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# Leather — Chemical tests — Determination of chromium (VI) and the reductive potential for chromium tanning agents

*Cuir — Essais chimiques — Détermination de la teneur en chrome (VI) et du potentiel de réduction des agents de tannage au chrome*



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# Foreword

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ISO 19071 was prepared by the Chemical Testing 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.

# Introduction

Under REACH regulations, manufacturers of chemicals are required to register their products before placing them on the market. Accordingly, a new method is given for the determination of chromium (VI) in chromium tanning agents.

Chromium tanning agents consist of chromium sulfate, containing additional hydroxyl groups in different amounts. These tanning agents exhibit a reductive potential. In the presence of reducing agents the recovery rate of chromium (VI) can be significantly lower than 90 %.

Consequently another procedure has to be selected to determine the exact chromium (VI) content. This is based on the standard addition procedure, and was developed in consultation with TEGEWA working group “Leather Auxiliaries” (TEGEWA is the Association of German Manufacturers of Textile, Leather and Washing Agent chemical products).

# Leather — Chemical tests — Determination of chromium (VI) and the reductive potential for chromium tanning agents

## 1 Scope

This International Standard specifies a test method for the determination of chromium (VI) content in chromium tanning agents. The results give information about the reductive potential of the chromium tanning agent.

## 2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

## 3 Principle



The chromium tanning agent is dissolved in water. After reaction of chromium (VI) with 1,5-diphenylcarbazide the resulting complex is extracted using *n*-hexanol. The concentration of the complex in the extract is determined by photometry at 540 nm.



Due to the presence of reducing agents in commercial chromium tanning agents, it is necessary to use the method of standard addition to determine the reductive potential. The procedure is repeated by adding different amounts of chromium (VI) to the original solution of the chromium tanning agent.

## 4 Reagents

All reagents used shall have at least analytical grade purity.

**4.1 Deionised water**, freshly prepared according to ISO 3696, grade 3.

**4.2 Phosphoric acid solution,** 700 ml *o*-phosphoric acid ($\rho$ = 1,71 g/ml[1)]) made up to 1 000 ml with water (4.1).

**4.3 Chromium (VI) stock solution [1 mg Cr(VI)/ml]**. Potassium dichromate, ($K_2Cr_2O_7$), is dried (16 ± 2) h at (102 ± 2) °C. Dissolve 2,829 g of the dried potassium dichromate in water into a 1 000 ml volumetric flask and make up to the mark with water (4.1).

**4.4 Chromium (VI) standard solution I [10 µg Cr(VI)/ml]**. Pipette 10 ml of the chromium (VI) stock solution into a 1 000 ml volumetric flask and make up to the mark with water (4.1).

**4.5 Glacial acetic acid**.

1) $\rho$ = mass concentration

**4.6 Diphenylcarbazide solution**. Dissolve 1,0 g of 1,5-diphenylcarbazide, $CO(NHNHC_6H_5)_2$, in 100 ml acetone and make acidic with one drop of glacial acid. The solution may be stored in a brown flask with stopper (5.3) in a refrigerator at approximately 4 °C for one week.

**4.7 *n*-Hexanol**.

**4.8 Sodium chloride**.

**4.9 Acetone**.

## 5 Apparatus

Usual laboratory equipment and, in particular, the following.

**5.1 Volumetric flasks**.

**5.2 Pipettes**.

**5.3 Brown coloured flask with stopper**, 100 ml.

**5.4 Separation funnel**, 100 ml.



**5.5 Horizontal mechanical shaker**, capable of 250 r/min shaking speed.

**5.6 Analytical balance**.



**5.7 Spectrophotometer**, capable of measuring the absorbance at wavelength 540 nm.

**5.8 Photometric cell**, 20 mm path length or any other suitable cell length.

## 6 Sampling and sample preparation

The chromium tanning agent shall be homogenized carefully prior to the collection of a representative sample.

NOTE Solid samples are used in the powdered state, if possible. Otherwise they are to be ground.

The analytical solution of the chromium tanning agent shall be used immediately after preparation.

## 7 Determination of chromium (VI) content using the standard addition procedure

### 7.1 General

Tanning agents usually have an unknown reductive potential. Therefore, the first added amounts of chromium (VI) have to be sufficiently high. Typical starting amounts for the first steps of standard additions are 60 µg chromium (VI) and 40 µg chromium (VI) (4.4).

### 7.2 Procedure

Each concentration level may be prepared separately and without any delay.

Weigh 1,000 g ± 0,001 g of chromium tanning agent for each concentration level (in total at least 4 levels) in separate 50 ml volumetric flasks. Dissolve the tanning agent in a small amount of water (4.1) before adding 60 µg, 40 µg, 30 µg and 20 µg chromium (VI) (4.4) and fill up with water to 50 ml.

Pipette 25 ml of the obtained solution in a 100 ml separation funnel. Add 0,5 ml of phosphoric acid solution (4.2) and 0,5 ml of diphenylcarbazide solution (4.6) and shake the funnel several times by hand. After at least 5 min, add approximately 3 g of sodium chloride (to improve the phase separation) and approximately 5 ml of *n*-hexanol to the separation funnel.

Shake the separation funnel for an additional 5 min (approximately) at 250 r/min in a horizontal shaker (5.5). Allow the separation funnel to stand for 2 min to 3 min to allow phase separation. Transfer the organic phase into a 25 ml volumetric flask *(first extraction)*.

Using the aqueous phase, repeat the extraction with approximately 5 ml of fresh *n*-hexanol as described above after addition of 0,5 ml of the solution of diphenylcarbazide *(second extraction).*

If the extract after a third extraction is not coloured red-purple, the extraction may be terminated. If not, the extraction shall be continued.

Make up the organic phases collected in the volumetric flask to 25 ml with *n*-hexanol. Measure the absorbance at 540 nm, 10 min after the end of extraction procedure, using the spectrophotometer (5.7) and the photometric cell (5.8). Use *n*-hexanol for the photometric cell of the reference beam.

The procedure as described shall be repeated with each concentration level of the added chromium (VI).

In the case of chromium tanning agents with an enhanced amount of reducing substances the standard addition has to be carried out with an increased amount of chromium (VI). To avoid dilution effects caused by adding high amounts of chromium (VI) stock solution, stock solutions with higher chromium (VI) concentrations shall be used in this case.



## 8 Quality control



The recovery rate of the control sample [15 µg chromium (VI)] has to be determined daily. The control sample is prepared according to Clause 7, using water as the matrix.

The chromium (VI) content of the calibration control samples is determined using a calibration curve of 5 µg, 10 µg, 20 µg, 25 µg and 35 µg chromium (VI). The calibration levels are prepared according to Clause 7, using water as the matrix.

## 9 Calculation and expression of the results

The absorption values obtained are used to calculate the chromium (VI) content of the chromium tanning agent according to the standard addition procedure.

The determined extinction is plotted against the ratio of the added amount of chromium (VI) to the sample amount.