INTERNATIONAL STANDARD

ISO 15320

First edition
2003-12-15

Pulp, paper and board — Determination of pentachlorophenol in an aqueous extract

Pâtes, papier et carton — Détermination du pentachlorophénol dans un extrait aqueux

Reference number
ISO 15320:2003(E)

PDF disclaimer

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

STANDARDSISO.COM : Click to view the full PDF of ISO 15320:2003

© ISO 2003

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 15320 was prepared by the European Committee for Standardization (CEN) in collaboration with Technical Committee ISO/TC 6, *Paper, board and pulps*, Subcommittee SC 5, *Test methods and quality specifications for pulps*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

Throughout the text of this document, read "...this European Standard..." to mean "...this International Standard...".

Content

Foreword

This document (EN ISO 15320:2003) has been prepared by Technical Committee CEN/TC 172 "Pulp, paper and board", the secretariat of which is held by DIN, in collaboration with Technical Committee ISO/TC 6 "Paper, board and pulps".

This European Standard EN ISO 15320:2003 including the Amendment shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by June 2004, and conflicting national standards shall be withdrawn at the latest by June 2004.

WARNING: The use of this European Standard may involves hazardous materials, e.g. methanol and pentachlorophenol, which are toxic substances, as well as acetic anhydryde, which is corrosive. This European Standard does not address all the safety and environmental problems associated with its use. It is the responsibility of the user of this European Standard to establish appropriate safety, health and environmental practices and determine applicability of safety regulations prior to use.

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

1 Scope

This European Standard specifies a test method for the determination of pentachlorophenol (PCP) in an aqueous extract in pulp, paper and board. Though it is developed for paper and board intended to come into contact with foodstuffs, it is applicable to all kinds of pulp, paper and board.

NOTE 1 It was investigated that a hot water extract (acc. to EN 647) is sufficient for the determination of PCP in pulp, paper and board.

The working range for the method is 0,05 mg/kg to 0,5 mg/kg.

NOTE 2 The upper limit of the working range could be increased if the aqueous extract is diluted.

2 Normative References

This European Standard 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 in this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

EN 645 *Paper and board intended to come into contact with foodstuffs – Preparation of a cold water extract*

EN 647 *Paper and board intended to come into contact with foodstuffs – Preparation of a hot water extract*

EN ISO 3696:1995 *Water for analytical laboratory use – Specification and test methods (ISO 3696:1987)*

3 Principle

A specimen of the material to be tested is extracted with cold water according to EN 645 or with hot water according to EN 647. The pentachlorophenol in the extract is concentrated using solid phase extraction on a phenyl column. The pentachlorophenol is then eluted from the phenyl column with hexane, acetylated using acetic anhydride and the amount of pentachlorophenol present determined using gas chromatography employing an ECD (electron capture detector) or MS (mass spectrometer) detector. The result is expressed as milligrams per kilogram of material.

4 Apparatus

4.1 Ordinary laboratory apparatus

4.2 Solid phase extraction (SPE) system and SPE columns

Propylphenyl columns, dimension 500 mg/3 ml.

4.3 Gas chromatograph

A conventional split/splitless injector gives suitable sensitivity when used in the splitless mode. Alternatively, an on-column injection mode may be used.

4.4 Capillary column

suitable for determination of acetylated derivates of pentachlorophenol. A column with the following features is given as an example.

- stationary phase:	polydimethylsiloxane with 5 % phenyl groups
- film thickness:	0,25 µm
- length:	30 m
- internal diameter:	0,32 mm.

4.5 Detector

— electron capture detector (ECD)

or

— mass spectrometer (MS) with the following features is given as an example:

a) ionisation: EI 70 eV (electron impact)

b) resolution: 1 amu (atomic mass unit)

c) runability: SIM mode (selected ion monitoring) (SIM is called SIR, selected ion recording for some instruments)

5 Reagents

5.1 General

All reagents shall be of a grade “pro analysis” (p.a.) or equivalent quality, respectively water of grade 2 according to EN ISO 3696:1995.

5.2 Methanol,

CH_3OH.

5.3 Hydrochloric acid,

HCl (0,1 mol/l).

5.4 n-Hexane,

C_6H_{14}.

5.5 Sulphuric acid,

H_2SO_4 (diluted 1+1).

5.6 Acetic anhydride,

$C_4H_6O_3$ (99 %).

5.7 Potassium carbonate solution,

K_2CO_3 (0,1 mol/l). Weigh 13,8 g potassium carbonate with an accuracy of 0,1 g and dissolve it in a beaker with a small amount of water. Transfer the solution to a 1000 ml volumetric flask and dilute to volume with water.

5.8 Reference solutions (for ECD)

5.8.1 Pentachlorophenol in methanol reference stock solution,

100 µg/ml. This solution is commercially available.

5.8.2 Pentachlorophenol in methanol dilute reference stock solution,

5 µg/ml. Pipette 1 ml of the stock solution (5.8.1) into a 20 ml volumetric flask and dilute to volume with methanol. Solution is stable more than 6 months in the refrigerator.

5.8.3 Pentachlorophenol in methanol reference solution,

0,5 µg/ml. Pipette 1 ml of the dilute stock solution (5.8.2) into a 10 ml volumetric flask and dilute to volume with methanol. Solution is stable more than 3 months in the refrigerator.

5.9 Internal standard solutions for ECD

5.9.1 2,3,6-trichlorophenol internal standard stock solution,

10 µg/ml, internal standard stock solution. This solution is commercially available.

5.9.2 2,3,6-trichlorophenol internal standard solution,

2 µg/ml, internal standard solution. Pipette 2 ml of the internal standard stock solution (5.9.1) into a 10 ml volumetric flask and dilute to volume with methanol. Solution is stable more than 3 months in the refrigerator.

5.10 Internal standard solutions for MS

5.10.1 ^{13}C6 labelled pentachlorophenol (labelled at all six carbons) internal standard stock solution,

10 µg/ml, internal standard stock solution. This solution is commercially available. It is an alternative to the 2, 3, 6-trichlorophenol methanol solution mentioned in 5.9.1 and can be applied only when a mass spectrometer is used as a detector.

5.10.2 ^{13}C6 labelled pentachlorophenol internal standard solution,

1 µg/ml, internal standard solution. Pipette 1 ml of the internal standard stock solution (5.10.1) into a 10 ml volumetric flask and dilute to volume with methanol. Solution is stable more than 3 months in the refrigerator.

6 Sampling and extraction

Sampling, preparation of sample and extraction shall be carried out in accordance with EN 645 (cold water extract) or EN 647 (hot water extract).

7 Procedure

The water extract shall be analysed. Filter according to EN 645 or EN 647.

7.1 Preparation

Take out 50 ml from the water extract. Add 200 µl of the internal standard solution (5.9.2 or 5.10.2) and acidify with 1 ml sulphuric acid (5.5).

7.2 Solid phase concentration

7.2.1 Conditioning

Pre-rinse a phenyl column (4.2) with 2 ml methanol and 5 ml 0,1 *M* HCl (5.3). Do not allow the column to run dry.

7.2.2 Concentration

Pour the acidified extract onto the column, elute at 2 ml/min to 3 ml/min. Subsequently, rinse the column with 5 ml pure analytical water (5.1) and suck it dry (approx. 5 min to 10 min).

7.2.3 Elution

For the receiver use a 50 ml conical flask or a separatory funnel, with 35 ml 0,1 *M* K_2CO_3 solution (5.7). Pour 2,5 ml hexane onto the phenyl column and wait until the first drop is seen in the lower end. Close the valve and elute after 2 min. Rinse with another 2,5 ml hexane.

7.3 Acetylation

Add 1 ml acetic anhydride (5.6) to the receiver and stir vigorously for approximately 3 min to allow the release of all carbon dioxide. Allow the two phases to separate. Fill the receiver with water until the hexane phase reach the neck of the receiver. Transfer the organic layer into a vial in order to avoid a reverse reaction. This extract has to be analysed within 24 h.

NOTE If the hexane solution is dried with e.g. sodium sulphate the solution can be stored for at least two weeks.

7.4 Gas chromatographic analysis

Choose the suitable conditions for determination of pentachlorophenol. Follow the instructions provided by the manufacturer of the instrument. The following conditions are given as an example.

- splitless injection:	1 µl;
- injector temperature:	250 °C;
- electron capture detector temperature:	350 °C;
- carrier gas, flow:	1 ml/min.
- temperature programme:	50 °C (1 min) at 20 °C/min to 180 °C and hold 2 min, then at 2 °C/min to 200 °C and hold for 1 min or 20 °C (1 min) to 280 °C and hold 5 min.

Carry out the detection either by the electron capture detector or by the use of a mass spectrometer. In both cases, follow the instructions provided by the manufacturer of the instrument.

If a mass spectrometer is used, with ^{13}C6-labelled pentachlorophenol as internal standard, the base peak, 266, is used for quantification of PCP, (266 = M + 2 minus ketene, $CH_2=C=O$, from the acetate). The corresponding ion from the ^{13}C6-labelled pentachlorophenol is 272 (266 + 6). Verification of PCP should be made from the retention time and the ratio between 264 and 266, which shall be close to 61/100 due to the chlorine isotope ratio.

If the value of PCP obtained exceeds the range covered by the calibration solutions, repeat the analysis from 7.1 with a more dilute sample solution.

8 Calibration

8.1 Calibration for electron capture detector, ECD

8.1.1 Preparation of calibration solutions

Prepare pentachlorophenol standard solutions for the calibration as follows:

Take 35 ml potassium carbonate solution (5.7) in a 50 ml conical flask or a separatory funnel (see 7.2.3). Add 200 µl of the internal standard solution (5.9.2). Make four solutions by adding various amounts of PCP (use the reference solutions (5.8.2 and 5.8.3).Shake for 3 min. Add 5 ml hexane (5.4) and 1 ml acetic anhydride and shake until the gas evolution has stopped (approximately 3 min). Fill up with pure analytical water until the organic phase is in the neck of the conical flask and can be removed with a pipette.

NOTE If the hexane solution is dried with e. g. sodium sulphate the solution can be stored for at least four weeks.

8.1.2 Gas chromatographic determination

Proceed to gas chromatographic determination as described in 7.4.

Carry out the gas chromatographic determinations in duplicate.

8.1.3 Establishing retention time of pentachlorophenol

Identify the retention time of pentachlorophenol relative to the retention time of the internal standard.

8.1.4 Calculation of the area ratio versus mass ratio

Measure the areas of the pentachlorophenol peaks and the peak of the internal standard.

Plot the area ratio A_r versus the mass ratio M_r in accordance with the formulas (1) and (2)

$$A_r = \frac{A_{pcp}}{A_{ist}} \tag{1}$$

$$M_r = \frac{M_{pcp}}{M_{ist}} \tag{2}$$

where

A_{pcp} is the area of the pentachlorophenol base peak;

A_{ist} is the area of the peak representing the internal standard base peak;

M_{pcp} is the mass of pentachlorophenol in the solution in µg;

M_{ist} is the mass of the internal standard in micrograms, in this case 0,4 µg.

Read the slope of the curve and obtain the response factor, *f*, which is a dimensionless number, independent of the injected volume and the acetylation yield.

$$f = \frac{M_{pcp} \times A_{ist}}{M_{ist} \times A_{pcp}} \tag{3}$$

Alternatively, read the response factor from the programme of the gas chromatograph.

NOTE The response for the ECD can change with time and the response factor should be checked regularly.

8.2 Calibration for mass spectrometer using 13C-labelled PCP

The response factor between PCP and the ^{13}C6 labelled pentachlorophenol is 1. That means that $A_r = M_r$ and $f = 1$.

A_{pcp} is the area of the pentachlorophenol base peak (266);

A_{ist} is the area of the peak representing the internal standard base peak (272);

9 Calculation

Identify the pentachlorophenol peak and measure its area, A_{pcp}. Measure also the area of the peak representing the internal standard, A_{ist}.