



Leather — Chemical determination of formaldehyde content —

Part 3: Determination of formaldehyde emissions from leather

Cuir — Dosage chimique du formaldéhyde —

Partie 3: Dosage des émissions de formaldéhyde du cuir

ICS 59.140.30

ISO/CEN PARALLEL PROCESSING

This draft has been developed within the European Committee for Standardization (CEN), and processed under the **CEN-lead** mode of collaboration as defined in the Vienna Agreement.

This draft is hereby submitted to the ISO member bodies and to the CEN member bodies for a parallel five-month enquiry.

Should this draft be accepted, a final draft, established on the basis of comments received, will be submitted to a parallel two-month approval vote in ISO and formal vote in CEN.

This draft International Standard is submitted to all ISO member bodies for voting, as a standard prepared by an international standardizing body in accordance with Council Resolution 42/1999. The proposer, *Chemical Test Commission of the International Union of Leather Technologists and Chemists Societies (Commission IUC, IULTCS)*, has been recognized by the ISO Council as an international standardizing body for the purpose of Council Resolution 42/1999.

To expedite distribution, this document is circulated as received from the committee secretariat. ISO Central Secretariat work of editing and text composition will be undertaken at publication stage.

Pour accélérer la distribution, le présent document est distribué tel qu'il est parvenu du secrétariat du comité. Le travail de rédaction et de composition de texte sera effectué au Secrétariat central de l'ISO au stade de publication.

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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 17226-3 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).

ISO 17226 consists of the following parts, under the general title *Leather — Chemical determination of formaldehyde content*:

- *Part 2: Method using colorimetric analysis*
- *Part 1: Method using high performance liquid chromatography*
- *Part 3: Determination of formaldehyde emissions from leather*

Leather — Chemical determination of formaldehyde content — Part 3: Determination of formaldehyde emissions from leather

1 Scope

This International Standard specifies a method to determine the emission of formaldehyde from leathers. This method is based on high performance liquid chromatography (HPLC). It is selective and allows also observing the emission of other low molecular aldehydes and ketones.

ISO 17226-3 refers to the release of formaldehyde to the gas phase. Therefore they are not comparable with the results of methods describe in part 1 and 2 which are based on an extraction with liquid water.

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

ISO 2419, *Leather - Physical and mechanical tests - Sample preparation and conditioning*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 4684, *Leather — Chemical tests — Determination of volatile matter*

3 Principle

A specimen with defined dimensions is held above demineralised water in a sealed bottle and is heated at constant temperature for a specific period. Afterwards the bottle is cooled and the formaldehyde absorbed into the water is analysed. The water is mixed with 2,4-dinitrophenylhydrazine, whereby aldehydes and ketones react to give the respective hydrazones. These are separated by means of a reversed-phase HPLC method, detected at 360 nm and quantified.

4 Reagents

Use only reagents of recognized analytical grade, unless otherwise stated. The water shall be grade 3 in accordance with ISO 3696:1987. All solutions are aqueous solutions.

4.1 Reagents for the formaldehyde stock solution

4.1.1 **Formaldehyde solution**, approximately 37 % (mass fraction).

4.1.2 **Iodine solution**, 0,05 mol/l, i.e. 12,68 g iodine per litre.

4.1.3 **Sodium hydroxide solution**, 2,0 mol/l.

4.1.4 Sulfuric acid solution, 2,0 mol/l.

4.1.5 Sodium thiosulfate solution, 0,1 mol/l.

4.1.6 Starch solution, 1 %, i.e. 1 g in 100 ml water.

4.2 Reagents for the HPLC method

4.2.1 Dinitrophenylhydrazine (DNPH) solution, consisting of 0,3 g DNPH (2,4-dinitrophenylhydrazine) dissolved in 100 ml concentrated *o*-phosphoric acid (85 % mass fraction). (DNPH recrystallized from 25 % mass fraction, acetonitrile in water)

4.2.2 Acetonitrile.

5 Apparatus

Use usual laboratory equipment and, in particular, the following.

5.1 One (1)L polyethylene bottle with hook implement integrated in the lid (see Figure 1). Hook made of stainless steel with seals, positioned inside the lid of the test bottle.

5.2 Volumetric flasks, of capacities 10 ml, 500 ml and 1 000 ml.

5.3 Erlenmeyer flasks, of capacities 100 ml and 250 ml.

5.4 Pipettes, of capacities 5 ml and 50 ml

5.5 Oven, capable of being maintained at $60 \pm 2^\circ\text{C}$

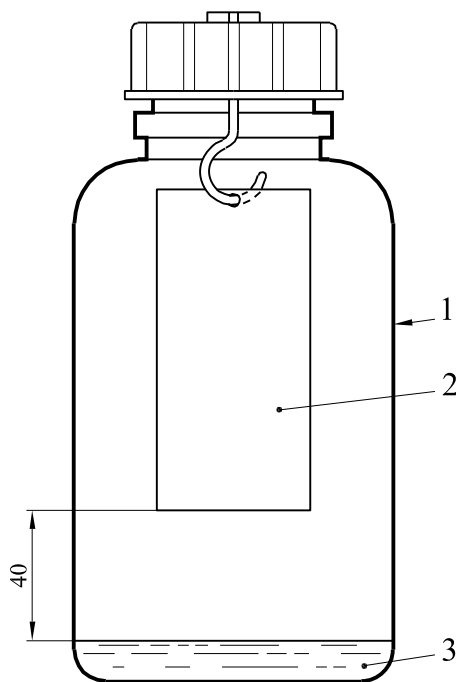
5.6 Analytical balance, , weighing to an accuracy of 1 mg.

5.7 HPLC system with UV detection, (e. g. 360 nm).

5.8 Press knife in accordance to ISO 2419 suitable to cut specimens of 100 x 40 mm.

5.9 Hole punch for holes with 3 - 4 mm diameter.

5.10 Membrane filter, polyamide, 0,45 μm .



Key

1 Polyethylene bottle

2 Sample

3 Water

Figure 1 — Polyethylene bottle with specimen and water

6 Methods

6.1 Procedure for the determination of formaldehyde in the stock solution

6.1.1 Preparation of the formaldehyde stock solution

Pipette 5 ml of the formaldehyde solution (4.1.1) into a 1 000 ml volumetric flask (5.2) which contains approximately 100 ml water and then fill the flask with demineralized water up to the mark. This solution is the formaldehyde stock solution.

6.1.2 Determination

Pipette 10 ml from this solution into a 250 ml Erlenmeyer flask (5.3) and mix with the 50 ml iodine solution (4.1.2). Add sodium hydroxide (4.1.3) until it turns yellow. Allow it to react for 15 min ± 1 min at 18 °C to 26 °C and then add 15 ml of sulfuric acid (4.1.4) while swirling.

After adding 2 ml of starch solution (4.1.6), titrate the excess iodine with sodium thiosulfate (4.1.5) until the colour changes. Make three individual determinations. Titrate at least two blank solutions in the same manner.

$$C_{FA} = \frac{(V_0 - V_1) \times c_1 \times M_{FA}}{2}$$

where

C_{FA} is the concentration of the formaldehyde stock solution, in milligrams per 10 ml (mg/10 ml);

V_0 is the titre of the thiosulfate solution for the blank solution, in millilitres (ml);

V_1 is the titre of the thiosulfate solution for the sample solution, in millilitres (ml);

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

c_1 is the concentration of the thiosulfate solution, in moles per litre (mol/l).

6.2 Procedure for the determination of formaldehyde emission by the HPLC method

6.2.1 Shipment and storage leather for this method

To avoid cross contamination and loss of formaldehyde during shipment and storage the leather samples should be sealed in an inert gastight plastic bag.

NOTE Multiple layer polyethylene bags with a metal layer inside are appropriate.

6.2.2 Sampling

Sample 6 specimens with (100 x 40) mm in accordance with ISO 2418 using a press knife (7.8) in accordance with ISO 2419. 5 specimens are used for the determination of formaldehyde emission. The 6th specimen is used for the determination of volatile matter.

To fasten the specimens 1 to 5, punch a hole of 3 – 4 mm near its centre and 10 mm from the upper edge.

6.2.3 Determination of volatile matter

If requested to calculate the result on the basis on dry substance use the 6th specimen to determine the volatile matter in accordance with ISO 4684. Do not grind or cut the specimen.

6.2.4 Determination of formaldehyde emission

Weight 3 of the specimens to 0.01 g.

Pipette 50 mL aliquots of demineralized water into each of a clean 1 L polyethylene bottle. Attach a specimen to each hook and seal the 5 bottles.

Pipette 50 mL aliquots of demineralized water into an additional clean 1 L polyethylene bottle. Seal the bottle without a specimen. Use this bottle for a blank test.

As soon as the bottles have been sealed store the bottles for 180 ± 15 minutes in a heated oven at $60 \pm 2^\circ\text{C}$.

Remove the bottles from the oven and allow it to cool at room temperature (1 h). Then remove the leather specimens from the bottles and continue immediately with analysing the formaldehyde absorbed in the water as described in 6.2.5.

6.2.5 Reaction with DNPH

Pipette 4,0 ml of acetonitrile (6.2.2), a 5,0 ml aliquot of water from the polyethylene bottle (6.2.4) and 0,5 ml of DNPH solution (4.2.1) into a 10 ml volumetric flask (5.2). Fill the volumetric flask with demineralized water up to the mark and shake it briefly by hand to mix the components. Allow it to stand at least 60 min, but not more than a maximum of 180 min. After filtering through a membrane filter (5.10), analyse the sample using HPLC. If the concentration is out of the calibration range, take smaller aliquots.

6.2.6 HPLC conditions (recommendations)

These conditions are only recommendations. The method used should be verified using the recovery rate determination (6.3).

Flow rate: 1,0 ml/min Mobile phase: acetonitrile/water, 60:40

Separation column: C18 reversed phase column with precolumn (1 cm, RP18)

UV detection wavelength: 360 nm

Injection volume: 20 µl

NOTE A Merck 100, CH 18,2 (highly coated, 12 % C) column is an example of a suitable separation column which is commercially available

6.2.7 Calibration of HPLC

Pipette 0,5 ml of the formaldehyde stock solution obtained in 6.1.1, with an exactly known formaldehyde content, into a 500 ml volumetric flask (5.2), pre-filled with approximately 100 ml water. Mix together and fill to the mark with water, and mix again. This solution is the standard solution for calibration purposes, i.e. the standard solution is approximately 2 µg formaldehyde/ml.

In each of six 10 ml volumetric flasks (5.2), add 4 ml acetonitrile (4.2.2), then add a concentration series of 0,5 ml; 1,0 ml; 2,0 ml; 3,0 ml; 4,0 ml; 5,0 ml, respectively, of the standard solution. Immediately upon addition of the formaldehyde solution, mix each flask and add 0,5 ml DNPH solution (4.2.1). Fill the flasks up to the mark with demineralized water and mix. After at least 60 min and not more than 180 min, analyse the samples using HPLC after filtration through a membrane filter (5.10). Effect the calibration through plotting a graph of the formaldehyde derivative peak area versus the concentration in micrograms per 10 ml.

6.2.8 Calculation of the formaldehyde content in leather samples

$$E_F = \frac{(A_{Sample} - A_{Blank}) \times 10}{m \times b} \times D$$

where

E_F is the amount of emitted formaldehyde in milligrams per kilogram (mg/kg) rounded to 0,1 mg/kg;

A_{sample} is the area of the leather sample determined by HPLC with UV-detection

A_{blank} is the area of the blank determined by HPLC with UV-detection

b is the slope of the calibration curve (10ml/µg)

D is the dilution factor (ml), usually 1, dilution is necessary if the determined area of the sample is out of the range of the calibration curve

m is the mass of leather weighed in grams (g).

6.3 Quality control

The chromatographic system has to be checked every day by definition of the recovery rate of a sample containing preferred 2 mg /l formaldehyde. The content of the sample has to be determined according the procedure described for the calibration.

7 Expression of results

Express the formaldehyde concentration to the nearest 0,1 mg/kg based on the mass of the leather sample tested.

If the results are to be reported on the basis of dry substance, multiply the results above by the factor $100/(100 - w)$, where w is the moisture content in percent (%) according to ISO 4684. If the results are presented on the basis of dry substance, clearly mention this in the test report.

If a single value differs more than 20% from the mean value test additional two specimens.

8 Test report

The test report shall include the following:

- a) reference to this document (i.e. ISO 17226-3);
- b) type, origin and designation of the analysed leather sample;
- c) mean value for the formaldehyde emission in mg/kg to nearest 0,1 mg/kg;
- d) if requested, mean value for the formaldehyde emission in mg/kg to nearest 0,1 mg/kg calculated on dry substance and volatile matter in %;
- e) number of tested specimens;
- f) any deviations from the analytical procedure, particularly any additional steps performed;
- g) the date of the test;
- h) if the results are determined on the basis of the dry substance this and the dry substance shall be reported.