INTERNATIONAL STANDARD

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Leather — Chemical tests — Determination of tetrachlorophenol-, trichlorophenol-, dichlorophenol-, monochlorophenol-isomers and pentachlorophenol content

Cuir — Essais chimiques — Détermination de la teneur en isomères de monochlorophénol, dichlorophénol, trichlorophénol, tétrachlorophénol et en pentachlorophénol

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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

ISO 17070 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 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.

This second edition of ISO 17070 cancels and replaces the first edition (ISO 17070:2006), which has been technically revised. ISO 17070:2006 previously replaced CEN/TS 14494.

The following changes have been made:

— the additional chlorinated phenol substances tetrachlorophenol-, trichlorophenol-, dichlorophenol-, and monochlorophenol-isomers are included;

— a new Clause 3 has been inserted to list the chlorophenol abbreviations;

— the examples of chromatographic conditions, previously in 7.4, have been moved to a new Annex A (the previous Annex A becomes Annex B).

Annexes A and B are informative.

Introduction

This International Standard describes a procedure where the chlorinated phenols (CP) are acetylated before the chromatographic detection and the amount of the detected chlorinated phenyl acetate is quantified via an internal standard correction.

Leather — Chemical tests — Determination of tetrachlorophenol-, trichlorophenol-, dichlorophenol-, monochlorophenol-isomers and pentachlorophenol content

1 Scope

This International Standard specifies a method for determining the content of tetrachlorophenol-, trichlorophenol-, dichlorophenol-, monochlorophenol-isomers, and pentachlorophenol, its salts, and esters in leather.

NOTE Bromophenol isomers can also be determined using this method.

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 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 Abbreviations

The following abbreviations are used for chlorinated phenols in this International Standard:

CP chlorinated phenols

DiCP dichlorophenol

MoCP monochlorophenol

PCP pentachlorophenol

TCG tetrachloroguaiacol (tetrachloro-*o*-methoxyphenol)

TeCP tetrachlorophenol

TriCP trichlorophenol

4 Principle

First of all, the leather sample is submitted to steam-distillation.

After extraction into *n*-hexane, the chlorinated phenols (CP) are acetylated by acetic anhydride and the chlorinated phenyl acetates are analysed by gas-chromatography with an electron capture detector (ECD) or mass selective detector (MSD). Quantification is performed by an external standard and a correction made with an internal standard.

5 Apparatus

5.1 Gas chromatography (GC), with ECD or MSD detector.

5.2 Analytical balance, weighing to an accuracy of 0,1 mg.

5.3 Suitable apparatus designed for steam distillation.

5.4 Shaking machine, capable of at least 200 cycles per minute.

5.5 Volumetric flasks, 500 ml and 50 ml.

5.6 Erlenmeyer (conical) flask, 100 ml.

5.7 Separating funnel, 250 ml, or **suitable vessel that allows separation of organic and aqueous phases**, that can be sealed for vigorous shaking.

5.8 Pasteur-pipettes, graduated pipettes, suitable auto-pipettes.

5.9 Strainer with paper filter, grade 4, diameter 125 mm.

6 Reagents

Unless otherwise specified, analytical grade chemicals should be used. Water shall be distilled or deionized, Grade 3 in accordance with ISO 3696.

6.1 Chlorinated phenol mix

A mix of the chlorinated phenols which contains the following isomers at a concentration of 100 µg/ml in acetone.

2-Chlorophenol	CAS[1)]-Number: 95–57–8
3-Chlorophenol	CAS-Number: 108–43–0
4-Chlorophenol	CAS-Number: 106–48–9
2,3-Dichlorophenol	CAS-Number: 576–24–9
2,4-Dichlorophenol	CAS-Number: 120–83–2
2,5-Dichlorophenol	CAS-Number: 583–78–8
2,6-Dichlorophenol	CAS-Number: 87–65–0
3,4-Dichlorophenol	CAS-Number: 95–77–2
3,5-Dichlorophenol	CAS-Number: 591–35–5
2,3,4-Trichlorophenol	CAS-Number: 15950–66–0
2,3,5-Trichlorophenol	CAS-Number: 933–78–8
2,3,6-Trichlorophenol	CAS-Number: 933–75–5

1) CAS Chemical Abstracts Service.

2,4,5-Trichlorophenol	CAS-Number: 95–95–4
2,4,6-Trichlorophenol	CAS-Number: 88–06–2
3,4,5-Trichlorophenol	CAS-Number: 609–19–8
2,3,4,5-Tetrachlorophenol	CAS-Number: 4901–51–3
2,3,4,6-Tetrachlorophenol	CAS-Number: 58–90–2
2,3,5,6-Tetrachlorophenol	CAS-Number: 935–95–5
Pentachlorophenol	CAS-Number: 87–86–5

NOTE This chlorinated phenol mix is available from laboratory chemical suppliers.

6.2 Tetrachloroguaiacol (TCG) (tetrachloro-*o*-methoxyphenol), at a concentration of 100 µg/ml in acetone (internal standard), melting point 118 °C to 119 °C.

6.3 Sulfuric acid, 1 mol/l.

6.4 *n*-hexane, for residue analysis.

6.5 Potassium carbonate, K_2CO_3.

6.6 Acetic anhydride, $C_4H_6O_3$.

6.7 Anhydrous sodium sulphate.

6.8 Distilled water, in accordance with Grade 3 of ISO 3696.

6.9 Triethylamine.

6.10 Acetone.

7 Sampling and preparation of samples

If possible, sample in accordance with ISO 2418. Cut the leather sample into small pieces or grind the leather in accordance with ISO 4044. The dimensions of the pieces shall not be larger than 2 mm to 3 mm. 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.

8 Procedure

8.1 Steam-distillation

Accurately weigh approximately 1,0 g of the leather sample into the distillation vessel (5.3). Add 20 ml of 1 mol/l sulfuric acid (6.3) and 100 µl of the TCG stock solution (6.2). Submit the contents of the vessel to a steam distillation by using a suitable steam distillation apparatus. Use a 500 ml volumetric flask (5.5) with 5 g K_2CO_3 (6.5) to collect the distillate.

Distill about 450 ml. Make up to volume (500 ml) with distilled water (6.8).

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

8.2 Liquid-liquid-extraction and acetylation

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

8.2.2 Add 20 ml *n*-hexane (6.4), 0,5 ml triethylamine (6.9), and 1,5 ml acetic anhydride (6.6) to the solution and shake for 30 min on a mechanical shaker (5.4) with a shaking rate of at least 200 shakes per min.

CAUTION — This step shall be carried out in a well-ventilated area or fume cupboard.

NOTE The derivatization 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 (at least 200 cycles/min). Do not try to shake by hand because this will produce inconsistent results. Pressure compensation should be carried out before fixing the separating funnel (5.7) to the mechanical shaker (5.4).

8.2.3 After phase separation, transfer the organic layer to a 100 ml conical flask (5.6) and shake the aqueous layer for a further 30 min with an additional 20 ml of *n*-hexane.

8.2.4 Dehydrate the combined *n*-hexane extracts by adding anhydrous sodium sulfate (6.7) to the flask (5.6) and leaving to stand for approximately 10 min.

8.2.5 Filter (5.9) the *n*-hexane extract quantitatively, washing with *n*-hexane into a 50 ml volumetric flask (5.5).

8.2.6 Make up to volume (50 ml) with *n*-hexane.

8.2.7 Analyse this solution by one of the gas chromatographic methods (5.1).

8.3 Preparation of calibration mixture for acetylated CP and TCG

8.3.1 Derivatization of chlorinated phenol mix and TCG standard for recovery rate

To calculate the recovery, prepare a CP/TCG standard mixture like the sample.

Measure 100 µl of the chlorinated phenol mix solution (6.1) and 100 µl TCG (6.2) into the distillation vessel together with 20 ml sulfuric acid (6.3). Treat this solution in the same way as the sample.

The recovery rate shall be higher than 90 %.

8.3.2 Chlorinated phenol mix (external standard)

Acetylate 20 µl of the chlorinated phenol mix solution (6.1) and 20 µl TCG-solution (6.2) in 30 ml of 0,1 mol/l K_2CO_3 in the same way as the sample (8.2.2 – 8.2.7) and transfer the organic layer into a 50 ml volumetric flask (5.5) and fill up to volume with *n*-hexane.

The final concentration for the GC is 0,04 µg/ml per compound.

This standard is included in the calculation.

NOTE This final concentration is suitable for CP concentrations of 5 mg/kg or more in leather. For determining lower concentrations of CP in leather, the final concentration of the external standard should be proportionally reduced.

8.4 Gas chromatography (GC)

Various types of gas chromatographic equipment can be used. The chromatographic conditions given in Annex A are examples of parameters that have been successfully used for this analysis. Annex B gives results for the reliability of the method.

9 Expression of results

Compare the areas of the single peaks with the areas of the standard which are analysed simultaneously and calculated.

Calculate the CP concentration as a mass fraction, w_{CP}, in milligrams per kilogram (mg/kg) of the leather sample, according to the following formula:

$$w_{CP} = \frac{A_{CP-S} \cdot c_{CP-St} \cdot A_{TCG-St} \cdot V \cdot \beta}{A_{CP-St} \cdot A_{TCG-S} \cdot m} \quad (1)$$

where

A_{CP-S} is the peak area of the sample;

A_{CP-St} is the peak area of the CP standard;

A_{TCG-S} is the peak area of the internal standard (TCG) in the sample;

A_{TCG-St} is the peak area of the internal standard (TCG) in the standard;

c is the concentration of the chlorinated phenol in the calibration standard in micrograms per millilitre, µg/ml (8.3.2);

m is the mass of the sample in grams, g;

V is the final sample volume in millilitres, ml;

β is the dilution factor.

Results based on dry matter:

$$w_{CP-dry} = w_{CP} \cdot D \quad (2)$$

where

D is the factor for conversion to dry matter: $D = 100/(100 - w)$;

w is the volatile matter determined using ISO 4684.

10 Test report

The test report shall include the following information:

a) a reference to this International Standard, i.e. ISO 17070;

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

c) the analytical result for each CP in milligrams per kilogram (mg/kg) rounded to one decimal place;

d) any deviations from the analytical procedure;

e) the date of the test.

