BS EN ISO 17072-1:2011

BSI Standards Publication

Leather — Chemical determination of metal content
Part 1: Extractable metals
(ISO 17072-1:2011)

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National foreword

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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 17072-1:2011) has been prepared by Technical Committee CEN/TC 289 “Leather”, the secretariat of which is held by UNI, in collaboration with the 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of an identical text or by endorsement, at the latest by August 2011, and conflicting national standards shall be withdrawn at the latest by August 2011.

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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.

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ISO 17072-1 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 method in IUC 27-1.

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.

ISO 17072 consists of the following parts, under the general title *Leather — Chemical determination of metal content*:

- *Part 1: Extractable metals*
- *Part 2: Total metal content*

INTERNATIONAL STANDARD

ISO 17072-1:2011(E)
IULTCS/IUC 27-1:2011(E)

Leather — Chemical determination of metal content —

Part 1:
Extractable metals

1 Scope

This part of ISO 17072 specifies a method for the determination of extractable metals in leather using extraction with an acid artificial-perspiration solution and subsequent determination with inductively coupled plasma/optical emission spectrometry (ICP-OES), or inductively coupled plasma/atomic emission spectrometry (ICP/AES), or inductively coupled plasma/mass spectrometry (ICP/MS), or atomic absorption spectrometry (AAS) or spectrometry of atomic fluorescence (SFA).

This method is especially suitable for determining the extractable chromium in chromium-tanned leathers.

This method determines extractable metals in leather; it is not compound-specific or specific to the oxidation state of the metals.

The method is also applicable for the determination of many extractable metals, including:

Aluminium (Al)
Antimony (Sb)
Arsenic (As)
Barium (Ba)
Cadmium (Cd)
Calcium (Ca)
Chromium (Cr)
Cobalt (Co)
Copper (Cu)
Iron (Fe)
Lead (Pb)
Magnesium (Mg)
Manganese (Mn)
Mercury (Hg)
Molybdenum (Mo)
Nickel (Ni)
Potassium (K)
Selenium (Se)
Tin (Sn)
Titanium (Ti)
Zinc (Zn)
Zirconium (Zr)

The quantification limit of extractable lead is 3 mg/kg (see Annex A).

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 105-E04:2008, *Textiles — Tests for colour fastness — Part E04: Colour fastness to perspiration*

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 11885, *Water quality — Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)*

ISO 15586, *Water quality — Determination of trace metals using atomic absorption spectrometry with graphite furnace*

ISO 17072-2:2011, *Leather — Chemical determination of metal content — Part 2: Total metal content*

ISO 17294-2, *Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) — Part 2: Determination of 62 elements*

ISO 17852, *Water quality — Determination of mercury — Method using atomic fluorescence spectrometry*

3 Principle

A sample of leather is ground and extracted at 37 °C ± 2 °C for 4 h ± 5 min in an acid artificial-perspiration solution. The extract solution is filtered, acidified and analysed by ICP, or SFA or AAS. If necessary, digest a portion of filtrate solution in accordance with ISO 17072-2.

The results are reported on the dry matter of the leather.

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

4 Reagents

WARNING — As concentrated acids are used, it is imperative to use all necessary personal protective equipment.

4.1 General

Unless otherwise stated, only analytical grade chemicals shall be used. All solutions are aqueous solutions.

4.2 Nitric acid, 60 % to 70 % concentration (by mass).

4.3 L-histidine monohydrochloride monohydrate, $C_6H_9O_2N_3 \cdot HCl{\cdot}H_2O$.

4.4 Sodium chloride.

4.5 Sodium dihydrogen orthophosphate dihydrate, $NaH_2PO_4{\cdot}2H_2O$.

4.6 Sodium hydroxide, 0,1 mol/l.

4.7 Element stock solutions, of the various metals with mass concentrations of 1 000 mg/l each.

4.8 Nitric acid, 0,1 mol/l.

4.9 Water, grade 3 in accordance with ISO 3696:1987.

5 Apparatus and materials

5.1 General

All glassware, the analytical devices and the materials, including filters, shall be suitable for analysis of trace metals.

Use normal laboratory apparatus and, in particular, the following.

5.2 Laboratory oven, capable of maintaining 102 °C ± 2 °C.

5.3 Analytical balance, with an accuracy of 0,1 mg.

5.4 Laboratory balance, with an accuracy of 0,01 g.

5.5 Membrane filters and holder, suitable for filtering aqueous solutions, with a pore size of 0,45 µm.

5.6 Filter paper, fast, qualitative type.

5.7 Volumetric flasks, of various sizes (50 ml, 100 ml, 1 000 ml).

5.8 Wide-necked conical flasks, of approximately 250 ml capacity, with stoppers.

5.9 Volumetric conical flasks, of various sizes.

5.10 Water bath, thermostatically controlled to 37 °C ± 2 °C, fitted with a flask shaker or stirrer.

5.11 Inductively coupled plasma/optical emission spectrometer (ICP/OES) or atomic emission spectrometer (ICP/AES) (see ISO 11885), with a hydride-generator module. The gases used shall be of analytical grade.

5.12 Flame or graphite-furnace atomic absorption spectrometer (AAS) (see ISO 15586), with a hydride-generator module and with a suitable hollow-cathode-lamp nitrous oxide burner head or high-solids nitrous oxide burner head. The gases used shall be of analytical grade.

5.13 Inductively coupled plasma/mass spectrometer (ICP/MS) (see ISO 17294-2). The gases used shall be of analytical grade.

5.14 Spectrometer of atomic fluorescence (SFA), for mercury analysis.

6 Sampling and sample preparation

6.1 If the leather piece available for testing is a whole hide or skin, then the test specimens shall be sampled in accordance with the standard procedures given in ISO 2418. If sampling in accordance with ISO 2418 is not possible (e.g. leathers are from finished products like shoes or garments), details about the sampling shall be given in the test report.

6.2 Grind the leather sample in accordance with ISO 4044. Test pieces that are wet (in excess of 30 % moisture) should be predried for at least 12 h, at a temperature not exceeding 50 °C ± 2 °C. The drying temperature should be selected while considering the influence of elevated temperature on the nature of the analyte.

6.3 Using the analytical balance (5.3), weigh accurately 2 g of the ground leather to the nearest 0,001 g and place in a wide-necked 250 ml conical flask (5.8).

6.4 Determine the volatile matter content in accordance with ISO 4684. The same sample of ground leather can be used for the extraction in 7.2.

7 Procedure

7.1 Preparation of acid artificial-perspiration solution in accordance with ISO 105-E04:2008, Clause 4

The solution shall be freshly prepared each day, containing, per litre:

- 0,5 g of L-histidine monohydrochloride monohydrate (4.3);
- 5 g of sodium chloride (4.4);
- 2,2 g of sodium dihydrogen orthophosphate dihydrate (4.5).

The solution is brought to pH 5,5 (±0,1) with 0,1 mol/l sodium hydroxide solution.

7.2 Extraction of leather sample

To the accurately weighed 2 g of ground leather sample (see 6.3) in the conical flask (5.8), add by pipette 100 ml of the acid artificial-perspiration solution (7.1) and, at 37 °C ± 2 °C, shake slowly in a water bath (5.10) for 4 h ± 5 min.

Filter the extract with a filter paper (5.6), then filter with a membrane filter (5.5).

For the direct measurement of the elements, take a suitable amount of extract for analysis and add 5 % (by volume) of nitric acid (4.2). Consider this addition in the dilution factor.

To control the contaminants, it will be necessary to carry out a blank procedure. An aliquot of acid perspiration is placed in a sample container and treated as a sample, in all respects, including all analytical procedures.

The above extraction conditions shall be followed exactly. Any deviation would lead to the wrong results.

7.3 Digestion of the extracted solution

If the solution is not clear after filtration and acidification, the following digestion procedures shall be used.

After filtration, use 25 ml of the filtrate solution for the digestion, following the procedures described in the ISO 17072-2:2011, Clause 6, according to the metal to be determined. Take into account that, after digestion, the final volume of solution to be analysed should be set to 25 ml. Otherwise, consider the dilution.

NOTE Depending on the required level of element, the determination of As, Sb, Sn, Se and Hg might need to be carried out using a hydride generator. In this case, part of the filtered extraction solution (without acidification) will be used according to the manufacturer's instructions. To determine mercury (Hg), it will be possible to use SFA.

7.4 Analysis by ICP, AAS and SFA

For calibration, prepare at least four standard reference solutions plus a calibration blank.

7.4.1 ICP

The solution obtained in 7.2 can be analysed directly, provided it contains a concentration of analysed metals within calibration limits. Otherwise, the solution should be diluted as appropriate.

Prepare standard reference solutions of the required metals in accordance with ISO 11885, using perspiration solution instead of water.

7.4.1.1 ICP/OES or ICP/AES

Set up the ICP/OES (or ICP/AES) spectrometer (5.11) in accordance with the manufacturer's instructions and use the recommended settings indicated in ISO 11885.

Prepare standard reference solutions of the required metals in accordance with ISO 11885, using perspiration solution instead of water. Analyse the solution obtained in 7.2 against the reference solutions of metals with known concentration using ICP/OES (5.11) at the characteristic wavelength of each individual element, either as it is or following an appropriate dilution.

7.4.1.2 ICP/MS

Set up the ICP/MS (5.13) in accordance with the manufacturer's instructions and use the recommended settings indicated in ISO 17294-2.

Analyse the solution obtained in 7.2 against the reference solutions of metals with known concentration using ICP/MS (5.13) at the characteristic ion mass of each individual element, either as it is or following an appropriate dilution.

7.4.2 AAS

Digest the extracted solution filtered as indicated in 7.3.

Prepare the atomic absorption spectrometer (5.12) following the manufacturer's instructions and use the recommended settings in accordance with ISO 15586.

7.4.3 Analysis by SFA technique

Hg analysis can be carried out using the SFA technique. If this is to be used, then the procedure described in ISO 17852 shall be followed.

8 Calculation and expression of results

Express the result by stating the mass fraction (content) of the analysed metal, in milligrams per kilogram (mg/kg), calculated on the dry mass of the leather, as follows:

$$w_x = \frac{w_{x,\mathrm{i}}}{m} \times V_1 \times F_\mathrm{d}$$

where

w_x is the mass fraction of the metal extracted from the leather, expressed in milligrams per kilogram (mg/kg) of analysed product, and rounded to the nearest first decimal place;

$w_{x,\mathrm{i}}$ is the concentration of the metal in question detected by the instrument, expressed in milligrams per litre (mg/l);

m is the dry mass of the sample, expressed in grams (g), calculated in accordance with ISO 4684;

V_1 is the volume of the acid artificial-perspiration solution for the extraction, expressed in millilitres (ml);

F_d is the dilution factor eventually derived from the digestion procedure or acidification.

It is possible, if required, to quote the results based on the dry, degreased mass of the leather sample. Details shall be noted in the test report.

9 Test report

The test report shall include at least the following information:

a) a reference to this part of ISO 17072 (i.e. ISO 17072-1:2011);

b) a description of the leather sample tested;

c) results of the determination;

d) results obtained for the amount of extracted metal, expressed in milligrams per kilogram (mg/kg);

e) details of any deviations from this standard test method.

Annex A
(informative)

Interlaboratory test results

Table A.1 — Lead interlaboratory test: statistical evaluation of results

Parameter	ISO 5725-2:1994	ISO 5725-5:1998
No. of considered laboratories	5	7
Overall mean value	0,56	0,62
Repeatability standard deviation	0,029	0,050
Relative repeatability standard deviation	5,22	8,13
Standard deviation between laboratories	0,566	
Reproducibility standard deviation	0,567	0,505
Relative reproducibility standard deviation	101,23	81,89
Repeatability factor	0,083	0,142
Reproducibility factor	1,604	1,429

Bibliography

[1] ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

[2] ISO 5725-5:1998, *Accuracy (trueness and precision) of measurement methods and results — Part 5: Alternative methods for the determination of the precision of a standard measurement method*

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