



Leather — Chemical tests — Determination of the preservative (TCMTB, CMK, OPP, OIT) content in leather

Cuir — Essais chimiques — Dosage des agents de conservation (TCMTB, CMK, OPP, OIT) dans le 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, *International Union of Leather Technologists and Chemists (Commission IUC, IULTCS)*, has been recognized by the ISO Council as an international standardizing body for the purpose of Council Resolution 42/1999.

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Contents

Page

Foreword	iv
1 Scope	1
2 Normative references	1
3 Principle	1
4 Reagents	1
5 Apparatus and materials.....	2
6 Procedure.....	2
6.1 Sampling and sample preparation.....	2
6.2 Preparation of analytical solution.....	2
6.3 Chromatographic conditions	2
6.4 Calibration	3
7 Calculation	3
8 Test report.....	4
Bibliography.....	5

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 13365 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).

Leather — Chemical tests — Determination of the preservative (TCMTB, CMK, OPP, OIT) content in leather

1 Scope

This International Standard specifies a test method for the determination of the amount of

2-(thiocyanomethylthio)-benzothiazole (TCMTB),

4-chloro-3-methylphenol (CMK),

2-phenylphenol (OPP) and

2-octylisothiazol-3(2H)-one (OIT)

in leather.

The determined preservative content shall be expressed in mg/kg leather.

NOTE 4-chloro-3-methylphenol (CMK) and 2-phenylphenol (OPP) may be determined also according to ISO 17070 and quantified by means of GC-MSD.

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, mechanical and fastness tests – Sampling location*

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

ISO 4684, *Leather - Chemical tests – Determination of volatile matter*

3 Principle

The leather sample is extracted with a suitable solvent with aid of ultrasonic waves. The filtered extract is analysed by HPLC with UV detection

4 Reagents

4.1 TCMTB, min 99,7 %

4.2 TCMTB stock solution, 500 mg/l in acetonitrile

- 4.3 CMK, min 99,5 %
- 4.4 CMK stock solution, 500 mg/l in acetonitrile
- 4.5 OPP, min 99,5 %
- 4.6 OPP stock solution, 500 mg/l in acetonitrile
- 4.7 OIT, min 97,0 %
- 4.8 OIT stock solution, 500 mg/l in acetonitrile
- 4.9 Acetonitrile, HPLC grade
- 4.10 Water, HPLC grade

5 Apparatus and materials

Usual laboratory apparatus is required and, in particular, the following.

- 5.1 Analytical balance, weighing to 0,1 mg
- 5.2 HPLC system with UV detection
- 5.3 Separation column: reversed phase C8 or C18 with corresponding pre-column
- 5.4 Ultrasonic bath, e.g. 40 kHz
- 5.5 Membrane filter 0,45 µm

6 Procedure

6.1 Sampling and sample preparation

If possible, sample in accordance with ISO 2418 and grind in accordance with ISO 4044. If sampling in accordance with ISO 2418 is not possible (e.g. leathers from finished products like shoes, garments) details about sampling shall be given together with the test report.

Wet intermediates like wet blue and wet white shall be dried as described in ISO 4044 prior to grinding.

6.2 Preparation of analytical solution

Weigh ($1 \pm 0,01$) g of ground leather to the nearest 0,001 g in a 100 ml conical flask. Pipette 20 ml acetonitrile (4.9) and add it to the leather. The leather sample is extracted in an ultrasonic bath (5.4) $1 \text{ h} \pm 5 \text{ min}$ (80 % ultrasound power) at room temperature. During extraction the temperature in the mixture increases to about 35 °C.

Subsequently, a part of the extract is filtered through a membrane filter (5.5) into a suitable vial.

The filtrate is analysed by HPLC (5.2) and detected preservatives are quantified.

6.3 Chromatographic conditions

Proposal:

Separation column:	CC 250/4 Nucleosil 100-5 C18 HD with pre-column
Flow rate:	0,8 ml/min
Mobile phase:	A: water, B: acetonitrile
Gradient:	60 % B 6 min isocratic, then linear to 95 % B in 9 min
Column oven:	30 °C
UV-detection:	275 nm
Injektion volume:	20 µl

6.4 Calibration

Calibration is carried out by means of an external standard. Prepare adequate dilutions (in acetonitrile) of preservative stock solutions (4.2, 4.4, 4.6, and 4.8). Calibration shall be done using at least 6 concentration levels. The calibration is effected through plotting a graph of the preservative peak area versus its concentration (µg/ml).

As very different preservative concentrations can be expected, it is not possible to cover the whole range with a single calibration curve.

7 Calculation

Calculate the content w_i of every preservative detected in mg/kg leather using the formula:

$$w_i = \frac{\beta \cdot V \cdot F \cdot 1000}{m \cdot 1000}$$

Where

- w_i is the mass fraction expressed in mg/kg of a certain preservative in leather
- β is the mass concentration of preservative obtained from the calibration in µg/ml
- V is the extract volume in ml
- F is the dilution factor
- m is the quantity of sample weighed in g.

The content of each preservative is given in mg/kg rounded to the nearest 0,1 mg.

The preservative content referred to dry matter, according to ISO 4684, can be calculated using the following equation:

$$w_{dm} = w \cdot D$$

Where

- w_{dm} is preservative content in mg/kg of sample referred to dry matter
- w_i is preservative content (w) expressed in mg/kg of sample being tested

D is recalculation factor to dry matter

$$D = \frac{100}{100 - w_w}$$

w_w is volatile matter content, based on ISO 4684, in percent by mass

8 Test report

The test report shall include the following:

- a) reference to this International Standard (ISO 13365);
- b) the type, origin and designation of the analysed product and the sampling method used;
- c) the analytical result for each preservative 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.

Bibliography

- [1] ISO 17070, *Leather – Chemical tests – Determination of pentachlorophenol content*