



Test method for the determination of chromium(VI) in chrome tanning agents

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

Chrome tanning agents consist of chromium sulphate containing additional hydroxyl groups in different amounts. They exhibit a reductive potential, and 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".

FILK-QMA 2026 - Method for the determination of chromium(VI) in chrome tanning agents

1. SCOPE

This method describes a procedure for the determination of chromium(VI) content in chrome tanning agents.

2. REFERENCES

- ISO 3696 Water for analytical laboratory use; Specification and test methods
- ISO 17075 Leather – Chemical tests – Determination of chromium(VI) content

3. PRINCIPLE

The chrome tanning agent is solved in water. After reaction with 1,5-diphenylcarbazide the resulting complex is extracted using n-hexanole. The concentration of the complex in the extract is determined by photometry at 540 nm.

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

4. CHEMICALS

All reagents used shall have at least analytical grade purity.

- 4.1 Phosphoric acid solution: 700 ml o-phosphoric acid ($\rho = 1.71 \text{ g/ml}$) made up to 1000 ml with distilled water.
- 4.2 Chromium(VI) stock solution (1mg Cr/ml): Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) is dried $16 \pm 2 \text{ h}$ at $102 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$. 2.829g of the dried potassium dichromate is dissolved in water in a volumetric flask and made up to 1000 ml with water.
- 4.3 Chromium(VI) standard solution I (10 $\mu\text{g Cr/ml}$): 10 ml of the chromium(VI) stock solution is pipetted in a 1000 ml volumetric flask and made up to the mark with water.

- 4.4 Chromium(VI) standard solution II (1 $\mu\text{g Cr/ml}$): 1 ml of the chromium(VI) stock solution is pipetted in a 1000 ml volumetric flask and made up to the mark with water.
- 4.5 Glacial acid
- 4.6 Diphenylcarbazide solution: 1.0g 1,5-diphenylcarabazide $\text{CO}(\text{NHNHC}_6\text{H}_5)_2$ is dissolved in 100 ml acetone and made acidic with one drop of glacial acid.
- 4.7 n-Hexanole
- 4.8 Sodium chloride
- 4.9 Distilled water of grade 3 (ISO 3696)

5. APPARATURES

- 5.1 Volumetric flask 25 ml, 50 ml, 100 ml
- 5.2 Pipettes 0.5 and 5 ml
- 5.3 Brown flask with stopper 100 ml
- 5.4 Separation funnel 100 ml
- 5.5 Horizontal mechanical shaker
- 5.6 Spectrophotometer or filterphotometer, wavelength 540 nm
- 5.7 Photometric cell, 2 cm length or any other suitable cell length

6. PROCEDURE

- 6.1 Basic Information: The determination of chromium(VI) in chrome tanning agents has to be carried out twice and independently for each sample. The analytical solution of the chrome tanning agent has to be used immediately after preparation.
- 6.2 Sampling and preparation of samples: The chrome tanning agent has to be homogenized carefully prior to the collection of a representative sample. Solid samples should be used in the powdered state if possible. Otherwise they should be ground.
- 6.3 Determination of chromium (VI) content
 - 6.3.1 *Determination of the zero-value:* $1 \pm 0.001 \text{ g}$ of chrome tanning agent is weighted in a 50 ml volumetric flask. The tanning agent has to be dissolved in a small amount of water before making up with water. This solution must be freshly made up for every determination. From the solution obtained, 25 ml are pipetted in a 100 ml separation funnel.

After addition of 0.5 ml phosphoric acid and 0.5 ml of diphenylcarbazide solution, the funnels have to be shaken slightly. After 5 minutes, 3 g of sodium chloride and 5 ml n-hexanole are added. The closed separation funnel has to be rotated for an additional 5 minutes at 250 rpm horizontally. The separation funnel is then stored for 2 to 3 minutes to reach phase separation. The organic phase has to be transferred into a 25 ml volumetric flask. The aqueous phase will be used to repeat the extraction with 5ml fresh n-hexanole as described after addition of 0.5 ml phosphoric acid and 0.5 ml of the solution of diphenylcarbazide (second extraction).



If the extract after a third extraction is not coloured red-purple the extraction can be terminated. If not, the extraction has to be continued.

The organic phases collected in the volumetric flask are made up to 25 ml with n-hexanole. The absorbance is measured at 540 nm 10 minutes after the end of extraction using spectrophotometer (5.6) and the photometric cell (5.7).

6.3.2 Determination of chromium (VI) using the standard addition procedure: 1 ± 0.001 g of a new sample of chrome tanning agent is weighted in a 50 ml volumetric flask in each case and solved with water. Before filling up with water to 50 ml, 60 µg chromium(VI) (chromium(VI) standard solution 4.3) is added. 25 ml of the obtained solution are pipetted in a 100 ml separation funnel. The extraction has to be carried out as described in 6.3.1

Repeat the procedure described in 6.3.2 with the following standard addition amounts: 50 µg, 40 µg, 30 µg and 20 µg.

(NOTE: In the case of a chrome tanning agent 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 cause by adding high amounts of chromium(VI) stock solution, stock solutions with higher chromium(VI) concentrations should be used in this case.)

7. QUALITY CONTROL

A control sample has to be determined daily. The procedure has to be carried out as described in part 6 using water as matrix and the amounts of chromium(VI) as previously used. The correlation coefficient has to reach a value of at least 0.999.

8. CALCULATION AND EXPRESSION OF RESULTS

The absorption values obtained are used to calculate the chromium (VI) content of the chrome tanning agent according to the standard addition procedure. The graph produced has to be checked regarding its linearity. The linear regression model has to describe the graph sufficiently.

Because of the reducing potential of the chrome tanning agent, it is possible that the lowest measured values are not laying on the linear graph because the chromium(VI) added is reduced. These values are excluded from the calculation of the linear equation graph. A value will be excluded if the correlation coefficient of the equation is lower than 0.90.

The graph is detailed as follows:

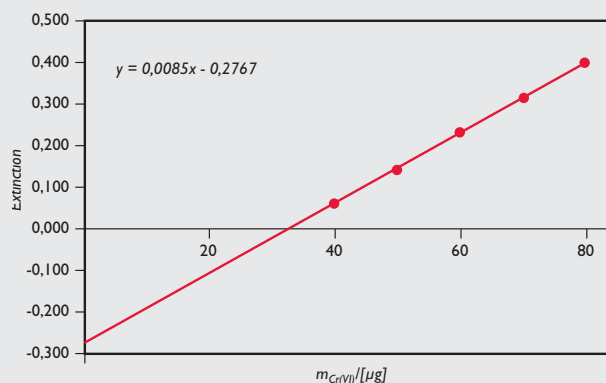
- If the correlation coefficient is higher than 0.90 no value has to be excluded.
- If the correlation coefficient is equal or lower than 0.90 the value without adding chromium(VI) stock solution (zero value) is excluded first and the calculation is repeated.
- If the correlation coefficient is still equal or lower than 0.90 further values are eliminated step by step beginning with the value for lowest addition of chromium(VI) stock solution.

The calculation of the content of chromium(VI) of the chrome tanning agent is described with the following equation

$$W_{Cr(VI)} = \frac{a}{b} + \frac{1}{m}$$

- $W_{Cr(VI)}$ Chromium(VI) of chrome tanning agent in mg/kg, to the nearest 0.1 mg/kg
 a constant value of the graph
 b gradient of the graph in 1/µg
 m amount of chrome tanning agent in g

Panel I: Determination of the chromium(VI) content of a chrome tanning agent with reductive potential



9. TEST REPORT

If the result of the calculation (8) is positive, the chrome tanning agent contains chromium(VI). This value has to be given in the test report as content of chromium(VI).

If the result of the calculation (8) is negative, the value describes the reductive potential of the chrome tanning agent. In this case the negative value has to be given in the test report including the following sentence: "The chrome tanning agent shows a reductive potential."

The test report shall include the following information:

- Average of the single determinations of content of chromium(VI),
- the results obtained to the nearest 0.1 in mg/kg,
- a reference to this document,
- a description of the sample tested,
- cell length used e.g. 2 cm,
- details of any deviation from the procedure. ☹

Legend

- The procedure was developed using chrome tanning agents containing different reducing compounds such as molasses or sulphur dioxide. Verified employed chrome tanning agents free of chromium(VI) and containing chromium(VI).
- Several experiments were carried out to select the extraction solvent. The extraction solvent has to ensure the separation of the organic and inorganic phase and to solve the reaction product of 1,5-diphenylcarabzide and chromium(VI). n-Hexanol was preferred since n-pentanol has toxic properties. The best extraction results were obtained if the aqueous phase is set acid at first. Consequently 1,5-dinitrophenylhydrazine is added. It means the reaction between chromium(VI) and 1,5-dinitrophenylhydrazin takes place in the aqueous phase. The extraction has to begin immediately and has to be carried out until the extract turns colourless.
- The solutions of the chrome tanning agents have to be prepared freshly since they are unstable over a long period of storage e. g. 4 hours.

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