



**SLOVENSKI STANDARD**  
**SIST-TS CEN/TS 14495:2004**  
**01-maj-2004**

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Leather - Chemical tests - Determination of chromium VI content

Leder - Chemische Prüfungen - Bestimmung des Chrom-VI-Gehaltes

Cuir - Essais chimiques - Détermination de la teneur en chrome VI

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**Ta slovenski standard je istoveten z: CEN/TS 14495:2003**

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ICS 59.140.30

English version

## Leather – Chemical tests – Determination of chromium VI content

This Technical Specification (CEN/TS) was approved by CEN on 27 October 2002 for provisional application.

The period of validity of this CEN/TS is limited initially to three years. After two years the members of CEN will be requested to submit their comments, particularly on the question whether the CEN/TS can be converted into a European Standard.

CEN members are required to announce the existence of this CEN/TS in the same way as for an EN and to make the CEN/TS available. It is permissible to keep conflicting national standards in force (in parallel to the CEN/TS) until the final decision about the possible conversion of the CEN/TS into an EN is reached.

CEN members are the national standards bodies of Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Slovakia, Spain, Sweden, Switzerland and United Kingdom.

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EUROPEAN COMMITTEE FOR STANDARDIZATION  
COMITÉ EUROPÉEN DE NORMALISATION  
EUROPÄISCHES KOMITEE FÜR NORMUNG

**Management Centre: rue de Stassart, 36 B-1050 Brussels**

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## Foreword

This document (CEN/TS 14495:2003) has been prepared by Technical Committee CEN/TC 289 "Leather", the secretariat of which is held by UNI.

The method described is suitable to quantify the chromium VI content in leathers down to 10 mg/kg and is suitable to show whether a leather complies with the criteria "maximum 10 mg/kg" as it is given e.g. by the European Commission decision of 17 February 1999 for the ecological criteria for the eco-label of leather for footwear.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to announce this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Slovakia, Spain, Sweden, Switzerland and the United Kingdom.

Annex A is informative.

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## 1 Scope

This European Technical Specification specifies a method for determining chromium VI in solutions leached from leather under defined conditions.

## 2 Normative references

This Technical Specification incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this Technical Specification only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

prEN 14676, Leather - Chemical tests - Determination of volatile matter

EN ISO 3696:1995, Water for analytical laboratory use - Specification and test methods (ISO 3696:1987)

EN ISO 4044, Leather - Preparation of chemical test samples (ISO 4044:1998)

EN ISO 2418:, Leather - Chemical, physical and mechanical and fastness tests - Sampling location (ISO 2418:2002)

EN ISO 2419, Leather – Physical and mechanical tests – Sample preparation and conditioning (ISO 2419:2002)

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## 3 Principle

Soluble chromium VI is leached from the sample 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 oxidises 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 dependant 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 Technical Specification.

## 4 Definitions

For the purposes of this Technical Specification the following applies:

chromium VI content is the amount of chromium VI in leather determined by this method after extraction with an aqueous salt solution at pH 7,5-8,0. Chromium VI content is reported as chromium VI in mg/kg. In cases where wet leathers, e.g. wet blues, are analysed, the content is given in mg/kg based on dry matter (prEN 14676)

## 5 Chemicals

All reagents used shall have at least analytical grade purity.

### 5.1 Extraction solution:

22,8 g dipotassiumhydrogenphosphate  $K_2HPO_4 \cdot 3H_2O$  dissolved in 1 000 ml water, adjusted to pH  $8,0 \pm 0,1$  with phosphoric acid (5.3). This solution shall be degassed with either argon or nitrogen

**5.2 Diphenylcarbazide solution:**

1,0 g 1,5-diphenylcarbazide  $\text{CO}(\text{NHNHC}_6\text{H}_5)_2$  is dissolved in 100 ml acetone  $(\text{CH}_3)_2\text{CO}$  and made acidic with one drop of glacial acetic acid  $\text{CH}_3\text{COOH}$ .

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  $d = 1,71 \text{ g/ml}$ , made up to 1 000 ml with distilled water.

**5.4 Chromium VI stock solution:**

2,829 g potassium dichromate  $(\text{K}_2\text{Cr}_2\text{O}_7)$  (5.8), is dissolved into water in a volumetric flask and made up to 1 000 ml with water. 1 ml of this solution contains 1 mg of chromium.

**5.5 Chromium VI standard solution:**

1 ml of solution (5.4), is pipetted into a 1 000 ml volumetric flask and made up to the mark with distilled water. 1 ml of this solution contains 1  $\mu\text{g}$  of chromium.

**5.6 Argon or nitrogen, oxygen free****5.7 Distilled water of Grade 3 (EN ISO 3696:1995)****5.8 Potassium dichromate  $(\text{K}_2\text{Cr}_2\text{O}_7)$ , dried for 16 h  $\pm$  2 h at 102 °C  $\pm$  2 °C****5.9 Methanol**

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**6 Apparatus**

**6.1** Suitable mechanical shaker, 50  $\text{revmin}^{-1}$  to 150  $\text{revmin}^{-1}$

**6.2** Conical flask, 250 ml, with stopper

**6.3** Aeration tube and flow meter

**6.4** pH meter with glass electrode

**6.5** Membrane filter, 0,45  $\mu\text{m}$  pore size (Teflon or Nylon)

**6.6** Volumetric flasks, 25 ml, 100 ml, 1000 ml

**6.7** Pipettes, nominal volumes 0,5/1,0/2,0/5,0/10/20/25 ml

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

**6.9** Photometric cell, quartz, 2 cm path length or any other suitable cell path length

**6.10** Glass or polypropylene cartridges filled with suitable reversed phase materials, e.g. RP 18

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

## 7 Procedure

### 7.1 Sampling and preparation of samples

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

Condition the ground test sample in accordance with EN ISO 2419 prior to weighting.

### 7.2 Preparation of analytical solution

Weigh  $2 \text{ g} \pm 0,01 \text{ g}$  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). and add the leather. Close the flask with a stopper.

The leather powder is extracted by shaking  $3 \text{ h} \pm 5 \text{ minutes}$  on a mechanical shaker.

The settings of the shaking apparatus shall be as such that the leather powder is in smooth circular movement without adhering to the wall of the flask. Too fast movement shall be avoided.

After 3 h of extraction 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 the complete procedure shall be started again.

Immediately after the extraction is completed the content of the conical flask is filtered through a membrane filter into a glass bottle with screw cap.

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

The cartridges are pre-treated in the following way: flush the cartridge (6.10) first with 5 ml methanol (5.9), afterwards with 5 ml distilled water (5.7) and directly afterwards with 10 ml of extraction solution (5.1). The cartridges (6.10) shall not be dried during or after the pre-treatment.

From the solution obtained in 7.2, 10 ml are taken and transferred quantitatively through the cartridge (6.10) on an SPE system with vacuum device (6.11). The eluate is collected in a 25 ml volumetric flask (6.6). The cartridge is flushed with 10 ml extraction solution (5.1), into the 25 ml flask. The flask is made up to volume with extraction solution (5.1). This solution is marked as  $S_1$ .

10 ml of solution  $S_1$  are pipetted into a 25 ml volumetric flask. The solution is diluted to 3/4 of the flask's volume with extraction solution (5.1). 0,5 ml of Diphenylcarbazide solution (5.2), is added and afterwards 0,5 ml of Phosphoric acid (5.3). The flask is made up to volume with extraction solution (5.1) and mixed well.

Allow to stand for 15 min.  $\pm 5 \text{ min.}$ . Measure the absorbance of the solution at 540 nm in a 2 cm cell against the blank solution (7.4). The absorbance obtained is registered as  $E_1$ .

For each sample another 10 ml aliquot of solution  $S_1$  is pipetted into a 25 ml volumetric flask and treated as described above but without the addition of the diphenylcarbazide solution (5.2). The absorbance of this solution is measured in the same way as before and registered as  $E_2$ .

### 7.4 Blank solution

Three quarters fill a 25 ml volumetric flask with extraction solution (5.1), add 0,5 ml of diphenylcarbazide solution (5.2) and 0.5 ml of phosphoric acid (5.3), make up to the mark with extraction solution (5.1) and mix well. This solution shall be stored in the dark. The blank solution is treated in the same way as the analytical solution, including the solid phase extraction.



## 7.5 Calibration

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

The calibrating solutions are prepared in 25 ml volumetric flasks.

A suitable calibration curve should be plotted by using at least a blank and four other standards, within the range 0,5 ml - 20 ml of standard solution (5.5). The given volumes of standard solution (5.5), are pipetted into 25 ml volumetric flasks, 0,5 ml diphenylcarbazide solution (5.2), and 0,5 ml of phosphoric acid (5.3), is added to each flask. Make up to volume with extraction solution (5.1), mix well and allow to stand for 15 min.  $\pm$  5 min.

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

The chromium VI concentrations in  $\mu\text{g} / \text{ml}$  are plotted against the absorbance measured. The chromium VI concentration is plotted on the x-axis, the absorbance on the y-axis.

NOTE In interlaboratory tests the 2 cm cell proved to be most suitable. In some cases it may however be suitable to use higher or lower cell path length.

## 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.

10 ml aliquot of the solution obtained in 7.2 are dosed with a suitable volume of chromium VI solution to double approximately the content of the chromium VI concentration of the extract ( $\pm$  25 %). The concentration of the spiking solution has to be selected in that way that the final volume of the spiked solution is maximum 11 ml. This solution is treated in the same way as the sample. (see 7.3)

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

### 7.6.2 Influence of the RP-material

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

This solution is treated in the same way as the leather extract. The content in this solution is determined in the same way as that of the leather extract and compared with the calculated content. In cases where no chromium VI was detected in the leather sample, the concentration of the solution shall be 6  $\mu\text{g}/100 \text{ ml}$ . The recovery rate shall be more than 90 %. If the recovery rate is equal to or lower than 90 % the RP material is not suitable for this procedure and has to be substituted.

NOTE 1 If added chromium VI can not 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 higher than 90 %, and after consideration 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 more than 80 %.