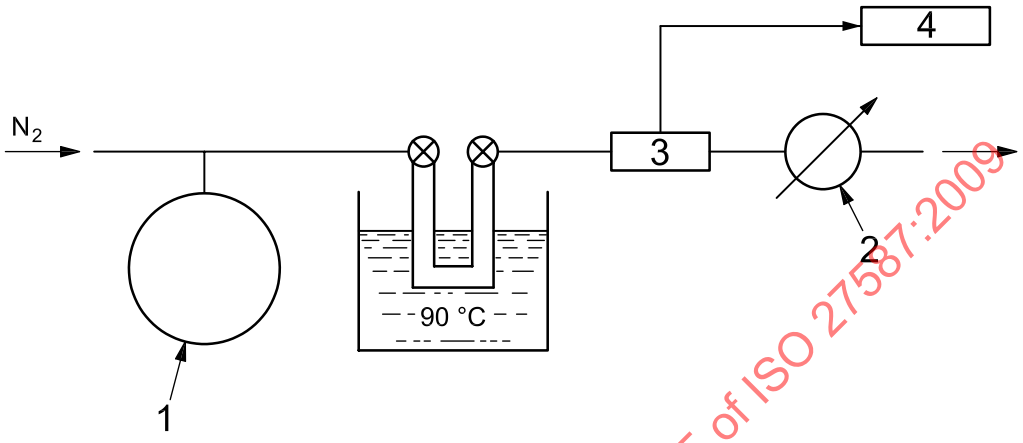
6.11 HPLC column, of the RP-C18 type.

6.12 Hair dryer.

7 Methods

7.1 Outline of sample preparation system

See Figure 1.



Key

1 gas tank
2 flow meter
3 DNPH cartridge
4 HPLC

Figure 1 — Schematic outline of sample preparation system

7.2 Sample preparation

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.

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 purging step may be omitted before further analyses if work is done without interruption. The sampling system is slightly pressurized; therefore, all stopcocks should be secured with joint clamps.

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. If this is not possible, use a larger diameter U-tube. Accurately weigh 0,5 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 in order to diminish the likelihood of condensed water giving erroneous results.

Apply a thin layer of stopcock grease (6.9) to the joints of the U-tube. Introduce the U-tube into the system and purge for 5 min with nitrogen (6.3) at a flow rate of 500 ml/min. Reduce the flow rate to between 150 ml/min to 350 ml/min. Introduce the DNPH cartridge (5.12) into the system and place the U-tube into the oil bath (6.1) preheated to 90 °C. Cover the cartridge and U-tube carefully with aluminum foil. During sampling, it may be necessary to readjust the flow rate.

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 visually.

Remove the DNPH cartridge from the system and elute with small portions of acetonitrile (5.13) in a 10 ml volumetric flask. 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 (recommendations)

Separation column:	CC 250/4 Nucleosil® 100-5 C18 HD[1)] with pre-column
Flow rate:	0,8 ml/min
Mobile phase:	Solvent A, water
	Solvent B, acetonitrile
Gradient:	55 % B linear to 95 % B in 20 min
Column oven:	30 °C
UV detection:	360 nm
Injection volume:	20 µl

9 Calibration

Calibration is carried out by means of an external standard in the range of 0,5 µg/10 ml to 50 µg/10 ml. The working range is limited by the capacity of the cartridge.

Prepare adequate dilutions (in acetonitrile) of the formaldehyde hydrazone solution (5.6). Calibration shall be done using at least six concentration levels. The calibration is effected through plotting a graph of the formaldehyde derivative peak area versus the concentration (µg/10 ml).

10 Calculation

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

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

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).

1) Nucleosil® 100-5 C18 HD is the trade name of a product supplied by Sorbent Technologies. 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.

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 (5.10). Proceed as described in 7.2. 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 stock solutions

Pipette 10 ml of formaldehyde stock solution S1 (5.9) 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.

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

where

ρ_S is the concentration of the formaldehyde stock 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 International Standard (ISO 27587);

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.