
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

Ta slovenski standard je istoveten z: EN 17134-2:2023

ICS:

59.080.01	Tekstilije na splošno	Textiles in general
71.040.50	Fizikalnokemijske analitske metode	Physicochemical methods of analysis

SIST EN 17134-2:2023**en,fr,de**

EUROPEAN STANDARD

EN 17134-2

NORME EUROPÉENNE

EUROPÄISCHE NORM

July 2023

ICS 59.080.01

Supersedes EN 17134:2019

English Version

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

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

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

This European Standard was approved by CEN on 12 June 2023.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the CEN-CENELEC Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN-CENELEC Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Republic of North Macedonia, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Türkiye and United Kingdom.



EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

CEN-CENELEC Management Centre: Rue de la Science 23, B-1040 Brussels

Contents

Page

European foreword.....	4
Introduction	5
1 Scope	6
2 Normative references.....	6
3 Terms and definitions	6
4 Principle	6
5 Reagents	6
6 Apparatus.....	10
7 Preparation of test samples and test specimens	10
8 Procedure.....	10
8.1 Extraction with KOH.....	10
8.2 Acetylation of extracted CPs.....	11
8.2.1 General procedure of acetylation.....	11
8.2.2 Preparation for GC analysis.....	11
8.2.3 Acetylation in case of low recovery rates.....	11
8.3 Acetylation of the calibration standards	11
8.4 Gas chromatography with mass selective detection	11
9 Expression of results.....	11
9.1 General.....	11
9.2 Calculation of the individual chlorophenols	12
9.3 Sum of chlorophenols	12
9.4 Precision of the test method	12
10 Test report.....	12
Annex A (informative) Example of parameters for GC-MS determination of CPs.....	13
A.1 Measuring technique	13
A.2 Chromatographic conditions	13
A.3 MS conditions	13
Annex B (informative) Reliability of the method.....	15
B.1 General.....	15
B.2 Results of interlaboratory trials.....	16
B.2.1 Results of the first interlaboratory trial	16
B.2.2 Results of the second interlaboratory trial from one real test specimen and two spikes of the real test specimen, with 4 laboratories	17
B.3 Influence of standard solutions	24
B.4 Influence of internal standards on the results of pentachlorophenol and other chlorophenols.....	29
Annex C (informative) Test method for free mono- and dichlorophenols	37
C.1 General.....	37

C.2	Reagents	37
C.3	Apparatus	37
C.4	Preparation of test samples	37
C.5	Procedure	37
C.5.1	Extraction and acetylation of extracted CPs	37
C.5.2	Acetylation of the calibration standards	37
C.6	Expression of results	38
C.7	Test report	38
	Bibliography	39

iTeh STANDARD PREVIEW
(standards.iteh.ai)

[SIST EN 17134-2:2023](https://standards.iteh.ai/catalog/standards/sist/bf44eb9b-194d-4412-b459-daf0fecdd11c2/sist-en-17134-2-2023)

<https://standards.iteh.ai/catalog/standards/sist/bf44eb9b-194d-4412-b459-daf0fecdd11c2/sist-en-17134-2-2023>

EN 17134-2:2023 (E)**European foreword**

This document (EN 17134-2:2023) has been prepared by Technical Committee CEN/TC 248 “Textiles and textile products”, the secretariat of which is held by BSI.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by January 2024, and conflicting national standards shall be withdrawn at the latest by January 2024.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN shall not be held responsible for identifying any or all such patent rights.

This document supersedes EN 17134:2019.

This document is part of a series of documents:

EN 17134-1¹, *Textiles and textile products — Determination of biocide additives — Part 1: 2-Phenylphenol and triclosan, method using liquid chromatography*

EN 17134-2, *Textiles and textile products — Determination of biocide additives — Part 2: Chlorophenol-based preservatives, method using gas chromatography*

EN 17134-3², *Textiles and textile products — Determination of biocide additives — Part 3: Permethrin, method using liquid chromatography*

A list of all parts in a series can be found on the CEN website: www.cencenelec.eu.

Any feedback and questions on this document should be directed to the users' national standards body. A complete listing of these bodies can be found on the CEN website.

According to the CEN-CENELEC Internal Regulations, the national standards organisations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Republic of North Macedonia, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Türkiye and the United Kingdom.

¹ Under preparation. Stage at the time of publication: prEN 17134-1:2023.

² Under preparation. Stage at the time of publication: prEN 17134-3:2023.

Introduction

In Europe, according to Regulation (EU) 2019/1021 of the European Parliament and of the Council of 20 June 2019 on persistent organic pollutants [1] 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 [2], 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).

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.

iTeh STANDARD PREVIEW
(standards.iteh.ai)

[SIST EN 17134-2:2023](https://standards.iteh.ai/catalog/standards/sist/bf44eb9b-194d-4412-b459-daf0fecdd11c2/sist-en-17134-2-2023)

<https://standards.iteh.ai/catalog/standards/sist/bf44eb9b-194d-4412-b459-daf0fecdd11c2/sist-en-17134-2-2023>

EN 17134-2:2023 (E)

1 Scope

This document specifies a test method using gas chromatography with a mass selective detector (GC-MS) for detection and quantification of chlorophenols (CPs), which are either freely present or released from salts and esters: pentachlorophenol (PCP), tetrachlorophenol- (TeCP), trichlorophenol- (TriCP), dichlorophenol- (DiCP) and monochlorophenol- (MoCP) isomers. The method is applicable to textile fibres, yarns, fabrics, coated fabrics, printed fabrics, plastic, and wooden parts of textile products (for example buttons).

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.

EN ISO 3696, *Water for analytical laboratory use - Specification and test methods (ISO 3696)*

EN ISO 4787, *Laboratory glass and plastic ware - Volumetric instruments - Methods for testing of capacity and for use (ISO 4787)*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminology 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 Principle

The sample is cut into small pieces and extracted with potassium hydroxide (KOH) solution at a defined temperature. The extracted CPs are subsequently acetylated and the chlorinated acetates are analysed and quantified using GC-MS. The quantitative determination is made by corrections with ¹³C- and ²H-labelled internal standards.

5 Reagents

Unless otherwise specified, all reagents shall be of a recognized analytical grade.

- 5.1 Water**, grade 3, according to EN ISO 3696.
- 5.2 Potassium hydroxide (KOH)**, CAS Registry Number³ (CAS RN[®]) 1310-58-3.
- 5.3 Potassium carbonate (K₂CO₃)**, anhydrous, CAS RN[®] 584-08-7.
- 5.4 n-Hexane**, CAS RN[®] 110-54-3.

³ CAS Registry Number[®] (CAS RN[®]) is a trademark of the American Chemical Society (ACS). This information is given for the convenience of users of this document and does not constitute an endorsement by CEN of the product named. Equivalent products may be used if they can be shown to lead to the same results.

5.5 **Acetic anhydride**, CAS RN® 108-24-7.

5.6 **Tetrachloroguaiacol (TCG)**, CAS RN® 2539-17-5, internal standard (IS).

5.7 **Acetonitrile**, CAS RN® 75-05-8.

5.8 Chlorophenols

The following 19 CPs given in Table 1 are probably relevant.

Table 1 — List of probably relevant CPs

Substance	Abbreviation	CAS RN®
2-chlorophenol	2-MoCP	95-57-8
3-chlorophenol	3-MoCP	108-43-0
4-chlorophenol	4-MoCP	106-48-9
2,3-dichlorophenol	2,3-DiCP	576-24-9
2,4-dichlorophenol	2,4-DiCP	120-83-2
2,5-dichlorophenol	2,5-DiCP	583-78-8
2,6-dichlorophenol	2,6-DiCP	87-65-0
3,4-dichlorophenol	3,4-DiCP	95-77-2
3,5-dichlorophenol	3,5-DiCP	591-35-5
2,3,4-trichlorophenol	2,3,4-TriCP	15950-66-0
2,3,5-trichlorophenol	2,3,5-TriCP	933-78-8
2,3,6-trichlorophenol	2,3,6-TriCP	933-75-5
2,4,5-trichlorophenol	2,4,5-TriCP	95-95-4
2,4,6-trichlorophenol	2,4,6-TriCP	88-06-2
3,4,5-trichlorophenol	3,4,5-TriCP	609-19-8
2,3,4,5-tetrachlorophenol	2,3,4,5-TeCP	4901-51-3
2,3,4,6-tetrachlorophenol	2,3,4,6-TeCP	58-90-2
2,3,5,6-tetrachlorophenol	2,3,5,6-TeCP	935-95-5
Pentachlorophenol	PCP	87-86-5

EN 17134-2:2023 (E)

5.9 Isotope labelled chlorophenols

The following 4 isotope labelled CPs given in Table 2 can be relevant as internal standards (IS).

Table 2 — List of probably relevant isotope labelled chlorophenols

Substance	Abbreviation	CAS RN®
2-chlorophenol-D ₄	2-MoCP-D ₄	93951-73-6
2,4-dichlorophenol-D ₃	2,4-DiCP-D ₃	93951-74-7
2,3,4,6-tetrachlorophenol- ¹³ C ₆	2,3,4,6-TeCP- ¹³ C ₆	1246820-81-4
Pentachlorophenol- ¹³ C ₆	PCP- ¹³ C ₆	85380-74-1

Instead of the isotope-labelled derivatives of tetra-, di- and monochlorophenol mentioned, other isotope-labelled analogues of the same chlorination levels, for example 4-chlorophenol-D₄, may be used as internal standards.

5.10 Potassium hydroxide (KOH) solution ($c = 1 \text{ mol/l}$)

Prepare an aqueous KOH solution at a concentration of 1 mol/l.

EXAMPLE Weigh 56,1 g KOH (5.2) into a 1 l volumetric flask and dissolve with 100 ml water (5.1) (WARNING: heat generation!). After cooling to room temperature fill up to 1 l with water (5.1).

5.11 Internal standard stock solution of isotope-labelled chlorophenols

Based on its requirements a laboratory shall decide which isotope-labelled CPs are required in an internal standard stock solution.

Table 3 shows which isotope-labelled CPs shall be used as internal standards (IS) for the quantification of CPs with particular chlorination levels. Alternative IS as outlined in 5.9 may be used.

Table 3 — Assignment of the isotope-labelled CPs to the CP groups

Isotope-labelled CP	CP group
2-chlorophenol-D ₄	MoCP
2,4-dichlorophenol-D ₃	DiCP, TriCP
2,3,4,6-tetrachlorophenol- ¹³ C ₆	TeCP
Pentachlorophenol- ¹³ C ₆	PCP

Prepare a stock solution of the isotope-labelled CPs required at a concentration suitable for the used analytical system, for example $c = 0,1 \text{ mg/ml}$.

EXAMPLE To get a stock solution of isotope-labelled CPs at concentrations of 0,1 mg/ml, dissolve 10 mg of each required isotope-labelled internal standard (5.9) in 100 ml KOH solution (5.10).

5.12 Extraction solution

The concentration of isotope-labelled CPs shall be adapted to the respective calibration range of the CPs (see solutions 5.16).

EXAMPLE To prepare 1 l extraction solution with a concentration of each isotope-labelled CP (5.11) of 0,1 µg/ml, transfer 1,0 ml stock solution isotope-labelled CPs (5.11) in a 1 l volumetric flask and fill it up with KOH

solution (5.10). If a more sensitive measuring instrument is used and the calibration is lowered, reduce the concentration of isotope-labelled internal CPs in the KOH accordingly.

5.13 Potassium carbonate (K₂CO₃) solution (c = 0,1 mol/l).

Prepare an aqueous K₂CO₃ solution at a concentration of 0,1 mol/l.

EXAMPLE Weigh 13,82 g K₂CO₃ into a 1 l volumetric flask, dissolve with water (5.1) and fill up to the mark.

5.14 Tetrachloroguaiacol (TCG) solution

Prepare a TCG solution in acetonitrile as internal standard solution for injection control at a concentration suitable for the used analytical system, for example c = 1 µg/ml.

EXAMPLE Dissolve 10 mg TCG (5.6) in 100 ml acetonitrile (5.7). Take 1,0 ml from this solution and dilute to 100 ml with acetonitrile (5.7).

5.15 CPs standard stock solution

Based on its requirements a laboratory shall decide which CPs from Table 1 in 5.8 need to be determined. Based on this decision, standard stock solutions at a concentration suitable for the analytical system used are required. CP standard stock solutions, either as single substance or mixed substance solutions (for example, c = 50 µg/ml in acetone), are available commercially as certified standard solutions or may be prepared from certified reference substances.

5.16 CPs calibration solutions

Prepare at least three calibration solutions of CPs from the CP standard stock solution(s) (5.15) at suitable concentrations for the analysis. Transfer the required volume of CP standard stock solution(s) (5.15) into a volumetric flask and fill it up to the mark with acetonitrile (5.7). Examples of concentrations that have been found suitable are provided in Table 4.

Table 4 — Examples of calibration solutions

Concentration of CPs in calibration solution µg/ml	Volume of CPs working solution (5.15) (for example c = 50 µg/ml) µl	Volume of volumetric flask ml
0,15	30	10
2,0	400	
4,0	800	
15	600	2
25	1 000	

EN 17134-2:2023 (E)**6 Apparatus**

The usual laboratory apparatus and laboratory glassware, according to EN ISO 4787, shall be used, in addition to the following:

- 6.1 Analytical balance**, weighing with an accuracy of 0,1 mg.
- 6.2 Gas-tight glass vial**, for example 20 ml headspace vial.
- 6.3 Heating block, sand bath or oven**, suitable to maintain the KOH solution at a temperature of (90 ± 1) °C.
- 6.4 GC vials**, for example 2 ml.
- 6.5 Pasteur pipettes, graduated pipettes, suitable autopipettes.**
- 6.6 Vortex shaker.**
- 6.7 Horizontal shaker**, capable of at least 200 min⁻¹.
- 6.8 Centrifuge.**
- 6.9 Gas chromatograph with mass selective detector (GC-MS).**

7 Preparation of test samples and test specimens

Dismantle the textile product and separate the different material types.

Each test specimen shall consist of a single material type, which is tested separately. If fabrics and prints cannot be separated, they may be tested together. Up to three test specimens (of equal mass) of the same material type may be tested together, taking into consideration the limits of detection (LoD) and quantification (LoQ).

Each material type is cut into pieces of about 0,3 cm to 0,5 cm edge length.

8 Procedure**8.1 Extraction with KOH**

Weigh approximately 1 g (minimum sample mass 0,2 g) of the cut test specimen (7) (to the nearest 0,01 g) in a glass vial (6.2). Add 10 ml extraction solution (5.12). After closing, the vial is transferred to a heating apparatus (6.3) and left for 16 h \pm 15 min at (90 ± 1) °C. The temperature in the vials is checked in a vial (6.2) with blank KOH extraction solution (5.12).

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. Alternatively, a larger amount of extraction solution shall be added. Thereby, the different specimen mass to solution ratio shall be considered in the calculation (9.2).

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

By applying KOH extraction, MoCPs and DiCPs can be released from unknown compounds, for example dyes. If it is only required to test for free MoCPs and DiCPs the procedure described in Annex C can be applied.

8.2 Acetylation of extracted CPs

8.2.1 General procedure of acetylation

To get a limit of quantification (LoQ) of 0,1 mg/kg use the following procedure: After extraction, the solution shall be cooled down to room temperature and shaken vigorously for approximately 1 min with a vortex shaker (6.6) or for approximately 10 min with a horizontal shaker (6.7).

Transfer 4 ml of the extract into a new glass vial (6.2) and add 6 ml potassium carbonate solution (5.13), 2 ml *n*-hexane (5.4), 250 µl TCG solution (5.14) and 1 ml acetic anhydride (5.5).

8.2.2 Preparation for GC analysis

Close the vial and shake it for (30 ± 1) min at a shaking rate of at least 200 min^{-1} on a horizontal shaker (6.7). An efficient mixing of the phases shall be ensured.

Let the two phases of the solution separate and centrifuge the vial, if required, before opening it. Open the vial carefully (WARNING: There can be an overpressure in the vial!) and transfer an aliquot from the upper phase into a GC vial (6.4) for analysis.

If a higher LoQ is required, it is possible to use less extract and/or more *n*-hexane (5.4). Perform a validation of the method with these changed conditions.

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

8.2.3 Acetylation in case of low recovery rates

For test specimens with very low recovery rates of the isotope-labelled internal standards, take the whole extract with the test specimen (8.1) and add 5 ml *n*-hexane (5.4), 625 µl TCG solution (5.14) and 2,5 ml acetic anhydride (5.5) instead of the above-mentioned volumes. The *n*-hexane phase will contain more matrix than from the solution without the test specimen. This can affect the instrumental analysis (8.4) but empirically the recovery rates of the isotope-labelled internal standards improve. Proceed with 8.2.2.

8.3 Acetylation of the calibration standards

Transfer 100 µl of each CP calibration solution (5.16) into new glass vials (6.2). Add 4 ml extraction solution (5.12), 6 ml potassium carbonate solution (5.13), 2 ml *n*-hexane (5.4), 250 µl TCG solution (5.14) and 1 ml of acetic anhydride (5.5) to each vial. Proceed analogous to 8.2.2.

8.4 Gas chromatography with mass selective detection

Determine the compounds listed in Table 1 and acetylated in 8.2 and 8.3 by GC-MS (6.9) as required. Examples of chromatographic and spectroscopic conditions are given in Annex A.

9 Expression of results

9.1 General

The quantitative determination is made using a multi-point calibration with at least three points. The calibration curve is constructed by plotting the area against the known standard concentrations with correction for the related isotope-labelled internal standards (Table 3). From the calibration curve, interpolate the concentration of chlorophenol (ρ_s), in µg/ml.

If the recovery of the isotope-labelled internal standards due to matrix effects is lower than the specified recovery of the laboratory's quality guideline, other valid methods, such as addition procedures, may be used to quantify the CP concentrations.

If the recovery rates of the isotope-labelled internal standards are very low, perform 8.2.3.

TCG is used to check whether the acetylation (8.3) and the injection were successful.