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Leather — Chemical tests — Determination of chromium(VI) content

Cuir — Essais chimiques — Détermination de la teneur en chrome(VI)

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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 17075:2007 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 Standardisation (CEN) Technical Committee CEN/TC 289, *Leather*, the secretariat of which is held by UNI, in accordance with the Agreement on technical co-operation 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 first edition of ISO 17075 cancels and replaces the first edition of CEN TS 14495:2003, which has been technically revised.

Leather — Chemical tests — Determination of chromium(VI) content

1 Scope

This International Standard specifies a method for determining chromium(VI) in solutions leached from leather under defined conditions. The method described is suitable to quantify the chromium(VI) content in leathers down to 3 mg/kg.

This document is applicable to all leather types.

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 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*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
chromium(VI) content
amount of chromium(VI) in leather determined by this method after extraction with an aqueous salt solution at pH 7,5 to 8,0

NOTE The chromium(VI) content is reported as chromium(VI) in milligrams per kilogram (mg/kg), expressed as the dry mass of the sample.

4 Principle

Soluble chromium(VI) is leached from the sample in phosphate buffer at pH 7,5 to 8,0 and substances which influence the detection are removed by solid phase extraction if necessary. The chromium(VI) in solution oxidizes 1,5-diphenylcarbazide to 1,5-diphenylcarbazone to give a red/violet complex with chromium which can be quantified photometrically at 540 nm.

The results obtained from the described method are strictly dependent on the extraction conditions. Results obtained by using other extraction procedures (extraction solution, pH, extraction time, etc.) are not comparable with the results produced by the procedure described in this standard.

5 Reagents

All reagents used shall have at least analytical grade purity.

5.1 Extraction solution.

Dissolve 22,8 g dipotassiumhydrogenphosphate $K_2HPO_4 \cdot 3H_2O$ in 1 000 ml water, adjusted to pH 8,0 ± 0,1 with phosphoric acid (5.3). Degas this solution with either argon or nitrogen.

5.2 Diphenylcarbazide solution.

Dissolve 1,0 g 1,5-diphenylcarbazide $CO(NHNHC_6H_5)_2$ in 100 ml **acetone** $(CH_3)_2CO$ and acidified with one drop of **glacial acetic acid** CH_3COOH.

The solution should be kept in a brown glass bottle. The shelf life is up to 14 days at 4 °C.

5.3 Phosphoric acid solution.

700 ml *o*-phosphoric acid, $\rho = 1{,}71$ g/ml, made up to 1 000 ml with distilled water.

5.4 Chromium(VI) stock solution.

Dissolve 2,829 g potassium dichromate ($K_2Cr_2O_7$) (5.8) in water in a volumetric flask and make up to 1 000 ml with water. 1 ml of this solution contains 1 mg of chromium.

5.5 Chromium(VI) standard solution.

Pipette 1 ml of solution (5.4) into a 1 000 ml volumetric flask and make up to the mark with extraction solution (5.1). 1 ml of this solution contains 1 µg of chromium.

5.6 Argon or nitrogen, oxygen-free.

Preference should be given to argon as an inert gas instead of nitrogen because argon has a higher specific mass than air.

5.7 Distilled water, Grade 3 quality as specified in ISO 3696.

5.8 Potassium dichromate ($K_2Cr_2O_7$), dried for 16 h ± 2 h at 102 °C ± 2 °C.

5.9 Methanol, HPLC grade.

6 Apparatus

6.1 Suitable mechanical shaker, 50 min^{-1} to 150 min^{-1}.

6.2 Conical flask, of capacity 250 ml, with stopper.

6.3 Aeration tube and **flow meter**.

6.4 pH meter, with glass electrode.

6.5 Membrane filter, 0,45 µm pore size (polytetrafluoroethylene or nylon).

6.6 Volumetric flasks, of capacity 25 ml, 100 ml and 1 000 ml.

6.7 Pipettes, various nominal volumes.

6.8 Spectrophotometer or **filterphotometer**, wavelength 540 nm.

6.9 Photometric cell, quartz, 4 cm length or any other suitable cell length.

6.10 Glass or polypropylene cartridges filled with suitable reversed phase material, e.g. reversed phase (RP) 18.

6.11 Solid Phase Extraction (SPE) system, with vacuum device or solvent resistant medical syringe.

7 Procedure

7.1 Sampling and preparation of samples

If possible, sample in accordance with ISO 2418 and grind leather in accordance with ISO 4044. Grinding should take place shortly prior to the extraction process. 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.

7.2 Preparation of analytical solution

Weigh 2 g ± 0,01 g of ground leather to the nearest 0,001 g. Pipette 100 ml of degassed solution (5.1) into a 250 ml conical flask (6.2). Displace oxygen by passing oxygen-free argon (or nitrogen) (5.6) into the flask for 5 min (50 ml/min ± 10 ml/min). Remove the aeration tube (6.3), add the leather and close the flask with a stopper. Record the extract volume as V_0.

Shake the leather powder suspension 3 h ± 5 min on a mechanical shaker to extract the chromium(VI).

Gently shake the suspension in a smooth circular movement to keep the leather powder from adhering to the wall of the flask. Avoid shaking it too quickly.

Immediately after completing 3 h of extraction, filter the content of the conical flask through a membrane filter into a glass bottle with screw cap. Check the pH of the solution. The pH of the solution shall be between 7,5 and 8,0. If the pH of the solution is not within this range, start the complete procedure again.

7.3 Determination of chromium (VI) in the solution obtained from the extraction procedure

Pretreat the cartridges in the following way:

a) flush the cartridge (6.10) first with 5 ml methanol (5.9),

b) afterwards with 5 ml distilled water (5.7) and

c) directly afterwards with 10 ml of extraction solution (5.1).

Do not dry the cartridges (6.10) during or after the pre-treatment.

From the solution obtained in 7.2, take 10 ml (V_1) and transfer this quantitatively through the cartridge (6.10) on an SPE system with vacuum device (6.11). Collect the eluate in a 25 ml volumetric flask (6.6). Flush the cartridge with 10 ml extraction solution (5.1) into the 25 ml flask. Make up the flask to volume (V_2) with extraction solution (5.1). Mark this solution as S_1.

Pipette (6.7) 10 ml (V_3) of solution S_1 into a 25 ml volumetric flask. Dilute the solution to 3/4 of the flask's volume with extraction solution (5.1). Add 0,5 ml of phosphoric acid solution (5.3) and afterwards 0,5 ml of diphenylcarbazide solution (5.2). Make up the flask to volume (V_4) with extraction solution (5.1) and mix well.

Allow to stand for 15 min ± 5 min. Measure the absorbance of the solution at 540 nm in a 4 cm cell against the blank solution (7.4). Record the absorbance obtained as A_1.

For each run, pipette another 10 ml aliquot of solution S_1 into a 25 ml volumetric flask and treat it as described above, but without the addition of the diphenylcarbazide solution (5.2). Measure the absorbance of this solution in the same way as before and record it as A_2.

7.4 Blank solution

Fill a 25 ml volumetric flask three quarters full with extraction solution (5.1), add 0,5 ml of phosphoric acid (5.3) and 0,5 ml of diphenylcarbazide solution (5.2) and make up to the mark with extraction solution (5.1) and mix well. Prepare this solution daily and store it in the dark. Treat the blank solution in the same way as the analytical solution, excluding the solid phase extraction.

7.5 Calibration

Prepare calibrating solutions from the standard solution (5.5). The chromium concentration in these solutions should cover the expected range of measurements.

Prepare the calibration solutions in 25 ml volumetric flasks (6.6).

Plot a suitable calibration curve by using at least six standards, within the range 0,5 ml to 15 ml of standard solution (5.5). Pipette the given volumes of standard solution (5.5) into 25 ml volumetric flasks. Add 0,5 ml of phosphoric acid (5.3) and 0,5 ml diphenylcarbazide solution (5.2) to each flask. Make up to volume with extraction solution (5.1), mix well and allow to stand for 15 min ± 5 min.

Measure the absorbance of the solutions in the same photometric cell as the samples at 540 nm against the blank obtained in 7.4.

Plot the chromium(VI) concentrations in micrograms per millilitre (µg/ml) against the absorbance measured. Plot the chromium(VI) concentration on the x-axis and the absorbance on the y-axis.

In interlaboratory tests, the 4 cm cell proved to be most suitable. The standard solutions described above are intended for analysis using a 4 cm cell. In some cases, however, it may be suitable to use higher or lower cell path length. Care shall be taken to ensure that the calibration range used is within the linear measuring range of the spectrophotometer. The measured extinction should not exceed 0,9 extinction units.

7.6 Determination of the recovery rate

7.6.1 Influence of the matrix

The determination of the recovery rate is important to provide information about possible matrix effects which can influence the results.

Spike a 10 ml aliquot of the solution obtained in 7.2 with a suitable volume of chromium(VI) solution to double approximately the content of the chromium(VI) concentration of the extract (± 25 %). Select the concentration of the spiking solution in that way that the final volume of the spiked solution is maximum 11 ml. Treat this solution in the same way as the sample (recording the absorbance as A_{1s} and A_{2s}). (See 7.3.)

The absorbance of the solution shall be within the range of the calibration curve, otherwise repeat the procedure using a smaller aliquot. The recovery rate shall be greater than 80 %.

NOTE 1 If the added chromium(VI) cannot be detected, this may be an indication that the leather contains reducing agents. In some cases, if the recovery rate according to 7.6.2 is greater than 90 %, and after intensive considerations, this may lead to the conclusion that this leather has no chromium(VI) content (below detection limit).

NOTE 2 The recovery rate is an indicator of whether the procedure works or whether matrix effects are affecting the results. Normally, the recovery rate is greater then 80 %.

7.6.2 Influence of the RP material

Pipette a volume of solution (5.5) which corresponds to the chromium(VI) content of the leather into a 100 ml volumetric flask and make up to volume with extraction solution (5.1).

Treat this solution in the same way as the leather extract. Determine the content in this solution in the same way as that of the leather extract and compare with the calculated content. In cases where no chromium(VI) was detected in the leather sample, the concentration of the solution shall be 6 µg/100 ml. The recovery rate shall be greater than 90 %. If the recovery rate is equal to or lower than 90 %, the RP material is not suitable for this procedure and shall be substituted.

8 Calculation and expression of results

8.1 Calculation of chromium(VI) content

$$w_{\mathrm{Cr(VI)}} = \frac{(A_1 - A_2) \times V_0 \times V_2 \times V_4}{V_1 \times V_3 \times m \times F}$$

where

$w_{\mathrm{Cr(VI)}}$ is the mass fraction, expressed in milligrams per kilogram (mg/kg), of soluble Cr(VI) in leather;

A_1 is the absorbance of sample solution with DPC;

A_2 is the absorbance of sample solution without DPC;

F is the gradient of calibration curve (y/x), expressed in millilitres per microgram (ml/µg);

m is the mass of the leather sample taken, expressed in grams (g);

V_0 is the extract volume of the initial sample, expressed in millilitres (ml);

V_1 is the aliquot taken from the extract volume of the initial sample, expressed in millilitres (ml);

V_2 is the total eluate (S_1) volume, after passage through the SPE column, to which the aliquot V_1 was made up, expressed in millilitres (ml);

V_3 is the aliquot taken from solution S_1, expressed in millilitres (ml);

V_4 is the final make-up volume of the aliquot from S_1, expressed in millilitres (ml).

Result based on dry matter:

$$w_{\mathrm{Cr(VI)\text{-}dry}} = w_{\mathrm{Cr(VI)}} \times D$$

where

D is the factor for conversion to dry matter:

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

w is the mass fraction of the volatile matter determined using ISO 4684, expressed as a percentage.

8.2 Recovery rate (according to 7.6.1)

$$\eta = \frac{\left[\left(A_{1s} - A_{2s}\right) - \left(A_1 - A_2\right)\right]}{\rho \times F} \times 100$$

where

η is the recovery rate, expressed in percent (%);

ρ is the mass concentration of chromium(VI) spiked, expressed in micrograms per millilitre (µg/ml);

F is the gradient of calibration curve, expressed in millilitres per microgram (ml/µg);

A_{1s} is the absorbance of solution after adding chromium(VI) and DPC;

A_{2s} is the absorbance of solution after adding chromium(VI), but without adding DPC;

A_1 is the absorbance of sample solution with DPC;

A_2 is the absorbance of sample solution without DPC.

8.3 Expression of results

The chromium(VI) content is given in milligrams per kilogram (mg/kg) rounded to the nearest 0,1 mg. The content is based on dry matter. The volatile matter (ISO 4684) is given in percent (%) rounded to the nearest 0,1 %.

The extraction matrix for leather is complex (for example, due to coloration) and results below 3 mg/kg show large variation and have limited reliability, therefore the limit of detection should be considered 3 mg/kg.

In the case of levels of chromium(VI) being detected above 3 mg/kg, the UV/VIS spectrum of the test solution should be compared with a standard solution (7.5) to determine whether the positive result is due to interfering substances.

9 Test report

The test report shall include the following information:

a) the chromium(VI) content obtained from 8.1;

b) a reference to this document (i.e. ISO 17075);

c) a description of the sample tested and details about sampling (7.1), if necessary;

d) the cell length used if not 4 cm;

e) the results obtained to 1 decimal place in milligrams per kilogram (mg/kg);

f) the volatile matter of the leather in percent (%);

g) the recovery rate in percent (%) if lower than 80 % or higher than 105 %;

h) details of any deviations from the procedure.

Annex A
(informative)

Reversed phase material

In interlaboratory trials, cartridges with 1 g RP 18 material and DIONEX cartridges (Dionex OnGuard-RP, part number 39595) have been tested and found to be suitable. Other potential cartridges are supplied by WATERS (WATERS Sep-Pak Plus tC_{18}) [1)]. Nevertheless, in some cases it may be advisable to also use other phases or more than 1 g of SPE material. In any case, the recovery rate has to be tested very carefully. Charcoal proved to be unsuitable for the decolourization of the extracts.

1) Dionex OnGuard-RP and WATERS Sep-Pak Plus tC_{18} are examples of suitable products available commercially. This information is given for the convenience of the users of this document and does not constitute an endorsement by ISO of these products.