SLOVENSKI STANDARD
SIST ENV 1798:1997

01-september-1997

Papir, karton in lepenka v neposrednem stiku z živili - Določanje sedmih izbranih vrst polikloriranih bifenilov (PCB)

Paper and board intended to come into contact with foodstuffs - Determination of 7 specified polychlorinated biphenyls (PCB)

Papier und Pappe für den Kontakt mit Lebensmitteln - Bestimmung von 7 ausgewählten polychlorierten Biphenylen (PCB)

Papier et carton destinés a etre en contact avec des produits alimentaires - Détermination de 7 polychlorobiphényles (PCB) spécifiés

Ta slovenski standard je istoveten z: **ENV 1798:1995**

ICS:

67.250	Materiali in predmeti v stiku z živili	Materials and articles in contact with foodstuffs
85.060	Papir, karton in lepenka	Paper and board

SIST ENV 1798:1997 **en**

EUROPEAN PRESTANDARD

PRÉNORME EUROPÉENNE

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ENV 1798

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ICS 67.040; 85.060

Descriptors: paper, paperboards, food products, food-container contact, chemical analysis, determination, polychlorobiphenyl, gas chromatography

English version

Paper and board intended to come into contact with foodstuffs - Determination of 7 specified polychlorinated biphenyls (PCB)

Papier et carton destiné à être en contact avec des produits alimentaires - Détermination de 7 polychlorobiphényles (PCB) spécifiés

Papier und Pape für den Kontakt mit Lebensmitteln - Bestimmung von 7 ausgewählten polychlorierten Biphenylen (PCB)

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CEN

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

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Content

Foreword

This European Prestandard has been prepared by the Technical Committee CEN/TC 172 "Pulp, paper and board", of which the secretariat is held by DIN.

According to the CEN/CENELEC Internal Regulations, the following countries are bound to announce this European Prestandard: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

0 Introduction

CEN/TC 172 has decided to publish this test method as a European Prestandard (ENV) 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 (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 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 7 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.

1 Scope

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

2 Normative references

This European Prestandard 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 Prestandard only when incorporated in it by amendment or revision. For dated references the latest edition of the publication referred to applies.

prEN ISO 186
Paper and board - Sampling to determine average quality

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. 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 by 30 mm internal diameter.

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).

4.5 Capillary column suitable for the determination of PCB in accordance to the specification laid down in 8.4.

5 Reagents

Unless otherwise specified, reagents of a grade suitable for residue analysis shall be used. Water should be double-distilled or 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 > 99,8 %)

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

		Ballschmiter 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) or

5.8.2 2,4,6-Tribromobiphenyl (TBBP)

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

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

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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 Prestandard 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 Prestandard and does not constitute an endorsement by CEN of this product.

5.10 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 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 and 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 and TBBP.

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 and TBBP.

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 and TBBP (5.10.2) , and dilute to 200,0 ml with hexane.

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 substances 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 prEN ISO 186. 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 Place the solid-phase disposable cartridge (4.3) on 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 manufacturers instructions.

7.3 Take a representative sample of the paper or board sample (100,0 g as received), cut into pieces of about 1 cm^2 and randomise by shaking in a large glass beaker.

7.4 Take nine 100,0 ml round-bottomed flasks. Add (2,00 ± 0,02) g portions of the paper (7.3) to eight of these flasks. Treat then as follows:

7.4.1 Sample MB (method blank)

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

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) along 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 drops per min 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 should be optimised with regard to sensitivity, linearity and reproducibility, according to manufacturers 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.