Leather — Chemical determination of formaldehyde content

Part 2: Method using colorimetric analysis (ISO 17226-2:2008)

ICS 59.140.30

British Standards

National foreword

This British Standard is the UK implementation of EN ISO 17226-2:2008. It partially supersedes DD CEN ISO/TS 17226:2003.

The UK participation in its preparation was entrusted to Technical Committee TCI/69, Footwear, leather and coated fabrics.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Foreword

This document (EN ISO 17226-2:2008) has been prepared by Technical Committee CEN/TC 289 "Leather", the secretariat of which is held by UNI in collaboration with Technical Committee ISO/TC IULTCS "International Union of Leather Technologists and Chemists Societies".

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by November 2008, and conflicting national standards shall be withdrawn at the latest by November 2008.

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Foreword

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ISO 17226-2 was prepared by the European Committee for Standardization (CEN) Technical Committee CEN/TC 289, *Leather*, in collaboration with the Chemical Test 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). This method is technically similar to the Colorimetric Section of the method IUC 19 which was declared an official method at the IULTCS Delegates meeting on 31st May 2003 in Cancún, Mexico.

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 sampling and the testing of leather. ISO recognizes IULTCS as an international standardizing body for the preparation of test methods for leather.

This first edition of ISO 17226-2, together with ISO 17226-1, cancels and replaces ISO/TS 17226:2003, which has been technically revised.

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

- *Part 1: Method using high performance liquid chromatography*
- *Part 2: Method using colorimetric analysis*

INTERNATIONAL STANDARD

ISO 17226-2:2008(E)
IULTCS/IUC 19-2:2008(E)

Leather — Chemical determination of formaldehyde content —

Part 2:
Method using colorimetric analysis

1 Scope

This part of ISO 17226 specifies a method for the determination of free and released formaldehyde in leathers. This method is based on colorimetric analysis.

The formaldehyde content is taken to be the quantity of free-formaldehyde and formaldehyde extracted through hydrolysis contained in a water extract from the leather under standard conditions.

This process is not absolutely selective for formaldehyde. Other compounds such as extracted dyes could interfere at 412 nm.

2 Conformance

When compared with ISO 17226-1, the two analytical methods should give similar trends but not necessarily the same absolute result. Therefore, in the case of dispute, ISO 17226-1 shall be used in preference.

3 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 3696:1987, *Water for analytical laboratory use — Specification and test methods*

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

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

ISO 17226-1, *Leather — Chemical determination of formaldehyde content — Part 1: Method using high performance liquid chromatography*

4 Principle

The leather sample is eluted with detergent solution at 40 °C. The eluate is treated with acetylacetone, whereby formaldehyde reacts to give a yellow compound (3,5-diacetyl-1,4-dihydrolutidine). The absorbance of this compound is measured at 412 nm. The amount of formaldehyde corresponding to the absorbance value for the test specimen is obtained from a calibration curve prepared under identical conditions.

5 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.

5.1 Reagents for the formaldehyde stock solution

5.1.1 Formaldehyde solution, approximately 37 % mass fraction.

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

5.1.3 Sodium hydroxide solution, 2,0 mol/l.

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

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

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

5.2 Reagents for the colorimetric method

5.2.1 Sodium dodecylsulfonate (detergent) solution, 0,1 %, 1 g in 1 000 ml water.

5.2.2 Solution 1, 150 g ammonium acetate + 3 ml glacial acetic acid + 2 ml acetylacetone (pentane-2,4-dione, CAS 123-54-6) in 1 000 ml water.

Prepare fresh daily and keep in a dark place. (It is sensitive to light.)

5.2.3 Solution 2, 150 g ammonium acetate + 3 ml glacial acetic acid in 1 000 ml water.

5.2.4 Dimedone solution, 5 g dimedone[1] in 1 000 ml water.

It is reported that dimedone cannot be readily dissolved in pure water. In such cases, dimedone can be dissolved in a small amount of ethanol and then made up to volume with water.

6 Apparatus

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

6.1 Volumetric flasks, of capacities 10 ml, 50 ml and 1 000 ml.

6.2 Erlenmeyer flasks, of capacities 25 ml, 100 ml and 250 ml.

6.3 Strainer with glass fibre filter, GF8 (or **glass filter strainer** G 3, diameter 70 mm to 100 mm).

6.4 Water bath, thermostatically controlled to 40 °C ± 0,5 °C, fitted with a flask shaker or stirrer.

6.5 Thermometer, with 0,1 °C graduations over the range 20 °C to 50 °C.

6.6 Analytical balance, weighing to an accuracy of 0,1 mg.

6.7 Spectrophotometer, with suitable cells capable of measuring absorbance at 412 nm.

The recommended cell path length is 20 mm.

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[1] Dimedone (CAS 126-81-8) or methone is 5,5'-dimethyl-1,3-cyclohexanedione.

7 Procedures

7.1 Procedure for the determination of formaldehyde in the stock solution

7.1.1 Preparation of the formaldehyde stock solution

Pipette 5 ml of the formaldehyde solution (5.1.1) into a 1 000 ml volumetric flask (6.1) which contains approximately 100 ml water. Then fill the flask with demineralized water up to the mark. This solution is the formaldehyde stock solution.

7.1.2 Determination

Pipette 10 ml from this solution into a 250 ml Erlenmeyer flask (6.2) and mix with 50 ml iodine solution (5.1.2). Add sodium hydroxide (5.1.3) 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 (5.1.4) while swirling.

After adding 2 ml of starch solution (5.1.6), titrate the excess iodine with sodium thiosulfate (5.1.5) until the colour changes. Make three individual determinations. Titrate at least two blank solutions in the same manner.

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

where

ρ_{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).

7.2 Procedure for the determination of formaldehyde in leather by the colorimetric method

7.2.1 Sampling and preparation of samples

If possible, sample in accordance with ISO 2418. If sampling in accordance with ISO 2418 is not possible (e.g. leathers from finished products like shoes, garments), provide details about sampling together with the test report. Grind leather in accordance with ISO 4044.

If the result is to be presented on the basis of dry substance, then test an additional sample of the same leather in accordance with ISO 4684 so that the moisture content can be calculated.

7.2.2 Extraction

Weigh 2 g ± 0,1 g leather into a suitable vessel. Pipette 50 ml of the detergent solution (5.2.1) into a 100 ml Erlenmeyer flask (6.2) and warm it to 40 °C. Transfer the pre-weighed leather quantitatively to the flask, then close it with a glass stopper (see next paragraph). Stir the content of the flask or shake smoothly at 40 °C ± 0,5 °C in a water bath (6.4) for 60 min ± 2 min. Immediately filter the warm extract solution by vacuum through a glass fibre filter (6.3) into a flask. Cool the filtrate, in a closed flask, down to room temperature (18 °C to 26 °C).

Do not modify the leather/solution ratio. Extraction and analysis should be performed within the same working day.

7.2.3 Reaction with acetylacetone

7.2.3.1 Pipette 5 ml of the filtrate obtained in 7.2.2 into a 25 ml Erlenmeyer flask (6.2) and add 5 ml of the Solution 1 (5.2.2). Fit the Erlenmeyer flask with a glass stopper. Stir the solution for 30 min ± 1 min at a temperature of 40 °C ± 1 °C. After cooling (in the dark), measure the absorbance spectrophotometrically at 412 nm against a blank solution made from a mixture from 5 ml detergent solution (5.2.1) + 5 ml Solution 1 (5.2.2). Register the absorbance obtained as E_{p}.

For the purpose of determining the absorbance resulting from the initial colour of the filtrate obtained in 7.2.2, pipette 5 ml of the filtrate (7.2.2) into a 25 ml Erlenmeyer flask (6.2) and add 5 ml of Solution 2 (5.2.3). Thereafter, the same method is applied as with the sample. Register the absorbance obtained as E_{e}.

7.2.3.2 Take a smaller aliquot for leathers with a high content of formaldehyde (> 75 mg/kg).

Make aliquots smaller than 5 ml up to 5 ml with water.

EXAMPLE Formaldehyde content is approximately 500 mg/kg.

Procedure: pipette 0,5 ml of the filtrate (7.2.2) into a 25 ml Erlenmeyer flask (6.2), add 4,5 ml water. Then follow the procedure as described in 7.2.3.1.

7.2.4 Checking reagents for absence of formaldehyde

Measure 5 ml detergent solution (5.2.1) + 5 ml Solution 1 (5.2.2) in relation to 5 ml of detergent solution (5.2.1) + 5 ml of water. The measured absorbance shall not be larger than 0,025 (measured in a 20 mm cell at 412 nm).

7.2.5 Testing other compounds which cause a colouring with acetylacetone

Mix 5 ml of the filtrate obtained in 7.2.2 with 1 ml dimedone solution (5.2.4) and warm it up to 40 °C ± 1 °C for 10 min ± 1 min. Add 5 ml of the Solution 1 (5.2.2) and keep the mixture at 40 °C ± 1 °C for 30 min ± 1 min. Upon cooling down to room temperature, take a spectrophotometer absorbance measurement at 412 nm against a similar solution, which instead of the Solution 1 (5.2.2) contains 5 ml of Solution 2 (5.2.3). This absorbance shall be less than 0,05 (measured in a 20 mm cell) when formaldehyde was found in the leather sample measurement.

In the case that the absorbance is greater than 0,05, carry out the procedure according to ISO 17226-1. If this is not possible, a note shall be made in the test report to the effect that other compounds were detected within the analysis that could cause a positive response for formaldehyde.

7.2.6 Calibration

Pipette 3 ml of the formaldehyde stock solution obtained in 7.1.1 with an exactly known amount of formaldehyde into a 1 000 ml volumetric flask (6.1), which has been pre-filled with 100 ml water. Mix together and fill the flask up to the mark with water and mix again thoroughly. This solution is the standard solution for calibration purposes, i.e. the standard solution is approximately 6 µg/ml.

From this solution, pipette 3 ml, 5 ml, 10 ml, 15 ml, 20 ml and 25 ml each into separate 50 ml volumetric flasks (6.1) and fill with water. These solutions cover the formaldehyde concentration range of 0,4 µg/ml to 3,0 µg/ml. (This corresponds to a formaldehyde in leather concentration range of 9 mg/kg to 75 mg/kg leather under the given conditions. For higher concentrations, use a smaller aliquot of filtrate.)

From these six solutions, pipette 5 ml of each and mix in a 25 ml Erlenmeyer (6.2) with 5 ml Solution 1 (5.2.2). Warm this mixture up to 40 °C ± 1 °C and shake at this temperature for 30 min ± 1 min.

Upon cooling down to room temperature (protect against light), take a spectrophotometer measurement at 412 nm against a blank solution consisting of 5 ml Solution 1 (5.2.2) and 5 ml water.

Prior to measuring, set the zero point of the spectrophotometer (6.7) with the blank sample [5 ml Solution 1 (5.2.2) and 5 ml water], which was treated under the same conditions as the calibration solutions.

Plot the concentrations in micrograms per millilitre (µg/ml) in a calibration graph against the measured absorbance, x-axis: concentration in micrograms per millilitre (µg/ml), y-axis: absorbance.

7.2.7 Calculation of the content of formaldehyde of the leather sample

$$w_{\mathrm{p}} = \frac{(E_{\mathrm{p}} + E_{\mathrm{e}}) \times V_{\mathrm{o}} \times V_{\mathrm{f}}}{F \times m \times V_{\mathrm{a}}}$$

where

w_{p}	is the concentration of formaldehyde in the sample in milligrams per kilogram (mg/kg), rounded off to 0,1 mg/kg;
E_{p}	is the absorbance of the filtrate after reaction with acetylacetone;
E_{e}	is the absorbance of the filtrate (initial colour);
V_{o}	is the volume of elution in millilitres (ml) (*standard conditions: 50 ml*);
V_{a}	is the aliquot taken from the filtrate in millilitres (ml) (*standard conditions: 5 ml*);
V_{f}	is the volume of solution obtained in 7.2.3 after reaction, in millilitres (ml) (*standard conditions: 10 ml*);
F	is the gradient of calibration curve (y/x), in millilitres per microgram (ml/µg);
m	is the mass of leather, in grams (g).

7.2.8 Spiking and recovery rate

Pipette 2,5 ml of the filtrate obtained in 7.2.2 into each of two 10 ml volumetric flasks (6.1). Add to one volumetric flask an exactly determined volume of the formaldehyde standard solution for calibration (7.2.6), to give approximately the same concentration as was found in the sample (see example below). Fill both volumetric flasks with water to the mark.

If the amount of formaldehyde in the leather is below 20 mg/kg, take a 5 ml aliquot instead of 2,5 ml.

EXAMPLE If in the leather sample the amount of formaldehyde is 30 mg/kg, then spike it with 0,5 ml of the formaldehyde standard solution (7.2.6).

Transfer the contents of the volumetric flasks to separate 25 ml Erlenmeyer flasks (6.2). Add 5 ml of Solution 1 (5.2.2) and stir for 30 min ± 1 min at 40 °C ± 1 °C.

After having cooled down (protect from light), take a measurement of the absorbance at 412 nm against a blank made of 5 ml detergent solution (5.2.1) + 5 ml Solution 2 (5.2.3). Register the absorbance of the spiked sample registered as E_{A}. The absorbance of the unspiked sample is recorded as E_{p}.

$$R_{\mathrm{R}} = \frac{\left(E_{\mathrm{A}} - E_{\mathrm{p}}\right) \times 100}{E_{\mathrm{zu}}}$$

where

E_{A}	is the absorbance of the spiked sample;
E_{p}	is the absorbance of the non-spiked sample;

E_{zu} is the expected absorbance for the quantity of formaldehyde that was added (from the calibration graph);

R_R is the recovery rate in per cent, rounded off to 0,1 %.

If the recovery rate (R_R) is not between 80 % and 120 %, the analysis should be repeated.

8 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.

9 Test report

The test report shall include the following:

a) reference to this document (i.e. ISO 17226-2);

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

c) the analytical procedure used;

d) the analytical results for the formaldehyde content;

e) any deviations from the analytical procedure, particularly any additional steps performed;

f) the date of the test;

g) if the results are determined on the basis of the dry substance this shall be reported.

Annex A
(informative)

Precision: reliability of the colorimetric method

The data in Table A.1 have been obtained in a collaborative trial with 15 laboratories on leather samples with unknown levels of formaldehyde.

Table A.1 — Reliability data of the colorimetric method

Leather sample	**Mean formaldehyde content** mg/kg	**Repeatability** r mg/kg	**Reproducibility** R mg/kg	**Recovery rate** %
A	9,49	1,74	3,86	96
B	19,14	2,23	7,10	94
C	30,41	2,94	8,52	98

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