# INTERNATIONAL STANDARD

# ISO 15318

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# Pulp, paper and board — Determination of 7 specified polychlorinated biphenyls (PCB)

*Pâtes, papiers et cartons — Détermination de 7 polychlorobiphényles (PCB) spécifiés*

Reference number
ISO 15318:1999(E)

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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 734 10 79
E-mail copyright@iso.ch
Web www.iso.ch

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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 member bodies casting a vote.

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

International Standard ISO 15318 was prepared by the European Committee for Standardization (CEN) in collaboration with ISO Technical Committee TC 6, *Paper, board for pulp*, Subcommittee SC 5, *Test methods and quality specifications for pulp*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

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

Annexes A, B and C form a normative part of this International Standard.

# Content

## Foreword

The text of EN ISO 15318:1999 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 supersedes ENV 1798:1995.

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 March 2000, and conflicting national standards shall be withdrawn at the latest by March 2000.

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, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

With regard to ENV 1798 : 1995-07 the following changes have been made:

a) extension of the scope to "pulp";

b) addition of detailed information on "precision";

c) transformation from a European Prestandard (ENV) to a European Standard (EN);

d) editorial updating.

## Introduction

CEN/TC 172 has decided to publish this test method as a European Standard (EN) because the validation of the test method on the level of the existing limit for PCB (2 ppm) was until now impossible due to the fact that there was no reference material with this level of PCB and all samples tested have a PCB content on the level of the detection limit (about 5 µg/kg of the congeners).

Prior to discontinuance of its use in 1971 a commercial PCB had been an ingredient in carbonless copy paper. The presence of these copy papers in waste paper can lead to contamination of recycled pulp, paper and board products with PCB.

The PCB contaminant has the same congener pattern as the PCB used earlier in carbonless copy papers and this identifies the source of PCB contamination.

In this method, seven specified PCB congeners (numbers 18, 28, 52, 101, 138, 153 and 180) are determined individually. Because the source of the PCB contamination can be identified from the congener pattern, the total PCB content of the paper may be estimated from these seven congeners.

For routine analyses, the spiking procedure of 5.10.5 and 7.4.4 may be omitted, provided that the result obtained from the analysis is less than 50 % of any present limit. This will require modification of clause 8 to take account of these changes. The use of this modification shall be stated in the test report. In the event of any dispute the full method shall be used.

**Warning:**

The use of this European Standard may involve hazardous materials, operations and equipment. It does not address all the safety problems associated with its use. It is the responsibility of the user of this European Standard to establish appropriate safety and health practices and determine the applicability of safety regulations prior to use.

## 1 Scope

This European Standard gives guidance on a test method which permits the determination of seven specified PCBs in pulp, paper and board. Annex A gives a procedure for estimating the total content of PCB from the congener content.

## 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 to this Standard only when incoroporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

EN ISO 186
Paper and board - Sampling to determine average quality (ISO 186 : 1994)

EN 27213
Pulps – Sampling for testing (ISO 7213 : 1981)

## 3 Principle

The test material is extracted with boiling ethanolic or methanolic potassium hydroxide solution. An aliquot of the extract is mixed with water and subjected to liquid-solid partitioning on a disposable $C_{18}$ solid phase extraction cartridge followed by elution with hexane or ISO-octane.

The PCBs contained in the hexane phase are quantified by capillary gas chromatography using an electron capture detector (ECD) or a mass selective detector (MSD). The pattern of the seven congener peaks is compared with the pattern of a technical PCB.

If the patterns correspond, the level of total PCB can be estimated from the congener content by application of an appropriate factor.

## 4 Apparatus and auxiliary aids

### 4.1 Ordinary laboratory apparatus

### 4.2 Extractor reservoir

An example is given in Annex B, where the reservoir comprises a glass tube approximately 200 mm long with an internal diameter of 30 mm.

The tube is tapered twice at the lower end to ensure that the connection to the disposable cartridge (4.3) is gas-tight and to allow drops to build up on the tip.

**4.3 Disposable solid-phase extraction cartridge** with a $C_{18}$ bonded phase (3,0 ml size and 200 mg).

**4.4 Gas chromatograph** with an electron capture detector (ECD) or a mass selective detector (MSD).

**4.5 Capillary column** suitable for the determination of PCB in accordance with the specification laid down in 8.1.

## 5 Reagents

Unless otherwise specified, reagents of a grade suitable for residue analysis shall be used. Water should be double-distilled or of equivalent quality. Methanol can be used in place of ethanol for all solutions if required and ISO-octane can be used in place of hexane.

### 5.1 Ethanol

($C_2H_5OH > 99,5$ %)

### 5.2 Methanol

($CH_3OH > 99,8$ %)

### 5.3 n-Hexane

($C_6H_{14} > 98,0$ %)

### 5.4 Sulphuric acid, concentrated

($d = 1,84$)

### 5.5 Reference substances

| | | Ballschmit Nomenclature |
|---|---|---|
| **5.5.1** | 2,2',5-Trichlorobiphenyl | 18 |
| **5.5.2** | 2,4,4'-Trichlorobiphenyl | 28 |
| **5.5.3** | 2,2',5,5'-Tetrachlorobiphenyl | 52 |
| **5.5.4** | 2,2',4,5,5'-Pentachlorobiphenyl | 101 |
| **5.5.5** | 2,2',3,4,4',5'-Hexachlorobiphenyl | 138 |
| **5.5.6** | 2,2',4,4',5,5'-Hexachlorobiphenyl | 153 |
| **5.5.7** | 2,2',3,4,4',5,5'-Heptachlorobiphenyl | 180 |

## 5.6 Comparison sample

Technical mixture of, for example, Chlophen[1] A 30 to A 60® or Arochlor[2] 1242 to 1260.

## 5.7 Gas-Chromatography (GC) resolution sample

**5.7.1** 2,4',5-Trichlorobiphenyl (TCBP, PCB 31)

## 5.8 Internal standards

**5.8.1** 2,4,6-Trichlorobiphenyl (TCBP, PCB 30)

**5.8.2** 2,4,6-Tribromobiphenyl (TBBP)

## 5.9 Ethanolic potassium hydroxide solution (2 % *w*/*v*)

Dissolve 30,0 g of potassium hydroxide in a solution 19:1 *v*/*v* ethanol/water (1500 ml). Allow to stand for 24 h, decant, and retain the clear solution.

## 5.10 Combined standard solutions

Prepare the following standard solutions using volumetric glassware throughout:

NOTE: Mixtures corresponding to 5.10.1 to 5.10.4 are commercially available.

### 5.10.1 Intermediate standard solutions A (200 μg/ml)

Take approximately 10,0 mg (to an accuracy of 0,1 mg) of reference congener substance 18 (5.5.1), transfer quantitatively to a 50,0 ml volumetric flask and make up to the mark with hexane. Shake to dissolve.

Repeat for congeners 28, 52, 101, 138, 153 and 180 (5.5), GC resolution sample 31 (5.7) and for TCBP or TBBP (5.8).

### 5.10.2 Intermediate standard solutions B (20 μg/ml)

Take 5,00 ml of solution A for congener 18 (5.10.1) and dilute to 50,0 ml using hexane.

Repeat for congeners 28, 52, 101, 138, 153 and 180, GC resolution sample 31, and for TCBP or TBBP (5.8).

### 5.10.3 Individual standard solutions for GC (0,1 μg/ml)

Take 1,00 ml of solution B for congener 18 (5.10.2) and dilute to 200,0 ml with hexane.

Repeat for congeners 28, 52, 101, 138, 153 and 180, GC resolution sample 31, and for TCBP or TBBP (5.8).

### 5.10.4 Combined standard solutions for GC (0,1 μg/ml)

Take 1,00 ml of solution B for each congener 18, 28, 52, 101, 138, 153 and 180, GC resolution sample 31, and TCBP or TBBP (5.8) , and dilute to 200,0 ml with hexane.

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1) Chlophen is the trade-name of a product supplied by Bayer. This information is given for the convenience of users of this Standard 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.

2) Arochlor is an example of a suitable product available commercially. This information is given for the convenience of users of this Standard and does not constitute an endorsement by CEN of this product.

### 5.10.5 Spiking solution (0,1 μg/ml)

Take approximately 10,0 mg (to an accuracy of 0,1 mg) of congener substances 18, 28, 52, 101, 138, 153 and 180 (5.5), transfer quantitatively to a 100,0 ml volumetric flask and make up to the mark with ethanol. Shake to dissolve.

Take 5,00 ml of this solution and dilute to 100,0 ml with ethanol.

Take 5,00 ml of this second solution and dilute to 250,0 ml with ethanolic potassium hydroxide solution (5.9).

### 5.10.6 Internal standard solution (0,1 μg/ml)

Take approximately 10,0 mg (to an accuracy of 0,1 mg) of internal standard substance TCBP or TBBP (5.8), transfer quantitatively to a 100,0 ml volumetric flask and make up to the mark with ethanol. Shake to dissolve.

Take 5,00 ml of this solution and dilute to 100,0 ml with ethanol.

Take 5,00 ml of this second solution and dilute to 250,0 ml with ethanolic potassium hydroxide solution (5.9).

## 6 Sampling

Sampling shall be carried out in accordance with EN ISO 186 or EN 27213. The sample shall be wrapped in aluminium foil between acquisition and testing, to prevent any change before the test.

## 7 Procedure

**7.1** Suitable safety measures shall be taken when the work laid down in this test method is carried out.

**7.2** Attach the solid-phase disposable cartridge (4.3) to the extractor reservoir (4.2) to give a gas-tight seal and condition with two charges of methanol (5.2) (typically 2 x 3,0 ml) followed by water (typically 2 x 3,0 ml) in accordance with the manufacturer's instructions.

**7.3** Take a representative sample of the pulp, paper or board sample (about 100 g as received), cut into pieces of about 1 $\text{cm}^2$ and randomise by shaking in a large glass beaker.

**7.4** Take nine 100 ml round-bottomed flasks. Add (2,00 ± 0,02) g portions of the paper or board, or for pulp (1,80 ± 0,02) g as oven dry (7.3) to eight of these flasks. Treat the nine flasks as follows:

### 7.4.1 Sample MB (method blank)

Add 2,00 ml internal standard solution (5.10.6) to the flask with no pulp, paper or board.

### 7.4.2 Sample SB (sample blank)

No further additions.

### 7.4.3 Samples S1 to S3 (triplicate samples)

Add 2,00 ml of the internal standard solution (5.10.6).

### 7.4.4 Samples C1 to C4 (calibration samples)

Add 2,00 ml of the internal standard solution (5.10.6) together with 1,00 ml, 2,00 ml, 3,00 ml or 4,00 ml of the spiking solution (5.10.5).

**7.5** Add ethanolic potassium hydroxide solution (5.9) to each of the flasks to give a total liquid volume of 50,0 ml.

Reflux for 60 min, cool to room temperature and pipette 25,0 ml of the extract into a conical flask containing 50,0 ml water. Mix immediately for 5 s.

**7.6** Pour the mixture immediately into the extractor reservoir with the conditioned cartridge attached (7.2). Apply pressure or vacuum to give a flow rate of 50 to 100 drops per min. Discard the eluent.

Remove the reservoir and dry the cartridge for approximately 10 min with the pressure or vacuum maintained. Place a separating funnel or a test tube (10,0 ml) at the cartridge outlet and pipette 0,5 ml n-hexane (5.3) into the cartridge. Allow the n-hexane to soak into the cartridge packing. Set the cartridge aside for 5 min to 10 min to allow the n-hexane to permeate the packing, and then add a further 0,5 ml n-hexane and elute carefully into the separating funnel using pressure or vacuum. Finally, add a further 1,0 ml n-hexane and elute with pressure.

**7.7** Wash the hexane extract successively with 2,0-ml portions of sulphuric acid (5.4) until no further colour is extracted. Transfer the hexane extract into a 2,0 ml volumetric flask and make up to the 2,0 ml mark with hexane.

The hexane phase is now ready for GC analysis.

## 8 Determination

### 8.1 Working conditions for gas chromatography

The gas chromatograph and electron capture detector or mass selective detector should be optimised with regard to sensitivity, linearity and reproducibility, according to the manufacturer's instructions.

The following are examples of columns and conditions that have proved suitable for this analysis.

| | |
|---|---|
| Capillary column (4.5): | cross-linked 5 % phenylmethyl silicone on fused silica. 50 m to 60 m length. 0,2 mm to 0,35 mm internal diameter. 0,1 μm to 0,3 μm phase. |
| Injector: | 250 °C to 270 °C split/splitless (vaporising) mode. |
| ECD detector: | 300 °C to 350 °C. |
| Oven: | temperature programmed from 100 °C (2 min) at 25 °C/min to 160 °C and hold 10 min, then at 5 °C/min to 280 °C and hold for 10 min, or, 130 °C (zero min) rising at 2,5 °C/min to 290 °C and hold 5 min. |

### 8.2 Establishing GC retention times

Analyse sequentially the individual standard solutions (5.10.3) to establish retention times for the internal standards, PCB congeners and GC resolution sample PCB 31.

### 8.3 Criteria for retention time reproducibility

Make three injections of the combined standards GC solution (5.10.4) and establish the variability (standard deviation) of the retention time for each component. This should typically not exceed 3 s or 0,5 % of the retention time, whichever is the greater.

### 8.4 Criteria for GC resolution

The resolution between congeners 28 and 31 serves for evaluation of the gas chromatograph. A resolution of $R > 0{,}5$ should be achieved.

## 8.5 GC analysis

Inject the nine final sample extracts (7.7) onto the GC in random order.

## 8.6 Assessment of method blank sample MB

The chromatogram for the method blank sample MB should display a peak for the internal standard (5.8) but should contain no significant peaks at the retention times (8.3) of the seven PCB congeners of interest (5.5).

## 8.7 Criteria for internal standard (s) suitability

The chromatogram for the sample blank SB should contain no interference at the internal standard retention time (s) greater than 5 % of the respective peak heights seen for the internal standard (s) in the pulp, paper or board samples S1 to S3.

If interferences are present for both internal standards, then an alternative internal standard has to be selected.

This shall be stated in the test report.

Isodrin, 1, 2, 3, 4-tetrachloronaphthalene, or hexabromobenzene have been used as alternatives with success.

## 8.8 Identification of PCB congeners by retention time

Identify the internal standard (5.8) and seven PCB congeners in the chromatograms C1 to C4 using the retention times established in 8.3. Calculate the reproducibility (coefficient of variation in %) of retention time for each of the PCB congeners and the internal standards. Similarly, identify the internal standard (5.8) and possible PCB congener peaks in the samples S1 to S3. The retention times of putative peaks in S1 to S3 should agree with the corresponding retention times for spiked samples to a tolerance of ± 2 .

## 8.9 Criteria for recovery

The recovery through the method of the internal standards and each of the seven PCB congeners should lie in the range 75 % to 115 %. This condition shall be met for each of the congeners subsequently reported as present in the pulp, paper or board sample. Recovery is assessed by a comparison of the GC results for calibration sample C2 and sample blank SB (8.5) and the combined GC standards solution (8.3).

## 8.10 Calculations

Tabulate the retention time and peak area (or height) for each congener identified together with the internal standard (s). Calculate the peak area ratio (PAR) for each congener identified versus the internal standard closest in retention time to that congener.

## 8.11 Graphical determination

For all samples C1 to C4 and S1 to S3 , plot the data graphically for each congener as shown in Annex C.

## 8.12 Results

Provided the criteria on retention time and recovery are satisfied, the level of each congener detected in the pulp, paper or board is found from the intercept of the standard addition line at the x-axis (Annex C).

A method for estimating the total PCB content of the pulp, paper or board is given in Annex A.

# 9 Confirmation

In cases where the result exceeds any relevant restriction criteria, the determination shall be confirmed as follows:

### 9.1 Confirmation by re-analysis on a different polarity phase

Repeat the determination from 8.1 onwards, employing a GC capillary column with a stationary phase different from that used at first.

The quantitative results thus obtained should agree with the previously found value(*s*) to within ± 15 % .

### 9.2 Confirmation by scanning gas chromatography/mass spectrometry (GC-MS)

Repeat the GC analysis of samples S1 to S3 using exactly the same GC conditions as employed in 8.5 with the MS scanning between 120 and 450 mass (m/z) units.

The ions for $[M]^+$, $[M\text{-}Cl]^+$ and $[M\text{-}2xCl]^+$ for each of the putative congener peak(s) should have the same relative ratio (± 15 %) as seen for standard(s) run under identical conditions.

Furthermore, there should be no additional ions greater than 10 % base intensity seen in the sample spectrum that are not present for the standard.

### 9.3 Confirmation by GC-MS in the selected ion mode

Re-analyse the set of samples from 8.2 onwards but using MS in place of the ECD or MSD. Detect the following ions assigned below for each of the congeners and internal standards.

**Table 1:**

| Class | Code | m/z |
|---|---|---|
| Trichlorobipenyls | 18, 28, 30 | 256 or 186 |
| Tetrachlorobiphenyl | 52 | 292 or 220 |
| Pentachlorobiphenyl | 101 | 326 or 254 |
| Hexachlorobiphenyls | 138, 153 | 360 or 290 |
| Heptachlorobiphenyl | 180 | 394 or 324 |
| Tribromobiphenyl | TBBP | 390 or 230 |

Calculations should employ peak area (or height) ratios from the GC-MS-SIM traces according to 8.10 onwards.

## 10 Expression of results

Calculate the results for each congener as the mean of the results from the parallel determinations. Express the results in milligrams per kilogram of pulp, paper or board as received. Round off the result to the nearest 0,01 mg/kg for results under 1 mg/kg, otherwise to the nearest 0,1 mg/kg. Report results below 0,01 mg/kg as < 0,01 mg/kg.

Calculate the total PCB content of the pulp, paper or board in accordance with Annex A, if required. Round off the result to the nearest 0,1 mg/kg. Report results below 0,1 mg/kg as < 0,1 mg/kg.

## 11 Precision

For an interlaboratory test the test method gave for the sum of determined congeners repeatability (*r*) and reproducibility (*R*) values as shown in table 2:

**Table 2: Repeatability and reproducibility found in an interlaboratory test**

|  | *r*<br>*n* = 3 | *R*<br>*n* = 5 |
|---|---|---|
| 0,2 mg/kg | < 10 % | < 25 % |
| 3,0 mg/kg | < 10 % | < 20 % |

## 12 Test report

The test report shall refer to this European Standard and state:

a) date and place of sampling;
b) date and place of testing;
c) identification of the material tested;
d) the results as stated in clause 10;
e) whether a confirmation test has been carried out and if so, its result;
f) reference to the technical PCB;
g) reference to the modified routine procedure, if relevant;
h) any departure from the specified procedure, or other circumstances that may have affected the results.