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IULTCS/IUC 27-2

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Leather — Chemical determination of metal content —

Part 2:
Total metal content

Cuir — Détermination chimique de la teneur en métal —

Partie 2: Teneur totale en métaux

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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document 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).

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.

This second edition cancels and replaces the first edition (ISO 17072-2:2011), which has been technically revised as follows:

- the Scope and Clauses 4, 5, 6, 7, 8, and 10 have been editorially and technically modified;
- 7.2 now refers to ISO 4044 for sample preparation, which requires the user to grind sufficiently large pieces of leather or cut small pieces of leather;
- 8.1, referring to the acid digestion, has been technically revised;
- 6.4 from ISO 17072-2:2011 has been included in 8.1 of this edition.

A list of all parts in the ISO 17072 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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Leather — Chemical determination of metal content —

Part 2:
Total metal content

1 Scope

This document specifies a method for the determination of the total metal content in leather using digestion of the leather and subsequent determination with inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS) or spectrometry of atomic fluorescence (SFA).

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

The method is applicable for determining the following metals:

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

This method is also suitable for determining Boron (B) in leather.

In the case of chromium-tanned leathers, it is often more relevant to use ISO 5398-1[1], ISO 5398-2[2], ISO 5398-3[3] or ISO 5398-4 [4].

Interlaboratory test results and the quantification limits possible with ICP-OES are given in Table A.1 and Table A.2 of Annex A.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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, *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 elements using atomic absorption spectrometry with graphite furnace*

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

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

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

4 Principle

Digestion of the sample of leather (see ISO 4044) is carried out using a ternary acid mixture or microwave digestion until complete mineralization is achieved. The residue is re-dissolved with water and analysed by AAS, ICP or SFA (for mercury).

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

5 Reagents

WARNING — The concentrated acids used in this method are very corrosive and/or oxidising liquids, which could raise the possibility of fire in the event of contact with ignitable materials and promote an existing fire considerably, or could decompose explosively with warming. They might cause acute or chronic health dangers as well. Moreover, they are hazardous to water. Suitable safety measures are therefore necessary.

5.1 General

Analytical grade chemicals shall be used for digestion with the Kjeldhal method. Ultrapure acid shall be used for microwave digestion. All solutions are aqueous solutions.

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

5.3 Sulfuric acid, 98 % concentration (by mass).

5.4 Perchloric acid, 60 % to 70 % concentration (by mass).

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

5.6 Hydrochloric acid, 37 %.

5.7 Water, grade 3 in accordance with ISO 3696.

6 Apparatus and materials

6.1 General

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

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

6.2 Laboratory oven, capable of maintaining (102 ± 2) °C.

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

6.4 Heating apparatus for Kjeldahl flasks, equipped with fume extraction.

6.5 Long-necked Kjeldahl digestion flask, 1 l volume, with reflux condenser.

6.6 Filtration device, using glass fibre (GFC) or membrane type filters.

6.7 Vacuum filter system for membrane filters.

6.8 Magnetic stirrer.

6.9 Glass boiling beads.

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

6.11 Flame or graphite-furnace atomic absorption spectrometer (AAS) (see ISO 15586), with a hydride-generator module, suitable burner heads, and hollow-cathode-lamps. The gases used shall be of analytical grade.

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

6.13 Atomic fluorescence spectrometer (SFA), for mercury analysis.

6.14 Volumetric flasks, capacity 50 ml and 100 ml.

7 Sampling and sample preparation

7.1 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.

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

7.3 Determine the dry matter content in accordance with ISO 4684.

8 Procedure

8.1 Acid digestion

Weigh accurately 1 g of the prepared leather to the nearest 0,001 g using an analytical balance (6.3) and place in a long-necked Kjeldahl digestion flask (6.5). Add, using a measuring cylinder, 10 ml to 20 ml of a ternary mixture of nitric acid (5.2), sulfuric acid (5.3) and perchloric acid (5.4) in a ratio of 3:1:1, and a few glass boiling beads (6.9). Place a funnel or splash bulb in the neck of the flask and heat to boiling. Leave to react on the heating apparatus (6.4) until digestion is complete and the red vapours of nitrogen dioxide have disappeared. Stop warming after digestion is complete. In the event of incomplete digestion, allow the flask to cool, add a further 10 ml to 20 ml of the ternary acid mixture and repeat the procedure.

For lead (Pb) determination, the digestion procedure shall be carried out separately, replacing sulfuric acid (5.3) with hydrochloric acid (5.6).

In the case of high volatile metals determination, check that this open acid digestion doesn't cause a partial loss of these elements.

WARNING — It is imperative that the leather sample is not in direct contact with perchloric acid because of the possible explosive reaction.

Allow to cool, re-dissolve with 30 ml of distilled water, filter if necessary, then transfer the filtrate to a 100 ml volumetric flask. With 30 ml of distilled water, thoroughly wash the flask used for digestion and the filter, transfer the water to the volumetric flask, and make up to volume.

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

8.2 Microwave digestion

The sample for analysis can also be prepared through application of microwave-assisted digestion (MAD) or other validated digestion technics. If this is to be used, then the procedure and the sample quantity shall be adapted. Weigh 0,1 g to 1,0 g of the prepared leather to the nearest 0,001 g.

8.3 Analysis by ICP, AAS and SFA

8.3.1 General

Prepare standard reference solutions of the required metals in accordance with ISO 11885 or ISO 15586 by ensuring that the acid concentration in the standard reference solutions is of the same order as that of the sample. For calibration, prepare at least four standard reference solutions plus a calibration blank.

8.3.2 ICP

8.3.2.1 General

The solution obtained in 8.1 or 8.2 can be analysed directly, provided it contains a concentration of analysed metals within calibration limits. Otherwise, the solution should be diluted as appropriate.

8.3.2.2 ICP-OES

Set up the ICP-OES spectrometer (6.10) in accordance with the manufacturer's instructions and use the recommended settings indicated in ISO 11885. If required, carry out the determination of As, Sb, Sn, Se and Hg using a hydride generator, following the manufacturer's instructions.

Analyse the solution obtained in 8.1 or 8.2 against the reference solutions of metals with known concentration using ICP-OES (6.10) at the characteristic wavelength of each individual element.

8.3.2.3 ICP-MS

Set up the ICP-MS (6.12) in accordance with the manufacturer's instructions and use the recommended settings indicated in ISO 17294-2.

Analyse the solution obtained in 8.1 or 8.2 against the reference solutions of metals with known concentration using the ICP-MS (6.12) at the characteristic ion mass of each individual element.

8.3.3 AAS

Prepare the atomic absorption spectrometer (6.11) following the manufacturer's instructions and use the recommended settings in accordance with ISO 15586. If required, carry out the determination of As, Sb, Sn, Se and Hg by using a hydride generator, following the manufacturer's instructions.

Analyse the solution obtained in 8.1 or 8.2 against the reference solutions of metals with known concentration using AAS (6.11), with a suitable hollow-cathode-lamp for each individual element.

8.3.4 Analysis by SFA technique

Set up the SFA (6.13) in accordance with the manufacturer's instructions and use the recommended settings indicated in ISO 17852.

Analyse the solution obtained in 8.2 against the reference solutions of mercury with known concentration using SFA (6.13).

9 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 in 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 determined 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 volumetric flask used for the digestion, expressed in millilitres (ml);

F_d is the dilution factor, if the solution obtained in 6.5 needs to be diluted.

If required, the results can be given based on the dry, degreased mass of the leather sample. Details shall be noted in the test report.

10 Test report

The test report shall include at least the following information:

a) the name of the laboratory;

b) a reference to this document, i.e. ISO 17072-2;

c) a description of the applied analytical system;

d) a description of the leather sample tested;

e) results of the dry matter determination;

f) results obtained for the amount of total metal, expressed in milligrams per kilogram of dry leather (mg/kg);

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

Annex A
(informative)

Interlaboratory test results and quantification limits

Table A.1 — Interlaboratory test for lead (Pb): statistical evaluation of results

Parameter	ISO 5725-2:1994[5]	ISO 5725-5:1998[6]
Number of laboratories	8	8
Overall mean value (mg/kg)	162,31	163,48
Repeatability standard deviation	5,216	5,498
Relative repeatability standard deviation	3,21	3,36
Standard deviation between laboratories	27,5	64
Reproducibility standard deviation	28,053	29,093
Relative reproducibility standard deviation	17,28	17,80
Repeatability factor	14,76	15,56
Reproducibility factor	79,39	82,33

Table A.2 — Quantification limit possible with ICP-OES

Metal Elements		Quantification limit (mg/kg)
Aluminium	Al	100
Antimony	Sb	25
Arsenic	As	25
Barium	Ba	10
Cadmium	Cd	10
Calcium	Ca	100
Chromium	Cr	10
Cobalt	Co	10
Copper	Cu	10
Iron	Fe	25
Lead	Pb	25
Magnesium	Mg	100
Manganese	Mn	10
Mercury	Hg	0,02
Molybdenum	Mo	25
Nickel	Ni	10
Potassium	K	100
Selenium	Se	25
Tin	Sn	10
Titanium	Ti	10
Zinc	Zn	10
Zirconium	Zr	10