INTERNATIONAL STANDARD

Leather — Chemical determination of formaldehyde content —

Part 2:
Method using colorimetric analysis

Cuir — Dosage chimique du formaldéhyde —

Partie 2: Méthode par analyse colorimétrique

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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 17226-2 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*

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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 $\pm$ 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.

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

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

$$w_p = \frac{(E_p + E_e) \times V_o \times V_f}{F \times m \times V_a}$$

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.

$$R_R = \frac{\left(E_A - E_p\right) \times 100}{E_{zu}}$$

where

E_A is the absorbance of the spiked sample;

E_p is the absorbance of the non-spiked sample;