SLOVENSKI STANDARD
SIST-TS CEN/TS 14494:2004

01-maj-2004

Usnje ï Kemiļ ni preskusi ï Doloļ evanje pentaklorofenola v usnju

Leather - Chemical tests - Determination of the content of pentachlorophenol in leather

Leder - Chemische Prüfungen - Bestimmung des Gehalts an Pentachlorphenol in Leder

Cuir - Essais chimiques - Détermination de la teneur en pentachlorophénol du cuir

Ta slovenski standard je istoveten z: **CEN/TS 14494:2003**

ICS:

59.140.30 Usnje in krzno Leather and furs

SIST-TS CEN/TS 14494:2004 **English language**

TECHNICAL SPECIFICATION
SPÉCIFICATION TECHNIQUE
TECHNISCHE SPEZIFIKATION

CEN/TS 14494

March 2003

ICS 59.140.30

English version

Leather – Chemical tests – Determination of the content of pentachlorophenol in leather

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.

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Ref. No. CEN/TS 14494:2003 E

Contents

Foreword

This document (CEN/TS 14494:2003) has been prepared by CEN/TC 289, "Leather" the Secretariat of which is held by UNI.

It is based on the English translation of *DIN 53313 Draft 1999* and describes a procedure where PCP is acetylated before the chromatographic detection and the amount of the detected PCP acetate is quantified via an internal standard correction.

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

Annex A is informative.

1 Scope

This Technical Specification specifies a method for determining the content of pentachlorophenol (PCP), its salts and esters in leather.

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).

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)

3 Principle

First of all the leather is submitted to steam distillation.

After extraction into *n*-hexane the PCP is acetylated by acetic anhydride and the PCP acetates analysed by gas chromatography with an ECD detector. Quantification is performed by an external standard and correction made with an internal standard.

4 Definitions

The concentration of pentachlorophenol can consist of free pentachlorophenol, its salts and esters. PCP is detected gas-chromatographically as it's derivative, PCP acetate. The PCP content is given in mg/kg sample.

5 Apparatus and auxiliary devices

5.1 Gas chromatograph with ECD or MSD

5.2 Analytical balance weighting to an accuracy of 0,1 mg

5.3 Suitable apparatus designed for steam distillation

5.4 Shaking machine

5.5 Volumetric flasks 500 ml, 50 ml

5.6 Erlenmeyer flask 100 ml

5.7 Separating funnel 250 ml

5.8 Pasteur-pipette, graduated pipette, suitable autopipette

6 Chemicals

Unless otherwise specified, analytical grade chemicals should be used. Water must be distilled or deionised, Grade 3 in accordance with EN ISO 3696:1995.

6.1 Stock solutions

6.1.1 Pentachlorophenol, 100 µg/ml in acetone

6.1.2 PCP acetate 10 µg/ml in *n*-hexane

6.1.3 PCP acetate Standard 0,04 mg/l PCP acetate (corresponds to 0,0346 mg PCP/l) in *n*-hexane

6.1.4 Tetrachloroguajacol TCG (Tetrachloromethoxyphenol) 100 µg/ml in acetone, marker and internal standard, melting point 118 °C - 119 °C

6.2 Sulphuric acid, 1M

6.3 *n*-hexane for residue analysis

6.4 Potassium carbonate, K_2CO_3

6.5 Acetic anhydride, $C_4H_6O_3$

6.6 Molecular sieve 10-20 mesh beads, pore diameter 0,3 nm. Or anhydrous sodium sulphate

6.7 Distilled water in accordance with Grade 3 of EN ISO 3696:1995.

6.8 Triethylamine

6.9 Acetone

7 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 weighing.

8 Procedures

8.1 Steam-distillation

Approximately 1,0 g of the leather sample is weighed accurately into the distillation vessel (5.3) and 20 ml 1M sulphuric acid (6.2) and 0,1 ml TCG stock-solution (6.1.4) are added. The content of the vessel is submitted to a steam distillation by using a suitable steam distillation apparatus. A 500 ml volumetric flask (5.5) with 5 g K_2CO_3 (6.4) is used as a receiver.

About 450 ml are distilled. Make up to volume with water.

In the case of extreme foaming the heat source should be reduced.

8.2 Liquid-Liquid Extraction and acetylation

100 ml of the distillate obtained in 8.1 is transferred into a 250 ml separating funnel (5.7).

20 ml *n*-hexane (6.3) and 1,5 ml acetic anhydride (6.5) and 0,5 ml triethylamine (6.8) are added to the solution and shaken for 30 minutes vigorously on a mechanical shaker (see NOTE).

After phase separation the organic layer is transferred to a 100 ml conical flask (5.6) and the aqueous layer is shaken again with 20 ml *n*-hexane.

The combined *n*-hexane extracts are dehydrated, with either molecular sieves or anhydrous sodium sulphate (6.6) in a 100 ml conical flask (5.6) for about 10 min.

Afterwards the *n*-hexane extract is decanted quantitatively under washing with *n*-hexane into a 50 ml volumetric flask (5.5).

It is made up to volume with *n*-hexane.

This solution is analysed by GC (5.1).

NOTE The derivatisation step is a two-phase-reaction and depends very strongly on the intensity of shaking. Use a suitable mechanical shaker with a high shaking frequency. Do not try to shake by hand because this will produce incorrect results.

8.3 Preparation of calibration mixture for acetylated PCP and TCG

8.3.1 Derivatisation of PCP and TCG Standard for recovery rate

To calculate the recovery, a PCP / TCG standard mixture is prepared like the sample.

Therefore 100 µl of stock-solution (6.1.1) and 100 µl TCG (6.1.4) is measured into the distillation vessel together with 20 ml sulphuric acid (6.2). This solution is treated in the same way as the sample.

NOTE The recovery rate shall be higher than 90 %.

8.3.2 PCP acetate Standard (External standard)

In addition a PCP acetate Standard (6.1.3) is analysed directly by gas-chromatography. The final concentration for the GC is 0,04 mg/l PCP acetate.

This standard is included in the calculation.

8.3.3 Derivatisation of TCG-Standard

20 µl of the TCG-solution (6.1.4) are acetylated in 30 ml of 0,1 M/l K_2CO_3 in the same way as the sample and the organic layer is transferred into a 50 ml volumetric flask (5.5).

A TCG-Standard is analysed in the same way as the sample.

8.4 Capillary Gas Chromatography (GC)

The described chromatographic conditions are only examples.

Capillary column:	fused quartz, (medium polarity) e.g. 95 % dimethyl-5 % diphenylpolysiloxane, length 50 m, inner diameter: 0,32 mm, film thickness: 0,25 µm
Detector/detector temperature:	ECD / 280 °C
Injection system:	split / splitless 60 seconds
Injection volume:	2 µl

Injector temperature:	250 °C
Carrier gas:	Helium
Make up gas:	Argon (95 %) / Methane (5 %)
Temperature Programme:	80 °C (1 min)
	6 °C/min ——> 280 °C (10 min)

9 Expression of results

The areas of the single peaks will be compared with the areas of the standard which are analysed at the same time and calculated.

The PCP concentration is calculated as a mass portion M in mg/kg leather sample according to the following equation:

$$M_{PCP} = \frac{A_{PCP} \cdot C_{PCPSt} \cdot V \cdot \beta \cdot F_{TCG}}{A_{PCPSt} \cdot E}$$

$$F_{TCG} = \frac{A_{TCG}\,calibration}{A_{TCG}\,Sample}$$

A = Peak area

C = Concentration PCP-Standard µg/ml (6.1.3) (0,04 mg PCP acetate is equivalent to 0,0346 mg free PCP)

E = Weight of sample in g

V = final sample volume in ml

ß = Dilution rate

F = Factor internal Standard (TCG)

Indices: PCPSt= Pentachlorophenol Standard

TCG: Internal Standard

10 Test report

The test report shall include the following:

a) reference to this Technical Specification;

b) type, origin and designation of the analysed leather sample and the sampling method used;

c) the analytical result for PCP content in mg/kg rounded to one decimal place;

d) any deviations from the analytical procedure;

e) date of the test.