SLOVENSKI STANDARD
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Tekstilije in tekstilni izdelki - Določevanje biocidnega dodatka - 2. del: Konzervansi na osnovi klorofenola, metoda z uporabo plinske kromatografije

Textiles and textile products - Determination of biocide additives – Part 2, Chlorophenol-based preservatives, method using gas chromatography

Textilien und textile Erzeugnisse - Bestimmung von Biozid-Zusatzstoffen - Teil 2: Konservierungsmittel auf Chlorphenolbasis, Verfahren mittels Gaschromatographie

Textiles et produits textiles - Détermination des additifs biocides - Partie 2 : Conservateurs à base de chlorophénol, méthode par chromatographie en phase gazeuse

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Textiles and textile products - Determination of biocide additives - Part 2, Chlorophenol-based preservatives, method using gas chromatography

Textilien und textile Erzeugnisse - Bestimmung von Biozid-Zusatzstoffen - Teil 2: Konservierungsmittel auf Chlorphenolbasis, Verfahren mittels Gaschromatographie

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
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Contents

Page

European foreword

This document (prEN 17134-2:2021) has been prepared by Technical Committee CEN/TC 248 “Textiles and textile products”, the secretariat of which is held by BSI.

This document is currently submitted to the CEN Enquiry.

This document will supersede EN 17134:2019.

Introduction

In Europe, according to REGULATION (EU) 2019/1021[1] of the European Parliament and of the Council of 20 June 2019 on persistent organic pollutants pentachlorophenol (PCP) and its salts and esters as constituents of articles are prohibited. According to COMMISSION DELEGATED REGULATION (EU) 2021/277 of 16 December 2020 amending Annex I to Regulation (EU) 2019/1021 of the European Parliament and of the Council on persistent organic pollutants as regards pentachlorophenol and its salts and esters, articles containing PCP in concentrations equal or lower than 5 mg/kg are allowed.

Further chlorinated phenols are restricted by voluntary specifications (ecolabel criteria, industry initiatives and standards).

This document specifies a method in which chlorophenols (CP) are acetylated before chromatographic detection and the amount of detected chlorophenol acetate is quantified by a correction with an internal standard.

WARNING - The use of this document involves hazardous materials. It does not purport to address all of the safety or environmental problems associated with its use. It is the responsibility of users of this document to take appropriate measures to ensure the safety and health of personnel and the environment prior to application of the document, and fulfil statutory and regulatory requirements for this purpose.

1 Scope

This document specifies a method to determine the content of free pentachlorophenol (PCP), and tetrachlorophenol- (TeCP), trichlorophenol- (TriCP), dichlorophenol- (DiCP), monochlorophenol- (MoCP) isomers. The procedure also releases chlorophenols from salts and esters. The method is applicable to natural and synthetic textiles, including coated fabrics and clothing components (e.g. buttons, zippers, etc.).

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

<std>ISO 3696, *Water for analytical laboratory use — Specification and test methods*</std>

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 Abbreviations

The following abbreviations are used in this document for chlorophenols:

CP	chlorophenols
MoCP	monochlorophenol
DiCP	dichlorophenol
TriCP	trichlorophenol
TeCP	tetrachlorophenol
PCP	pentachlorophenol
2-MoCP-d4	2-chlorophenol-d_4
2,3-DiCP-d3	2,3-dichlorophenol-d_3
TeCP-13C6	2,3,4,6-tetrachlorophenol-$^{13}C_6$
PCP-C13	pentachlorophenol-$^{13}C_6$
TCG	tetrachloroguaiacol (= tetrachloro-*o*-methoxyphenol)

The following abbreviations are used in this document for the designation of textile fibres:

CO	cotton
PES	polyester
CV	viscose
EL	elastane
LI	linen
PA	polyamide

5 Principle

The sample is extracted with a potassium hydroxide solution (KOH solution) for 16 h at 90 ° C.

During subsequent extractive derivatization with *n*-hexane and acetic acid anhydride, CPs are acetylated and the chlorinated acetates are analyzed using gas chromatography with a mass-selective detector (MSD). The quantitative determination is made by correction with ^{13}C and ^{2}H labelled internal standards. For pentachlorophenol, the ^{13}C derivative of PCP is used, for tetrachlorophenols the ^{13}C derivative of 2,3,4,6-tetrachlorophenol, for tri- and dichlorophenols 2,3-dichlorophenol-d_3 and for monochlorophenols 2-chlorophenol-d_4. TCG serves as an internal standard for injection control.

6 Apparatus

6.1 Gas chromatograph (GC), with mass selective detector (MSD).

6.3 Heating block, sand bath or drying cabinet, suitable for a temperature of 90 °C ± 1 °C in the KOH solution.

6.4 Gas-tight glass vials, for example headspace vials, (20 ml) .

6.5 GC vials, about 2 ml.

6.6 Pasteur pipettes, graduated pipettes, suitable autopipettes

6.7 Vortex shaker

6.8 Horizontal shaker, capable of at least 200 min^{-1}

7 Reagents

7.1 General

Unless otherwise stated, chemicals of analytical grade shall be used.

7.2 Chlorophenol mixture Stock solution

A mixture of chlorophenols which, at a concentration of 50 µg/ml in a suitable solvent (for example

Acetonitrile) contains the following isomers:

2-chlorophenol	CAS 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
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-tetrachlorphenol	CAS number: 935-95-5
pentachlorophenol	CAS number: 87-86-5

NOTE This mixture of chlorophenols is available from laboratory chemical suppliers.

7.3 Tetrachloroguaiacol (tetrachloro-*o*-methoxyphenol) CAS number: 2539-17-5

7.4 Isotope labelled internal standards

2-chlorophenol-d_4	CAS number: 93951-73-6
2,3-dichlorophenol-d_3	CAS number: 93951-74-7
2,3,4,6-tetrachlorophenol-$^{13}C_6$	CAS number:1246820-81-4
pentachlorophenol-$^{13}C_6$	CAS number: 85380-74-1

Instead of the isotope-labelled derivatives of tetra-, di- and monochlorophenol mentioned, other isotope-labelled analogues of the same chlorination levels, e.g. 4-chlorophenol-d_4, may also be used as internal standards.

7.5 *n*-Hexane, for residue analysis.

7.6 Potassium hydroxide solution (KOH), aqueous solution (1 mol/l).

Weigh 56,1 g KOH into a 1 l volumetric flask and dissolve with 100 ml water (7.12) (caution: heat generation!). After cooling, fill up to 1 l with water (7.12).

7.7 Tetrachloroguiacol (TCG) solution, at a concentration of 1 µg/ml in acetonitrile (internal standard for injection control)

Dissolve 10 mg TCG in 100 ml acetonitrile (7.14). Take 1,0 ml from this stock solution and dilute to 100 ml with acetonitrile (7.14).

7.8 Stock solution isotope-labelled internal standards in KOH solution, each 0,1 mg/ml

Dissolve 10 mg of each isotope-labelled internal standard (7.4) in 100 ml KOH solution (7.6).

7.9 Extraction solution (containing isotope-labelled internal standards)

1,0 ml stock solution isotope-labelled internal standards (7.8) is filled up with KOH solution (7.6) in a 1 l volumetric flask, the concentration of each of the isotope-labelled internal standards (7.4) is 0,1 µg/ml .

The concentration of isotope-labelled internal standards shall be adapted to the respective calibration range of the chlorophenols (see solutions 7.15 to 7.19). If a more sensitive measuring instrument is used and the calibration is lowered, then the concentration of isotope-labelled internal standards in the KOH solution should also be reduced.

7.10 Potassium carbonate (K_2CO_3), aqueous solution (0,1 mol/l).

Weigh 13,82 g K_2CO_3 into a 1 l volumetric flask, dissolve with water (7.12) and fill up to 1 l.

7.11 Acetic anhydride ($C_4H_6O_3$), for analysis.

7.12 Water, grade 3, according to ISO 3696.

7.13 Acetone

7.14 Acetonitrile

7.15 Working solution calibration level 1, for daily calibration

30 µl stock solution chlorophenol mixture (7.2) is filled up with acetonitrile (7.14) in a 10 ml volumetric flask; the concentration of chlorophenols is 0,15 µg/ml.

7.16 Working solution calibration level 2, for daily calibration

400 µl stock solution chlorophenol mixture (7.2) is filled up with acetonitrile (7.14) in a 10 ml volumetric flask; the concentration of chlorophenols is 2,0 µg/ml.

7.17 Working solution calibration level 3, for daily calibration

800 µl stock solution chlorophenol mixture (7.2) are filled up with acetonitrile (7.14) in a 10 ml volumetric flask; the concentration of chlorophenols is 4 µg/ml.

7.18 Working solution calibration level 4, for daily calibration

600 µl stock solution chlorophenol mixture (7.2) is filled up with acetonitrile (7.14) in a 2 ml volumetric flask; the concentration of chlorophenols is 15 µg/ml.

7.19 Working solution calibration level 5, for daily calibration.

1 000 µl stock solution chlorophenol mixture (7.2) is filled up with acetonitrile (7.14) in a 2 ml volumetric flask; the concentration of chlorophenols is 25 µg/ml.

The concentrations of the calibration solutions (7.15 to 7.19) are examples and should be adjusted according to the specified limit values and the linearity of the device.

8 Sampling

From the material to be examined, a representative test specimen shall be taken and cut into pieces of about 0,5 cm × 0,5 cm.

9 Procedure

9.1 General

If it is only required to test for free mono- and dichlorophenols, the procedure described in Annex C shall be applied.

9.2 Extraction with KOH

Place approximately 1 g (minimum sample weight 0,2 g) of the cut test specimen (to the nearest 0,01 g) in the reaction vessel (6.4). Add 10 ml extraction solution (7.9). After closing, the vessel is transferred to a heating apparatus (6.3) and left for 16 h ± 15 min at (90 ± 1) °C. The temperature in the reaction vessel is checked with extraction solution. If the test specimen to be examined is too voluminous to be

completely covered with KOH solution for the period of extraction, the test specimen shall be weighed down with glass balls or a comparable inert object to ensure complete wetting, or a suitable larger amount of extraction solution shall be added (take into account the different specimen weight to liquor ratio in the calculation).

NOTE Deviations from the specified extraction time and temperature can lead to significant deviations in the result.

9.3 Extractive acetylation

After extraction, the test specimen shall be cooled down to room temperature and shaken vigorously (1 min vortex shaker (6.7) or 10 min horizontal shaker (6.8)). Transfer 4 ml of the KOH extraction solution into a new reaction vessel (6.4) and add 6 ml potassium carbonate solution (7.10), 2 ml *n*-hexane (7.5), 250 µl TCG solution (7.7) and 1 ml acetic acid anhydride (7.11).

After closing the vessel, shake it for 30 min at a shaking rate of at least 200 min^{-1} on a horizontal shaker (6.8). An efficient mixing of the phases shall be ensured.

After shaking, centrifugation may improve phase separation. The vessel is then opened carefully (caution: overpressure!). Transfer an aliquot (for example 1 ml) from the upper phase to a GC vial (6.5) for analysis.

Take 4 ml of extraction solution and add 2 ml of *n*-hexane to reliably detect a value of 0,05 mg/kg chlorophenols. For device configurations that allow lower limits of detection, the volume of extraction solution used for acetylation may be reduced or the amount of *n*-hexane added may be increased. The same volumes shall be used for calibration and test specimens. A validation with the changed conditions shall be executed.

By reducing the weight of the test specimen higher limit values can be covered.

9.4 Derivatization of the chlorophenol mixtures and the TCG standards (calibration for daily use)

100 µl of each chlorophenol working solution (7.15 to 7.19), 4 ml extraction solution (7.9), 6 ml potassium carbonate solution (7.10), 2 ml *n*-hexane (7.5), 250 µl TCG solution (7.7) and 1 ml of acetic acid anhydride (7.11) shall be added into a separate reaction vessel (6.4). After closing the vessel, shake it for 30 min at a shaking rate of at least 200 min^{-1} on a horizontal shaker (6.8). The vessel is centrifuged after shaking and then carefully opened (caution: overpressure!). Transfer an aliquot (for example 1 ml) from the upper phase from each reaction vessel to a GC vial (6.5) for analysis. Depending on the device, a basic calibration is carried out for detection and determination and for the linear working area.

9.5 Gas chromatography (GC)

Various types of gas chromatographic equipment may be used. The chromatography conditions specified in Annex A are an example of parameters that have been successfully applied in the analysis.