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BSI Standards Publication

Characterization of waste — Determination of selected polychlorinated biphenyls (PCB) in solid waste by gas chromatography with electron capture or mass spectrometric detection

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National foreword

This British Standard is the UK implementation of EN 15308:2016. It supersedes BS EN 15308:2008 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee EH/4, Soil quality.

A list of organizations represented on this committee can be obtained on request to its secretary.

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English Version

Characterization of waste - Determination of selected polychlorinated biphenyls (PCB) in solid waste by gas chromatography with electron capture or mass spectrometric detection

Caractérisation des déchets - Détermination de polychlorobiphényles (PCB) sélectionnés dans les déchets solides par chromatographie en phase gazeuse avec détection par capture d'électrons ou spectrométrie de masse

Charakterisierung von Abfällen - Bestimmung ausgewählter polychlorierter Biphenyle (PCB) in festem Abfall unter Anwendung der Kapillar-Gaschromatographie mit Elektroneneinfang-Detektion oder massenspektrometrischer Detektion

This European Standard was approved by CEN on 21 September 2016.

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European foreword

This document (EN 15308:2016) has been prepared by Technical Committee CEN/TC 444 "Test methods for the characterization of solid matrices", the secretariat of which is held by NEN.

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of an identical text or by endorsement, at the latest by April 2017, and conflicting national standards shall be withdrawn at the latest by April 2017.

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This document supersedes EN 15308:2008.

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Introduction

Polychlorinated biphenyls (PCB) have been widely used as additives in industrial applications where chemical stability has been required. This stability on the other hand creates environmental problems when PCBs are eventually released into the environment. Since some of these PCB compounds are highly toxic, their presence in the environment (air, water, soil, sediment and waste) is regularly monitored and controlled. At present determination of PCB is carried out in these matrices in most of the routine laboratories following the preceding steps for sampling, pretreatment, extraction, clean-up by measurement of specific PCB by means of gas chromatography in combination with mass spectrometric detection (GC-MS) or gas chromatography with electron capture detector (GC-ECD).

Taking into account the different matrices and possible interfering compounds, this European Standard does not contain one single possible way of working. Several choices are possible, in particular relating to clean-up. Detection with both Mass Spectrometry and Electron Capture is possible. Two different extraction procedures and nine clean-up procedures are described. The use of internal and injection standards is described in order to have an internal check on choice of the extraction and clean-up procedure. This European Standard has been validated on seven solid waste which are typically contaminated with PCB (building debris, cable shredder, contaminated soil, electronic waste, sealant waste, shredder light fraction and waste wood). Validation data are given in Annex A (informative).

1 Scope

This European Standard specifies a method for quantitative determination of seven polychlorinated biphenyl congeners (PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153 and PCB-180) in solid waste using high-resolution gas chromatography with electron capture or mass spectrometric detection. The basic content of this standard is identical to that of the Horizontal PCB-standard and is therefore also applicable to soil, sludge and treated bio-waste. The detection and the quantification limits in this method are dependent on sample intake, the level of interferences as well as instrumental limitations. Under the conditions specified in this standard, minimum amounts of individual PCB congeners equal or above 0,01 mg/kg dry matter can typically be determined with no interferences present.

NOTE For the analysis of PCB in insulating liquids, petroleum products, used oils and aqueous samples is referred to EN 61619, EN 12766–1 and EN ISO 6468 respectively.

The method may be applied to the analysis of other PCB congeners not specified in the scope, but its suitability should be proven by proper in-house validation experiments.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 12766-1, *Petroleum products and used oils - Determination of PCBs and related products - Part 1: Separation and determination of selected PCB congeners by gas chromatography (GC) using an electron capture detector (ECD)*

EN 12766-2, *Petroleum products and used oils - Determination of PCBs and related products - Part 2: Calculation of polychlorinated biphenyl (PCB) content*

EN 14346, *Characterization of waste - Calculation of dry matter by determination of dry residue or water content*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
polychlorinated biphenyl
PCB
biphenyl substituted by one to ten chlorine atoms

3.2
congener
member of the same kind, class or group of chemicals

Note 1 to entry: Any one of the two hundred and nine individual PCB.

Note 2 to entry: The IUPAC congener numbers are for easy identification; they do not represent the order of chromatographic elution.

3.3
calibration standard
solution prepared from a secondary standard and/or stock solutions of native polychlorinated biphenyl congeners (PCB) and used to calibrate the response of the instrument with respect to analyte concentration

3.4
internal standard
$^{13}C_{12}$-labelled PCB or other PCB that are unlikely to be present in waste samples added to the sample before extraction and used for quantification of PCB content

3.5
injection standard
$^{13}C_{12}$-labelled PCB or other PCB that is unlikely to be present in waste samples added to the sample extract before injection into the gas chromatograph, to monitor variability of instrument response and the recovery of the internal standards

3.6
critical pair
pair of congeners that needs to be separated to a predefined degree (e. g. $R = 0{,}5$) to ensure chromatographic separation meets minimum quality criteria

3.7
resolution
R_S
difference in retention times between the maxima of the two peaks *i* and *j*, which constitute the critical pair, divided by the arithmetic mean of the peak widths of *i* and *j* at base, calculated as:

$$R_s = \frac{2\left(t_{Rj} - t_{Ri}\right)}{\left(w_{bi} + w_{bj}\right)} \quad (1)$$

where

t_{Rj} and t_{Ri} are the retention times of the two peaks *i* and *j* (sec), and

w_{bi} and w_{bj} are the peak widths of *i* and *j* (sec) at base

4 Principle

A proper test portion is extracted with a mixture of organic solvents by an appropriate extraction technique (e.g. shaking, soxhlet, sonication), partitioned against water and the organic layer separated. The obtained extracts are concentrated and, if appropriate, cleaned-up. Sample clean-up procedures may include sulphuric acid treatment, Dimethylsulfoxide/n-Hexan partitioning, column chromatography on alumina and silica. Tetrabutylammonium sulfite (TBA) or copper may be used to remove sulfur if required. The extract is analysed by gas chromatography with either mass spectrometric (GC-MS) or electron capture detection (GC-ECD). In case of GC-MS analysis quantification is performed by the isotope dilution technique. In case of GC-ECD, extracts are analysed using two columns of different polarity. Quantification is conducted by the internal standard method.

In case of plastic shredder a pure non-polar solvent should be used for extraction to prevent dissolving of the polymer matrix as far as possible.

5 Reagents

5.1 General

All reagents shall be of recognized analytical grade. Running a blank determination as described in 11.1 shall check the purity of the reagents used.

5.2 Reagents for extraction and drying

5.2.1 Acetone (2-propanone), $(CH_3)_2CO$.

5.2.2 Hexane like solvents with a boiling range of 36 °C to 98 °C, e.g. petroleum ether, n-hexane, n-heptane.

5.2.3 Anhydrous sodium sulfate, heated for at least 6 h to 550 °C ± 20 °C, cooled to about 200 °C in the furnace and then to ambient temperature in a desiccator containing magnesium perchlorate or another suitable drying reagent.

The anhydrous sodium sulfate shall be kept carefully sealed.

5.3 Reagents for clean-up procedures

5.3.1 Aluminium oxide clean-up:

5.3.1.1 One of two types of alumina, acidic or basic, which can be used in the clean-up of sample extracts:

— acidic alumina, activate by heating to 130 °C for a minimum of 12 h;

— basic alumina, activate by heating to 600 °C for a minimum of 24 h.

Preparation of deactivated aluminium oxide, the aluminium oxide is deactivated with 10 % water. To 90 g of aluminium oxide (5.3.1.1) add 10 g of water. Shake until all lumps have disappeared. Allow the aluminium oxide to condition before use for some 16 h, sealed from the air.

ICN Alumina Super I or an equivalent may be used without activation.

5.3.2 TBA sulfite reagent for sulfur removal:

5.3.2.1 Tetrabutylammonium reagent (TBA sulfite reagent): saturate a solution of tetrabutylammonium hydrogen sulfate in a mixture of equal volumina of water and 2-propanol, $c((C_4H_9)_4NHSO_4)$ = 0,1 mol/l, with sodium sulfite.

25 g of sodium sulfite should be sufficient for 100 ml of solution.

5.3.3 Pyrogenic copper for sulfur removal:

WARNING — Pyrogenic copper is spontaneously inflammable. Suitable precautions should be taken.

5.3.3.1 Copper-(II)sulfate pentahydrate, $CuSO_4 \cdot 5\ H_2O$.

5.3.3.2 Hydrochloric acid, c(HCl) = 2 mol/l.

5.3.3.3 Zinc granules, Zn, particle size 0,3 mm to 1,4 mm.

5.3.3.4 Anionic detergent aqueous solution (e.g. 35 % *m/V* n-dodecane-1-sulfonic acid sodium salt ($CH_3(CH_2)_{11}SO_3Na$)).

5.3.3.5 Deoxygenated water.

5.3.4 Silica – silver nitrate clean up:

5.3.4.1 Silica gel, particle size 60 µm to 200 µm.

5.3.4.2 Silver nitrate, $AgNO_3$.

5.3.4.3 Preparation of silica gel impregnated with silver nitrate.

Dissolve 10 g of $AgNO_3$ in 40 ml of water and pour this mixture in portions to 90 g silica. Shake the mixture until it is homogenous and leave standing it for 30 min. Put the mixture into a drying oven at 70 °C. Within 5 h increase the temperature from 70 °C up to 120 °C. Activate the mixture for 15 h at 125 °C. Store the mixture in brown glass bottles.

5.3.5 Commercially available benzenesulfonic acid/silica gel cartridges, 3 ml.

5.3.6 Dimethylsulfoxide/n-hexane partitioning:

5.3.6.1 Dimethylsulfoxide (DMSO).

5.3.6.2 n-Hexane, C6H14.

5.3.7 Sulphuric acid clean-up:

5.3.7.1 Sulphuric acid, H_2SO_4, 95 % to 97 %.

5.3.8 Silica gel/sulphuric acid clean-up:

5.3.8.1 Silica/H_2SO_4 44 %: Pour 28 g of activated silica and 22 g of sulfuric acid in a flask, stopper air tight and shake thoroughly until disappearance of all agglomerates.

5.3.8.2 Silica/NaOH 33 % 1 mol/l: pour 33,5 g of activated silica and 16,5 g 1 mol/l NaOH in a flask, stopper air tight and shake thoroughly until disappearance of all agglomerates.

5.3.9 Commercially available silica cartridges, 3 ml or 6 ml.

5.3.10 Florisil clean up:

5.3.10.1 Florisil®[1)] 100 mesh to 200 mesh, activated by heating to 600 °C for a minimum of 2 h.

5.3.10.2 Iso-octane, C_8H_{18}.

5.3.10.3 Iso-octane/Toluene 95/5.

1) Florisil® is a trade name for a prepared diatomaceous substance, mainly consisting of anhydrous magnesium silicate. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product. Equivalent products may be used if it can be shown to lead to comparable results.

5.4 Reagents for gas chromatographic analysis

5.4.1 Operating gases for gas chromatography, of high purity and in accordance with manufacturer's specifications.

5.5 Standard compounds

5.5.1 Calibration standards

Use the following PCB for the calibration:

— PCB-28: 2,4,4'-trichlorobiphenyl (CAS number: 7012–37–5);
— PCB-52: 2,2',5,5'-tetrachlorobiphenyl (CAS number: 35693–99–3);
— PCB-101: 2,2',4,5,5'-pentachlorobiphenyl (CAS number: 37680–37–2);
— PCB-118: 2,3',4,4',5-pentachlorobiphenyl (CAS number: 31508–00–6);
— PCB-138: 2,2',3,4,4',5'-hexachlorobiphenyl (CAS number: 35056–28–2);
— PCB-153: 2,2',4,4',5,5'-hexachlorobiphenyl (CAS number: 35065–27–1);
— PCB-180: 2,2',3,4,4',5,5'-heptachlorobiphenyl (CAS number: 35065–29–3).

5.5.2 Internal and injection standards

5.5.2.1 MS detection

The labelled PCB congeners to be considered as internal standards are listed below.

— ^{13}C-2,4,4'-trichlorobiphenyl (PCB-28);

— ^{13}C-2,2',5,5'-tetrachlorobiphenyl (PCB-52);

— ^{13}C-2,2',4,5,5'-pentachlorobiphenyl (PCB-101);

— ^{13}C-2,3',4,4',5-pentachlorobiphenyl (PCB-118);

— ^{13}C-2,2',3,4,4',5'-hexachlorobiphenyl (PCB-138);

— ^{13}C-2,2',4,4',5,5'-hexachlorobiphenyl (PCB-153);

— ^{13}C-2,2',3,4,4',5,5'-heptachlorobiphenyl (PCB-180).

^{13}C-2,2',3,3',5,5',6-heptachlorobiphenyl (PCB-178), other ^{13}C-labelled PCB or PCB that are unlikely to be present in waste samples may be used as internal and injection standards as well.

The application of isotopic dilution mass spectrometry is recommended but adding ^{13}C-labelled internal standards to the test portion before extraction is associated with high costs. Hence, if only an aliquot of the extract is subjected to the clean-up adding ^{13}C-labelled internal standards to this aliquot might be a good option to ensure high quality of the analysis and to reduce costs.

5.5.2.2 ECD detection

Also for ECD-detection internal and injection standards shall be added. Use at least one of the following standards unlikely to be present in waste samples and not interfering with the analytes as internal standard

— PCB-29 – 2,4,5-trichlorobiphenyl (CAS number: 15862–07–4);

— PCB-30 – 2,4,6-trichlorobiphenyl (CAS number: 35693–92–6);

— PCB-143 - 2,2',3,4,5,6'-hexachlorobiphenyl (CAS number: 68194–15–0);

— PCB-155 - 2,2',4,4',6,6'-hexachlorobiphenyl (CAS number: 33979–03–2);

— PCB-198 - 2,2',3,3',4,5,5',6,-octachlorobiphenyl (CAS number: 68194–17–2);

— PCB-207 - 2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl (CAS number: 52663–79–3);

— PCB-209 - 2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl (CAS number: 2051–24–3).

For quantification (internal standard) PCB-198 and PCB-209 are recommended because of little interferences found in practice. Use of PCB-30 and PCB-209 for relative retention is recommended, see EN 12766–1.

5.5.2.3 PCB congeners for resolution check

— PCB-28 – 2,4,4'-trichlorobiphenyl (CAS number: 7012-37-5);

— PCB-31 – 2,4',5-trichlorobiphenyl (CAS number: 16862-07-4).

6 Apparatus

6.1 Extraction and clean-up procedures

6.1.1 General

6.1.1.1 Customary laboratory glassware.

All glassware and material that comes into contact with the sample or extract shall be free of PCB and interfering compounds.

6.1.2 Extraction procedures

6.1.2.1 Glass sample bottles of proper size according to the amount of sample taken with glass stopper or screw top and polytetrafluorethene seal (PTFE).

6.1.2.2 Shaking device.

With horizontal movement (200 min^{-1} to 300 min^{-1}).

6.1.2.3 Water bath, adjustable up to 100 °C.

6.1.2.4 Separatory funnels of appropriate volume.

6.1.2.5 Conical flasks of appropriate volume.

6.1.2.6 Soxhlet extraction apparatus, consisting of round bottom flask e.g.100 ml, Soxhlet extractors and soxhlet thimbles e.g. 27 mm × 100 mm, vertical condensers e.g. 300 mm, with water-bath or heating mantle as heating device.

6.1.2.7 Evaporator.

Kuderna Danish or other evaporators, e.g. a rotary evaporator.

6.1.2.8 Analytical balance.

6.1.3 Clean-up procedures

6.1.3.1 Quartz wool or silanized glass wool.

WARNING — Working with quartz wool imposes a risk to health through the release of fine quartz particles. Inhalation of these should be prevented by using a fume cupboard and wearing a dust mask.

6.1.3.2 Boiling chips, glass or porcelain beads.

6.1.3.3 Calibrated test tubes with a capacity of 10 ml to 15 ml and ground glass stopper.

6.1.3.4 Glass chromatography columns of e.g. 600 mm length and 5 mm internal diameter.

6.1.3.5 Empty SPE-cartridge of e.g. 6 ml volume.

6.2 Gas chromatograph

Equipped with a capillary column, mass spectrometric detector (MS) or electron capture detector (ECD) based on ^{63}Ni. The injector shall be either an on-column injector, a split/splitless injector or a programmable temperature vaporizer injector.

NOTE 1 Working with an encapsulated radioactive source, as present in an ECD requires a license according to the appropriate national radiation protection regulations.

NOTE 2 Using ECD, gas chromatographs equipped with two detectors and with facilities for connecting two capillary columns to the same injection system are very well suited for this analysis; with such apparatus the confirmatory analysis can be performed simultaneously.

6.3 Capillary columns

The columns consist of a non-polar stationary phase, e.g. 5 % phenyl-methyl silicone, coated onto a fused silica capillary column or an equivalent chemically bonded phase column. Use a chromatogram of a standard solution containing PCB-28 and PCB-31 (5.5.2.3) at equal concentrations. Run the test under identical conditions as samples for the determination of the resolution of the critical pair PCB-28/PC-B31.The resolution of this pair shall be better than 0,5. In general column lengths should be 25 m to 60 m, internal diameter 0,18 mm to 0,32 mm and film thickness 0,1 µm to 0,5 µm.

Using ECD-detection, a column coated with a moderate polar phase, e.g. CP-Sil 19, OV 1701 or equivalent, shall be used to confirm the result obtained on the non-polar column. Confirmation analysis using a second column is not necessary in case the analytical result is much below any regulatory level.

7 Safety precautions

Anyone dealing with waste and sludge analysis shall be aware of the typical risks of that kind of material irrespective of the parameter to be determined. Waste and sludge samples may contain hazardous (e.g. toxic, reactive, flammable, infectious) substances, which can be liable to biological and/or chemical reaction. Consequently it is recommended that these samples should be handled with special care. The gases, which may be produced by microbiological or chemical activity, are potentially flammable and will pressurize sealed bottles. Bursting bottles are likely to result in hazardous shrapnel,

dust and/or aerosol. National regulations should be followed with respect to all hazards associated with this method.

8 Interferences

Some organic chlorinated compounds (e.g. tetrachlorobenzyltoluenes, polychlorinated naphthalenes, polychlorinated terphenyls, toxaphenes, also sulfur) give rise to interferences since their behaviour is very similar to that of PCB during sample clean-up and gas chromatographic separation. It is possible that several PCB congeners elute within one peak. On many capillary columns PCB-138 coelutes with PCB-160, PCB-163 and PCB-164. Hence PCB-138 concentration may represent the sum of those congeners (also in case of mass spectrometric detection) The same is true for PCB-101 and PCB-90. Typically the concentrations of the co-eluating congeners compared to those of the target congeners are low.

Presence of considerable amounts of mineral oil in the sample may interfere with the quantification of PCB in GC-MS analysis. In such cases, GC-ECD may be the preferred method or clean-up of the sample extract according to 11.3.8 using DMSO/n-hexane partitioning to remove the mineral oil from sample extract is recommended.

9 Sample storage

In principle, the samples shall be analysed as soon as possible after sampling. This applies in particular to the examination of microbiologically active solids. Field moist samples can be stored at a temperature of 4 °C ± 2 °C in sample containers in a dark place for a maximum of one week. If the sample cannot be processed within seven days, it shall be stored at temperatures below –18 °C. Dried samples shall be stored at room temperature in a dark place.

10 Pretreatment

10.1 General

The goal of a pretreatment procedure is to prepare a test sample in which the content of the PCB congeners is not significantly changed compared to the laboratory sample. Due to the different properties of the various kinds of materials there is no general procedure available. Recommendations for sample pretreatment are given in EN 15002 and ISO 14507.

10.2 Drying

Depending on the nature of the sample material and the extraction solvent to be used a drying step might be needed. If it is necessary, air-dry the complete sample or dry it in a ventilated drying oven at 40 °C or in a freeze dryer. The drying time depends on the technique chosen and the nature of the sample.

For sludge, freeze-drying is strictly applied.

10.3 Particle size reduction

In order to achieve a homogeneous and representative test portion, one or more particle size reduction steps might be needed. The choice of the technique depends on the nature of the sample and on the particle size needed. Typically, particle size reduction is a multi-step operation that implies the use of a sequence of different techniques like crushing, cutting or grinding.

Grinding of samples which have a plastic or paste-like consistency requires embrittlement with liquid nitrogen and particle size reduction to less than 0,5 mm, e.g. by using an ultra-centrifugal mill.

In case of plastic materials (e.g. cable shredder) the material to be granulated is poured in portions into liquid nitrogen and ground in a centrifugal mill (10 000 rounds/min to 15 000 rounds/min) cooled with liquid nitrogen. It should be noted that the mill is constantly kept cool by addition of liquid nitrogen in short intervals. The plastic material should be filled into the mill constantly in small portions without causing any significant slowing down of the grinder.

11 Procedure

11.1 Blank

Perform a blank determination following the paragraphs of the procedure applied to samples (selected extraction and clean-up). Use the same amounts of reagents that are used for pretreatment, extraction, clean up and analysis of samples. Analyse the blank immediately prior to analysis of the samples to demonstrate freedom from contamination.

11.2 Extraction

11.2.1 Extraction by shaking or sonification

Weigh a test portion of 10 g to 25 g to the nearest 0,1 g in a stoppered flask. Add a definite volume of the internal standard solution. Isotopically labelled internal standards may be added after extraction to an aliquot of the extract where appropriate. Typically the concentration of the individual internal standards in the final extract will be 0,1 µg/ml. Add 50 ml of acetone to the test sample. Extract by shaking thoroughly for 30 min on a shaking device or by sonification. Then add 50 ml of hexane-like solvent (5.2.2) and extract again thoroughly during 30 min. After the solids have settled decant the supernatant. Wash the remaining solids with 50 ml of hexane-like solvent (5.2.2) and decant again. Collect the extracts in a separatory funnel and remove the acetone by shaking twice with 400 ml of water. Dry the extract over anhydrous sodium sulfate. Filtrate or decant the extract and rinse the sodium sulfate three times with 10 ml of hexane-like solvent (5.2.2) and add the rinsings to the extract. Reduce the volume of the extract according to the applied clean-up procedure.

In case of waste material with a high proportion of plastic, e.g. plastic shredder, extraction with an acetone containing solvent leads to a high amount of co-extractives. In these cases, extraction should be performed twice with 50 ml of hexane-like solvent (5.2.2).

11.2.2 Soxhlet extraction

Weigh a test portion of 10 g to 25 g to the nearest 0,1 g in the extraction thimble. Add a definite volume of the internal standard solution. Isotopically labelled internal standards may be added after extraction to an aliquot of the extract where appropriate. Typically the concentration of the individual internal standards in the final extract will be 0,1 µg/ml. Add approximately 70 ml of the extraction mixture acetone/hexane-like solvent (5.2.1/5.2.2) 1:1 to the extraction vessel. Extract the sample for a minimum of 100 extraction cycles. Transfer the extract in a separatory funnel and remove the acetone by shaking twice with 400 ml of water. Dry the extract over anhydrous sodium sulfate. Filtrate or decant the extract and rinse the sodium sulfate three times with 10 ml of hexane-like solvent (5.2.2) and add the rinsings to the extract. Reduce the volume of the extract according to the applied clean-up procedure.

In case of waste material with a high proportion of plastic, e.g. plastic shredder, extraction with an acetone containing solvent leads to a high amount of co-extractives. In these cases, extraction should be performed with 50 ml of hexane-like solvent (5.2.2).

NOTE Other extraction techniques, e.g. accelerated solvent extraction (ASE), are also applicable provided that their suitability has been proven.

11.3 Clean-up

11.3.1 General

Clean-up of extracts shall be conducted if compounds are expected to be present that can interfere with the PCB congeners of interest in the gas chromatogram or if those compounds can influence the GC-procedure (i.e. contamination of the detection system). If no or negligible interfering substances are present, no clean-up is necessary. Before applying the clean-up to real samples the laboratory shall ensure that recoveries of all relevant congeners including internal standards are at least 70 %. If polar compounds have to be removed take special care on the recoveries of the low chlorinated PCB. A suitable injection standard shall be added to the final extract before GC-ECD or GC-MS analysis after the final clean-up and concentration to the desired volume have been performed.

11.3.2 Aluminium oxide clean-up

Prepare a chromatography column by placing a small plug of quartz wool (6.1.3.1) in the chromatography tube (6.1.3.4) and adding 2,0 g ± 0,1 g of aluminium oxide (5.3.1.1).

Apply the extract to the dry packed column; rinse the sample vessel twice with 1 ml of hexane-like solvent (5.2.2). Add the rinses to the column as soon as the liquid level has reached the surface of the column packing. Elute with approximately 20 ml of hexane-like solvent (5.2.2). Collect the entire eluate. Concentrate to the desired volume. If a new batch of aluminium oxide is used the solvent volume to elute the specified PCB congeners completely from the column shall be determined using a proper PCB standard solution

Commercially available disposable aluminium oxide cartridges may be used as an alternative if found equally suitable.

11.3.3 Silica cartridge clean-up

Pre-wash the silica cartridges (5.3.4) with n-hexane like solvent (5.2.2). Do not allow the cartridges to become dry. When the solvent is within 1 mm of the packing apply an aliquot of 1 ml of the sample extract (11.2) to the column. Elute the PCB with n-hexane like solvent (5.2.2) at 1 ml/min (approximately 5 ml of n-hexane like solvent (5.2.2) are required for complete elution of the PCB congeners of interest when using a cartridge with 3 ml capacity). Collect the entire eluate. Concentrate to the desired volume.

11.3.4 Silica H_2SO_4 clean-up

Prepare a chromatography column by pouring consecutively 1 g of silica NaOH (5.3.8.2), 5 g of silica H_2SO_4 (5.3.8.1) and 2 g of anhydrous Na_2SO_4 (5.2.3) in a clean chromatography column. Add a sufficient amount of n-hexane and elute until the top of the n-hexane like solvent (5.2.2) phase reaches the top of the Na_2SO_4 layer. Place with the aid of a Pasteur pipette the extract on top of the Na_2SO_4 layer and make it penetrate into the Na_2SO_4 layer. Elute with ca 60 ml of n-hexane like solvent (5.2.2) and collect the entire n-hexane like solvent (5.2.2) fraction. Concentrate to the desired volume.

11.3.5 Florisil® clean-up

Add into a glass column (6.1.3.4) 5 mm of anhydrous sodium sulfate (5.2.3), 1,5 g Florisil (5.3.10.1), and again 5 mm of sodium sulfate. To fix the mixture, place glass wool (6.1.3.1) on the top. Rinse the column with approx. 50 ml iso-octane (5.3.10.2). Apply the extract to the column. Rinse the extraction tube/vessel two times with 1 ml iso-octane / toluene (95/5) (5.3.10.3) and add the rinsings onto the column. Then, elute the PCBs with 7 ml to 9 ml iso-octane /toluene. Collect the entire eluate and concentrate to the desired volume. If a new batch of Florisil is used the necessary solvent volume to elute the specified PCB congeners completely from the column shall be determined using a proper PCB standard solution.

Alternatively empty 6 ml SPE-cartridges (6.1.3.5) filled with 2 g of Florisil (5.3.10.1) can be used instead of glass chromatography columns (6.1.3.4). For preconditioning, application of the sample and elution of the PCBs see above. Note that the cartridges should not run dry during the clean-up procedure.

Commercially available Florisil-SPE-cartridges could also be used. In this case the suitability for the clean-up procedure should be evaluated.

11.3.6 TBA clean-up

Add 2 ml of TBA sulfite reagent (5.3.2) to 1 ml of concentrated extract and shake for 1 min. Add 10 ml of water and shake again for 1 min. Separate the organic phase from the water with a Pasteur pipette and add a few crystals of anhydrous sodium sulfate to remove the remaining traces of water.

11.3.7 Pyrogenic copper clean-up

11.3.7.1 Preparation of pyrogenic copper

Dissolve 45 g copper(II) sulfate pentahydrate (5.3.3.1) in 480 ml water containing 20 ml hydrochloric acid (5.3.3.2) in a 1 000 ml beaker. Take 15 g of zinc granules (5.3.3.3) add 25 ml water and one drop of anionic detergent solution (5.3.3.4) in another 1 000 ml beaker.

Stir with a magnetic stirrer at a high speed to form a slurry. Then, while stirring at this high speed, carefully add the copper(II) sulfate solution drop by drop using a glass rod. Hydrogen is liberated and elemental pyrogenic copper is precipitated (red coloured precipitate). Stirring is continued until the hydrogen generation almost ceases. Then the precipitated copper is allowed to settle. The supernatant water is carefully removed and the product washed with deoxygenated water (5.3.3.5) three times, to eliminate residual salts. Then the water is carefully replaced with 250 ml acetone (5.2.1) (while continuously stirring the mixture). This operation is repeated twice more to ensure complete removal of water. Then the above procedure is repeated three times with 250 ml hexane (5.2.2), to ensure elimination of the acetone. Carefully transfer the copper with hexane into a ground glass stoppered flask. The copper shall be covered with n-hexane completely and stored in a refrigerator. The shelf life of the pyrogenic copper is approximately two weeks. The clean-up efficiency will then decline. The copper will change colour as the clean-up efficiency decreases.

11.3.7.2 Pyrogenic copper — Clean-up procedure

Add 1 ml to 2 ml of the extract to a test or centrifuge tube. Add approximately 100 mg of pyrogenic copper powder (prepared according 11.3.7.1), thoroughly mix and remove the extract after phase separation.

Centrifugation for about 5 min at approximately 3 500 rpm (it is recommended to ensure that there is no visible turbidity) improves phase separation.

11.3.8 $AgNO_3$/silica clean-up

Add into a glass column (6.1.3.4), Na_2SO_4, resulting in a layer of e.g. 5 mm height, 2 g of the $AgNO_3$/silica mixture (5.3.4.2) and again Na_2SO_4, 5 mm height. Rinse the column with approximately 50 ml of n-hexane like solvent (5.2.2). Discard the eluate. Transfer the concentrated extract (ca. 2 ml) with a pipette onto the column. Rinse the vessel three times each with 2 ml of n-hexane like solvent (5.2.2) and add the rinsings onto the column. When the meniscus of the solvent reaches the surface of the Na_2SO_4, add 40 ml of n-hexane like solvent (5.2.2) onto the column. Collect the entire eluate and concentrate it to the desired volume.

If the eluate is still coloured after the clean-up, the procedure should be repeated.

11.3.9 DMSO/n-hexane partitioning clean-up

Transfer the whole extract to a separatory funnel (6.1.2.4) of 100 ml and extract the PCB with 25 ml of DMSO. Repeat twice. Transfer the combined DMSO extracts to a separatory funnel of 500 ml, add 100 ml of pure water and extract the PCB with 50 ml of n-hexane. Repeat once. Combine the n-hexane extracts and concentrate to the desired volume.

Extracts of samples containing a high amount of aliphatic compounds may require clean-up by dimethylsulfoxide/hexane partitioning. This clean-up step should only be applied in case of GC-MSD and not for GC/ECD.

11.3.10 Benzenesulfonic acid/silica cartridge clean-up

Condition the silica cartridges by eluting three times with 2 ml portions of n-hexane, discard the eluate and vacuum dry the columns. Apply 500 µl of the extract to the column and let slowly seep into the column. After 30 s, add 2 x 1 ml n-hexane like solvent (5.2.2) to the column and wait once again for 30 s. Elute the PCB from the column with 3 x 0,5 ml of n-hexane like solvent (5.2.2). Collect the entire eluate.

11.4 Gas chromatographic analysis

11.4.1 General

Both mass spectrometric (MS) and electron capture (ECD) detection are allowed, but in special cases only one technique will give the proper results. In general MS is recommended.

In the following cases ECD-detection may be preferred:

— Presence of considerable amounts of mineral oil in the sample;

— Determination of PCB patterns in the sample;

— Screening to select the samples having PCB concentrations higher than the minimum reporting values.

For both detection techniques the internal standard method is used for quantification.

NOTE Removal of mineral oil may be difficult because the polarity of these compounds can be comparable to those of PCB.

11.4.2 Optimizing the gas chromatograph

Optimize the gas chromatograph (6.2) in such a way that separation is achieved as described in 6.3.

Typical GC settings are given in Annexes A and B.

11.4.3 Detectors

11.4.3.1 Electron capture detector

The ECD shall be operated at temperatures of 300 °C to 350 °C. Use the manufacturer's recommended settings to give the best conditions for linearity of the detector response. The make-up gas flow rate shall be between 20 ml/min and 40 ml/min, and shall be selected to give the best sensitivity to PCB.

11.4.3.2 Mass spectrometer

Typical MS settings are given in Annex A.

Table 1 — Diagnostic ions to be monitored in the selected ion monitoring mode

PCB congener	Native m/z	^{13}C-labelled m/z	Relative abundance %
trichloro PCB-28,-31	256[a] 258 186	268[a] 270	100 98
tetrachloro PCB-52	289,9 291,9[a] 220	301,9 303,9[a]	77 100
pentachloro PCB-101, –118	325,9[a] 327,9 256	337,9[a] 339,9	100 65
hexachloro PCB-138, –153	359,8[a] 361,8 289,9	371,8[a] 373,8	100 81
heptachloro PCB-178, –180	393,8[a] 395,8 323,9	405,8[a] 407,8	100 98
[a] Quantification ions, other m/z values correspond to qualifier ions.			

The detection of PCB congeners is carried out using a low-resolution mass spectrometer. The mass spectrometer is tuned in accordance with the manufacturer's instructions. Chromatograms are recorded in full scan or selected ion monitoring/recording mode (SIM/SIR). The ions to be selected are given in Table 1. For each native congener two ions making part of the chlorine isotope cluster of the molecular ion and one specific fragment ion are chosen. The relative abundance of the 2 ions of the molecular isotope cluster shall meet the criteria set in 11.4.5.3. The most abundant ion of the molecular isotope cluster shall be used for quantification.

Ion chromatograms are given in Annex A for a standard solution and a soil sample extract.

11.4.4 Check on method performance

The recovery *R%* of each internal standard, added to the sample prior to extraction, can be calculated by comparing the response of the internal standard with that of the injection standard, added to the final extract:

$$R\% = \frac{A_{\mathrm{d}} \times m_{\mathrm{inj}}}{A_{\mathrm{inj}} \times m_{\mathrm{d}} \times s_{\mathrm{d}}} \times 100 \qquad (2)$$

where

A_{d} and A_{inj} are the responses of respective internal standard and injection standard in the ion chromatograms of the sample extract;

m_{inj} is the mass of injection standard in µg spiked to the final extract;

m_{d} is the mass of internal standard in µg spiked to the sample prior to extraction;

s_{d} is the relative response factor of the labelled internal standard relative to the injection standard, as recorded for the calibration solution.

The values calculated for the concentrations of native congeners in the sample are only considered to be acceptable if the recoveries of the internal standards are higher than 50 % and do not exceed 110 %. In other cases the values should be reported as indicative.

NOTE The suggested range of acceptable recoveries of the internal standards have been verified in the validation inter-comparison study conducted in 2007.

11.4.5 GC-MS determination

11.4.5.1 Calibration of the method using the internal standard method

11.4.5.1.1 General

Run the GC-MS analysis with the calibration solutions.

Calculate the relative response factor for the native PCB and the ^{13}C-labelled PCB (internal standard, IS) after obtaining a calibration curve by plotting the ratio of the mass concentrations against the ratio of the peak areas (or peak heights) using Formula (3):

$$\frac{A_{\mathrm{n}}}{A_{\mathrm{IS}}} = s \times \frac{\rho_{\mathrm{n}}}{\rho_{\mathrm{IS}}} + b \qquad (3)$$

where

A_{n} is the measured response of the native PCB, e.g. peak area;

A_{IS} is the measured response of the PCB internal standard, e.g. peak area;

s is the slope of the calibration function or relative response factor;

ρ_{n} is the mass concentration of the native PCB in the calibration solution in µg/ml;

ρ_{IS} is the mass concentration of the PCB internal standard in the calibration solution in µg/ml;

b is the intercept of the calibration curve with the ordinate.

Two types of calibration are distinguished: the initial calibration (11.4.5.1.2) and the daily calibration (validity check of the initial calibration); the last one is called recalibration (11.4.5.1.3).

The initial calibration serves to establish the linear working range of the calibration curve. This calibration is performed when the method is used for the first time and after maintenance and/or repair of the equipment.

The recalibration checks the validity of the linear working range of the initial calibration curve and is performed before each series of samples.

11.4.5.1.2 Initial calibration

Record the GC-MS chromatograms of a series of at least 5 standard solutions (5.5.1/5.5.2.1) with concentrations, which cover the intended concentration range. Construct a calibration graph for each compound.

11.4.5.1.3 Validity check of the calibration function

For each batch of samples, inject at least two calibration standards with concentrations of (20 ± 10) % and (80 ± 10) % of the established linear range and calculate the concentrations using Formula (1). If the measured values fall within the ± 10 % of the reference values the initial calibration line is assumed to be valid. If not, a new calibration line shall be established according to 11.4.5.1.2.

11.4.5.2 Measurement

Record the ion chromatograms of the extracts obtained under 11.2. On the basis of the absolute retention times identify the peaks that can be assigned to the PCB congeners and corresponding internal standards (see 11.4.5.3 for identification criteria).

11.4.5.3 Identification

A native or labelled PCB congener is identified as being present in a standard, blank, or sample when all of the criteria listed below are met. If the criteria are not met, the PCB congener has not been identified and the results shall not be reported for regulatory compliance purposes.

— The signals for the two diagnostic masses specified in Table 1 shall be present in the mass chromatogram and their retention times shall be within ± 0,03 min based on the retention time of the corresponding ^{13}C-labelled PCB.

— The signal to noise ratio (S/N) for the GC peak at each mass shall be greater than or equal to 3 for each PCB detected in a sample extract, and greater than or equal to 10 for all PCB congeners in the calibration standard.

— The ratio of the integrated peak areas of the two ions from the molecular ion isotope cluster shall be within ± 10 % theoretical chlorine isotope ratio.

— The relative intensities (relative to the diagnostic peak having the highest response in the calibration standard solution) of all the selected diagnostic ions measured in the sample do not deviate by more than ± (0,1 I_{std} + 10) % from the relative intensities determined in the calibration standard solution (I_{std} is the relative intensity of the diagnostic ion in the calibration standard solution).

NOTE EN ISO 22892 can also be consulted to assist in identification of PCB.

11.4.5.4 Calculation

Calculate the mass content of the individual PCB from the multipoint calibration Formula (3) by using Formula (4):

$$\omega_{\mathrm{n}} = \frac{\left(\frac{A_{\mathrm{n}}}{A_{\mathrm{d}}} - b\right) \times q_{\mathrm{d}} \times 100}{s \times m \times d_{\mathrm{m}}} \qquad (4)$$

where

ω_{n} is the content of the PCB congener found in the sample in mg/kg on the basis of the dry matter;

A_{d} is the measured response of the corresponding internal standard in the sample extract;

A_{n} is the measured response of the PCB congener in the sample extract;

s is the slope of the calibration function or relative response factor;

b is the intercept of the calibration curve with the ordinate;

q_{d} is the mass of the internal standard added to the sample in µg;

m is the mass of the test sample used for extraction in g;

d_{m} is the content of the dry matter of the sample, determined according to EN 14346.

11.4.6 GC-ECD determination

11.4.6.1 Calibration

11.4.6.1.1 General

Run the GC-ECD analysis with the calibration solutions.

Calculate the relative response factor for the native PCB and the corresponding internal standard after obtaining a calibration curve by plotting the ratio of the mass concentrations against the ratio of the peak areas (or peak heights) using Formula (3).

Two types of calibration are distinguished: the initial calibration (11.4.6.1.2) and the daily calibration (validity check of the initial calibration); the last one is called recalibration (11.4.6.1.3). The initial calibration serves to establish the linear working range of the calibration curve. This calibration is performed when the method is used for the first time and after maintenance and/or repair of the equipment.

The recalibration checks the validity of the linear working range of the initial calibration curve and is performed before each series of samples.

11.4.6.1.2 Initial calibration

Record the GC-ECD chromatograms of a series of at least five standard solutions (5.5.1/5.5.2.1) with concentrations, which cover the intended concentration range. Construct a calibration graph for each compound.

NOTE It is allowed to work with nonlinear calibration graphs.

11.4.6.1.3 Recalibration

For each batch of samples, inject at least two calibration standards with concentrations of (20 ± 10) % and (80 ± 10) % of the established linear range and calculate the concentrations using Formula (1). If the measured values fall within the ± 10 % of the reference values the initial calibration line is assumed to be valid. If not, a new calibration line shall be established according to 11.4.6.1.2.

If using nonlinear calibration graphs, recalibration shall be conducted as described in 11.4.6.1.2.

11.4.6.2 Measurement

Record the GC-ECD chromatograms of the extracts obtained under 11.2. With the aid of the relative retention times identify the peaks belonging to the PCB congeners and corresponding internal standards (see 11.4.6.3 for identification criteria). Check the presence of any assigned compound by repeating the gas chromatographic analysis, using GC-MS or using a column with a moderate polar phase (6.3) in combination with ECD.

If the area is above the level of the linear range a diluted extract shall be injected for proper quantification.

11.4.6.3 Identification

A PCB congener is identified as being present in a standard, blank or sample when all of the criteria listed below are met. If the criteria are not met, the PCB congener has not been identified and the results shall not be reported for regulatory compliance purpose.

— The signals for the PCB congener of interest shall be present in the gas chromatogram obtained on both capillary columns (non-polar, medium polar) used for separation and their relative retention time shall be within ± 0,2 % based on the relative retention time of the corresponding PCB in the calibration solution.

— The signal to noise ratio (S/N) for the GC peak at each mass shall be greater than or equal to three for each PCB detected in a sample extract, and greater than or equal to 10 for all PCB congeners in the calibration standard.

— Inspect ECD chromatograms for peak patterns to provide further evidence for the presence or absence of particular PCB congeners. Moreover, peak patterns give an indication for the presence of interfering compounds when they are compared with congener patterns in the chromatograms of technical PCB formulations run under identical conditions.

12 Calculation

Calculate the mass content of the individual PCB from the multipoint calibration Formula (3) by using Formula (4).

The calculation method in Annex D can be applied for the calculation of the total content of PCB.

13 Test report

The test report shall contain at least the following information:

a) a reference to this European Standard;

b) references to the methods used for extraction and clean-up;

c) a complete identification of the sample;

d) the results of the determination; in case of dual column GC-ECD analysis both results shall be reported;

e) any detail not specified in this document or which are optional, as well as any other factors that might have affected the result.

If the total PCB content is needed as final result, a calculation method, based on the analytical results, is proposed in Annex D.

Annex A
(informative)

Performance characteristics

A.1 General

The method performance characteristics given in this Annex have been established in a European inter-comparison study on seven solid wastes which are typically contaminated with PCB (building debris, cable shredder, contaminated soil, electronic waste, sealant waste, shredder light fraction and waste wood). Additionally a PCB standard solution with a defined concentration was used for quality assurance purposes. The study was carried out in 2007.

A.2 Type of samples and sample preparation

a) Contaminated soil

The sample was taken from an old industrial site. In order to achieve the desired concentration it was mixed with non contaminated soil. The homogenized material was air-dried and sieved (5 mm). After milling in a ball mill the material was sieved again (1 mm) and finally homogenized by shaking in a plastic drum.

b) Building debris

The sample was collected from a building on a chemical industry site. It consists of parts of concrete, brick and gypsum. The material was crushed in a jaw crusher into particles < 10 mm. After milling in a ball mill the material was sieved again (1 mm) and finally homogenized by shaking in a plastic drum.

c) Waste wood

After grinding using a cutting mill two subsequent milling processes with sieves of 2 mm and 1 mm were performed in order to obtain visually homogenous material. In order to achieve the desired concentration the material was spiked with an extract of contaminated soil in acetone. After air-drying, the material was homogenized in a plastic drum.

d) Sealant waste

This sample was collected from windows in a public school. In order to achieve the desired concentration the material was mixed with non contaminated samples. The mixture consisted of sealants based on silicone and polyacryl polymers. The sample was grinded with a cutting mill using liquid nitrogen. Three subsequent milling processes with sieves of 5 mm, 2 mm and 1 mm were performed. The material was finally homogenized in a plastic drum.

e) Electronic waste

Boards from different electronic devices were crushed manually into smaller pieces and grinded using a cutting mill. Two subsequent milling processes with sieves of 5 mm and 2 mm were performed. After sieving (1 mm), the material was grinded again with a centrifugal mill (ring sieve 0,75 mm) and finally homogenized in a plastic drum.

f) Shredder light fraction

This material is a fraction of waste from used devices and vehicles. Typically it consists of 25 % to 35 % plastics, 20 % to 30 % elastomers, 10 % to 16 % glass, 3 % to 5 % lacquers, 3 % to 6 % textiles, 3 % to 6 % wood/fibrous materials, 0,5 % to 4 % alumina, 1 % to 3 % copper, 3 % to 13 % iron, 10 % to 20 % soil material and street dirt. The material was grinded using a cutting mill. The material was then sieved. The fraction < 1 mm was taken and homogenized in a plastic drum.

g) Cable shredder

The sample material was grinded with a centrifugal mill (ring sieve 0,50 mm) using liquid nitrogen. The resulting material required further air drying, grinding and sieving. Finally the fraction < 2 mm was taken and homogenized in a plastic drum.

h) Standard solution

Commercially available solutions of 7 PCB congeners in iso-octane were mixed and diluted to the desired concentrations with cyclohexane. The concentration of the individual congeners was in the range of 0,2 µg/ml to 1,2 µg/ml.

A.3 Homogeneity and stability

Within-bottle homogeneity of samples was tested by eight repeated analyses from one sample container. For testing between-bottle homogeneity of bottles, eight repeated analyses from different sample vessels were performed. Data for homogeneity testing are given in Table A.1 (from 1 sample container) and Table A.2 (from 8 sample bottles).

Stability of samples during the study was tested. Results showed that all analytes were sufficiently stable.

Table A.1 — Homogeneity testing within bottle

Analyte	**Contami-nated soil**	**Building debris**	**Cable shredder**	**Electronic waste**	**Sealant waste**	**Shredder light fraction**	**Standard solution**	**Waste wood**
	RSD %	RSD %	RSD %	RSD %	RSD %	RSD %	RSD %	RSD %
PCB 28	3,4	2,9	14,8	4,4	2,0	8,5	0,0	6,5
PCB 52	2,4	1,8	6,5	19,8	3,8	7,4	0,7	6,5
PCB 101	3,3	2,2	8,7	28,8	3,9	8,1	1,8	6,3
PCB 118	3,2	2,0	5,5	30,3	4,0	3,8	3,7	5,9
PCB 153	3,1	2,3	5,5	29,0	4,4	16,1	2,1	5,6
PCB 138	4,5	1,4	5,0	30,0	3,6	7,6	0,6	4,9
PCB 180	3,1	1,8	6,7	14,7	7,4	4,7	0,7	4,7
sum PCB_7	2,8	1,6	7,2	26,8	3,6	7,4	0,7	4,2
RSDRelative standard deviation								

Table A.2 — Homogeneity testing between bottles

Analyte	Contami-nated soil	Building debris	Cable shredder	Electronic waste	Sealant waste	Shredder light fraction	Standard solution	Waste wood
	RSD %	RSD %	RSD %	RSD %	RSD %	RSD %	RSD %	RSD %
PCB 28	6,7	5,0	7,1	1,7	4,7	5,2	0,0	5,4
PCB 52	6,1	5,6	4,1	5,7	4,6	5,1	0,7	3,3
PCB 101	6,0	4,0	6,4	5,2	4,7	4,9	1,8	2,3
PCB 118	5,0	3,0	6,7	6,8	4,4	4,8	3,7	2,3
PCB 153	4,4	4,0	7,7	8,9	4,8	7,3	2,1	5,4
PCB 138	4,8	3,9	4,5	6,1	4,2	7,0	0,6	4,6
PCB 180	4,6	2,4	8,6	6,0	3,8	7,8	0,7	4,1
sum PCB_7	4,9	3,6	5,0	6,0	4,4	5,0	0,7	1,8
RSD Relative standard deviation								

A.4 Extraction

The standard describes three possibilities for extraction: soxhlet extraction, extraction by shaking and by sonification. About 25 % each of the participants used soxhlet extraction or ultrasonification, the other 50 % used shaking. The results of the validation study showed comparability of the extraction methods.

A.5 Clean-up

The standard describes several possibilities for clean-up. The participants used most of them: $AgNO_3$-silica (22 %), benzenesulfonic acid-silica (22 %), Florisil (3 %), silica gel (13 %), silica H_2SO_4 (19 %) or no clean-up (8 %). There was no indication that the results were influenced by choice of clean-up procedure.

A.6 Detection

The standard describes two possible GC detectors: mass spectrometric (GC-MSD) and electron capture detector (GC-ECD). 50 % of the participants used GC-ECD and GC-MSD respectively. No significant differences in results due to the choice of detection technique were observed.

A.7 PCB standard solution

A standard solution of known reference concentrations of 7 PCB congeners was analysed by the participants. Table A.3 shows the overall mean values with respect to the reference values.

Table A.3 — Analytical results of standard solution

Analyte	Mean value µg/ml	Reproducibilty standard deviation µg/ml	Reference concentration µg/ml
PCB 28	0,191	0,031	0,200
PCB 52	0,650	0,088	0,600
PCB 101	0,965	0,097	1,000
PCB 118	0,214	0,035	0,200
PCB 138	1,208	0,144	1,200
PCB 153	0,214	0,035	0,200
PCB 180	0,787	0,075	0,800
Sum PCB_7	4,174	0,391	4,200

The results of the performance tests on the different waste samples are presented in Table A.4 below.

Table A.4 — Performance characteristics for the determination of polychlorinated biphenyls in waste

Sample	Analyte	O %	p	N	Outliers	x mg/kg	s_R mg/kg	$C_{V,R}$ %	s_r mg/kg	$C_{V,r}$ %
Building debris	PCB-028	5	20	40	1	1,203	0,454	37,7	0,069	5,7
	PCB-052	0	20	40	0	1,985	0,726	36,6	0,12	6,1
	PCB-101	0	20	40	0	7,992	3,306	41,4	0,366	4,6
	PCB-118	5,3	19	38	1	7,098	1,771	25,0	0,568	8,0
	PCB-138	0	20	40	0	8,84	2,741	31,0	0,513	5,8
	PCB-153	10	20	40	2	5,998	1,426	23,8	0,268	4,5
	PCB-180	5	20	40	1	3,581	0,913	25,5	0,342	9,6
	Sum PCB_7	5,3	19	38	1	35,2	8,384	23,8	1,322	3,8
Cable shredder	PCB-028	20	15	33	3	0,647	0,115	17,8	0,05	7,7
	PCB-052	25	16	34	4	0,498	0,147	29,5	0,035	7,0
	PCB-101	0	16	34	0	0,829	0,231	27,8	0,051	6,2
	PCB-118	6,7	15	32	1	0,601	0,172	28,6	0,043	7,1
	PCB-138	12,5	16	34	2	0,857	0,229	26,8	0,028	3,3
	PCB-153	12,5	16	34	2	0,704	0,124	17,7	0,021	2,9
	PCB-180	7,1	14	30	1	0,293	0,064	21,7	0,018	6,2

Sample	Analyte	O %	*p*	*N*	Outliers	*x* mg/kg	s_R mg/kg	$C_{V,R}$ %	s_r mg/kg	$C_{V,r}$ %
	Sum PCB_7	14,3	14	30	2	4,659	1,17	25,1	0,131	2,8
Contaminated soil	PCB-028	10	20	40	2	0,565	0,178	31,5	0,028	5,0
	PCB-052	10	20	40	2	0,886	0,316	35,7	0,093	10,5
	PCB-101	10	20	40	2	3,69	1,259	34,1	0,155	4,2
	PCB-118	0	19	38	0	4,125	1,751	42,4	0,277	6,7
	PCB-138	0	20	40	0	4,843	2,044	42,2	0,344	7,1
	PCB-153	0	20	40	0	3,53	1,562	44,3	0,219	6,2
	PCB-180	10	20	40	2	1,942	0,45	23,2	0,198	10,2
	Sum PCB_7	0	19	38	0	19,818	8,488	42,8	0,966	4,9
Electronic waste	PCB-028	22,2	19	35	2	0,008	0,003	33,6	0,002	21,0
	PCB-052	26,3	19	39	5	0,209	0,045	21,4	0,009	4,1
	PCB-101	0	19	39	0	0,815	0,366	44,9	0,071	8,7
	PCB-118	5,6	18	37	1	0,751	0,213	28,3	0,091	12,1
	PCB-138	0,0	19	39	0	0,879	0,322	36,6	0,118	13,5
	PCB-153	5,3	19	39	1	0,597	0,237	39,6	0,105	17,6
	PCB-180	5,9	17	37	1	0,133	0,051	38,3	0,025	19,1
	Sum PCB_7	0,0	19	39	0	3,653	1,548	42,4	0,341	9,3
Sealant waste	PCB-028	13,3	15	36	2	2,13	1,21	56,9	0,081	3,8
	PCB-052	5,3	19	38	1	311,9	84,4	27,1	9,002	2,9
	PCB-101	5,3	19	38	1	923,8	246,7	26,7	37,31	4,0
	PCB-118	0,0	18	36	0	783,8	192,5	24,6	34,64	4,4
	PCB-138	0,0	19	38	0	892,5	320,4	35,9	39,05	4,4
	PCB-153	5,3	19	38	1	554,4	130,3	23,5	27,36	4,9
	PCB-180	5,3	19	38	1	107,3	26,8	25,0	6,526	6,1
	Sum PCB_7	0,0	18	36	0	3534,8	891,5	25,2	128,5	3,6
Shredder light fraction	PCB-028	10	20	40	2	0,538	0,238	44,2	0,029	5,3
	PCB-052	15	20	40	3	0,393	0,104	26,5	0,015	3,9
	PCB-101	5	20	40	1	0,513	0,199	38,8	0,028	5,4

Sample	Analyte	O %	*p*	*N*	Outliers	*x* mg/kg	s_R mg/kg	$C_{V,R}$ %	s_r mg/kg	$C_{V,r}$ %
	PCB-118	5,3	19	38	1	0,399	0,141	35,4	0,022	5,4
	PCB-138	0	19	38	0	0,82	0,344	41,9	0,068	8,3
	PCB-153	5	20	40	1	0,669	0,277	41,4	0,06	9,0
	PCB-180	0	19	38	0	0,421	0,197	46,9	0,027	6,4
	Sum PCB_7	5,3	19	38	1	3,769	1,403	37,2	0,132	3,5
Waste wood	PCB-028	10	20	40	2	0,256	0,11	42,8	0,013	5,0
	PCB-052	10	20	40	2	0,335	0,107	31,9	0,011	3,4
	PCB-101	10,5	19	38	2	0,524	0,174	33,3	0,025	4,8
	PCB-118	5,3	19	38	1	0,511	0,12	23,5	0,036	7,0
	PCB-138	10,0	20	40	2	0,642	0,246	38,3	0,032	5,0
	PCB-153	5,3	19	38	1	0,483	0,125	25,8	0,035	7,3
	PCB-180	10,5	19	38	2	0,281	0,045	16,2	0,008	2,7
	Sum PCB_7	5,3	19	38	1	3,081	0,76	24,7	0,172	5,6

p Number of laboratories before elimination of outliers
N Number of observed values
O Percentage of outliers
x Mean value
s_R Estimate of the reproducibility standard deviation
$C_{V,R}$ Coefficient of variation of reproducibility
s_r Estimate of the repeatability standard deviation
$C_{V,r}$ Coefficient of variation of rep

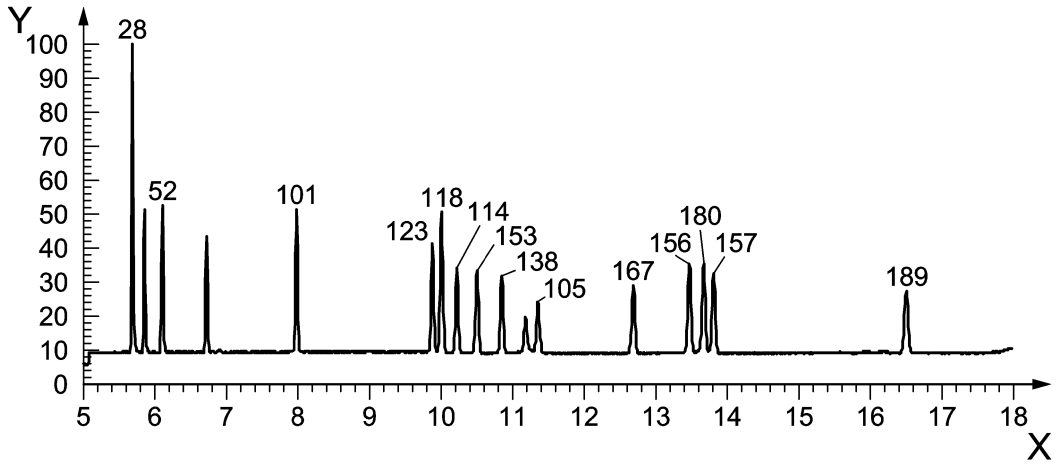
Annex B
(informative)

Examples of GC-MS chromatograms of a calibration standard solution and a contaminated soil sample

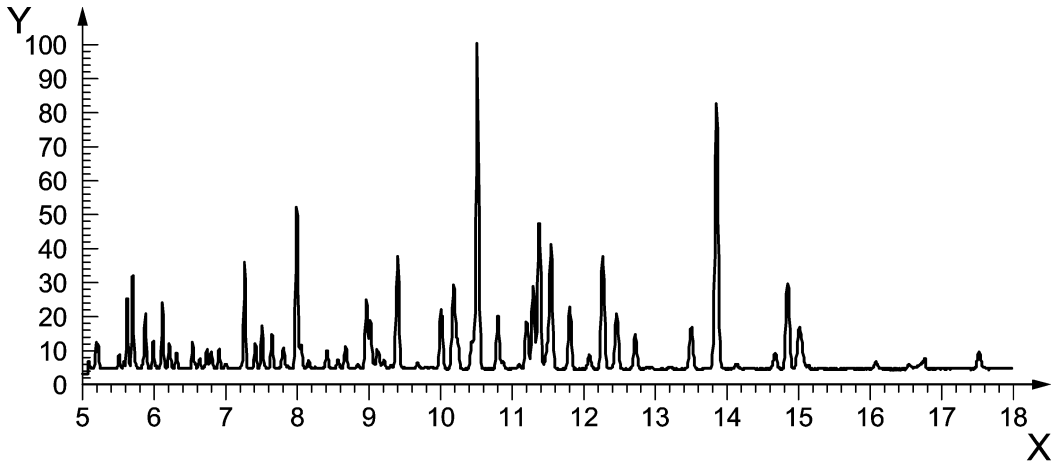
GC-MS total ion (TIC) and selected ion (m/z) chromatograms for native and labelled PCB congeners were recorded under the GC-MS conditions given below.

Capillary column:	HT-5, 25 m x 0,22 mm x 0,10 µm or equivalent
Oven temperature programme:	125 °C, 1 min
	25 °C/min to 200 °C
	4 °C/min to 260 °C
	60 °C, 1 min
Total run time:	20 min
Injector temperature:	300 °C
Splitless injection:	1 µl, keep the split 1 min closed
Carrier gas:	Helium 0,7 ml/min constant flow
MS Interface temperature:	280 °C
Source temperature:	230 °C
Ionization energy:	70 eV

Examples of GC-MS total ion chromatograms are presented in Figure B.1 for a calibration solution with 14 PCB congeners and for a contaminated soil extract.



a)



b)

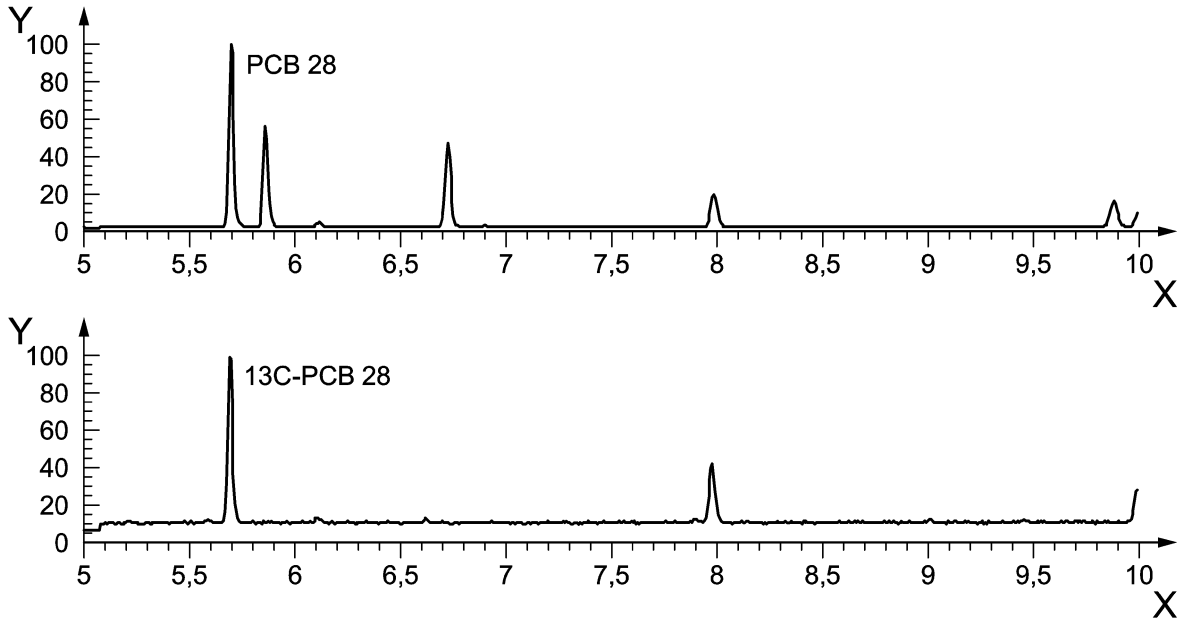
Key

X time in min

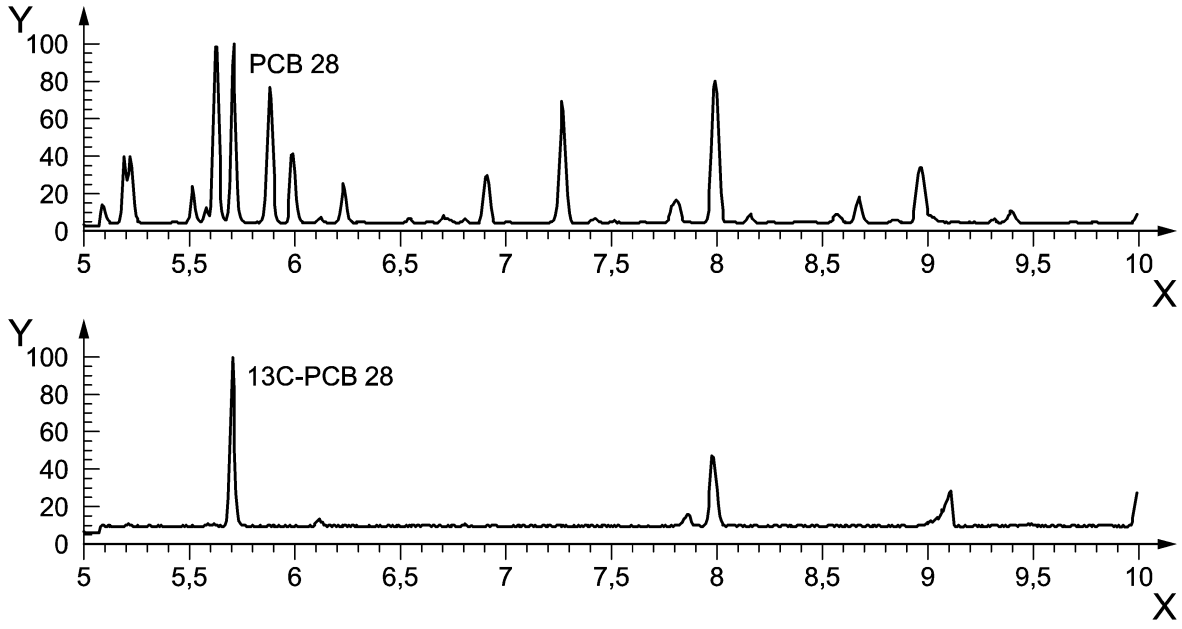
Y relative abundance in per cent

Figure B.1 — GC-MS total ion chromatogram of a calibration solution (14 congeners) and a contaminated soil extract

Examples of selected ion chromatograms for PCB-28 and ^{13}C-PCB-28 are presented in Figure B.2 for a calibration solution and for a contaminated soil extract.



a)



b)

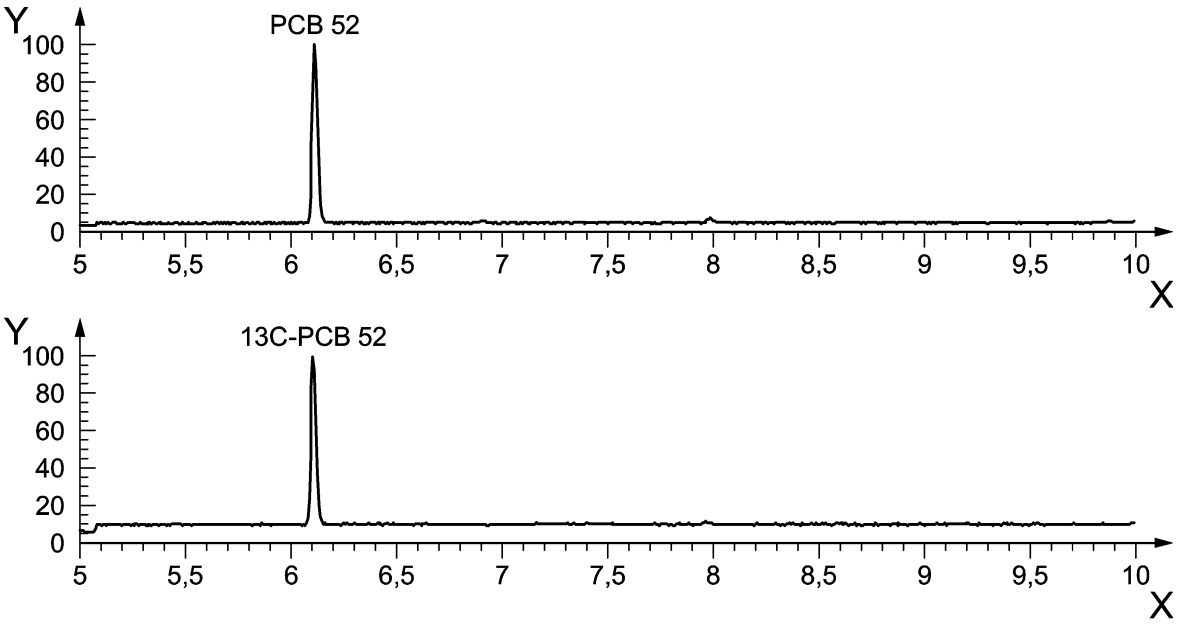
Key

X time in min

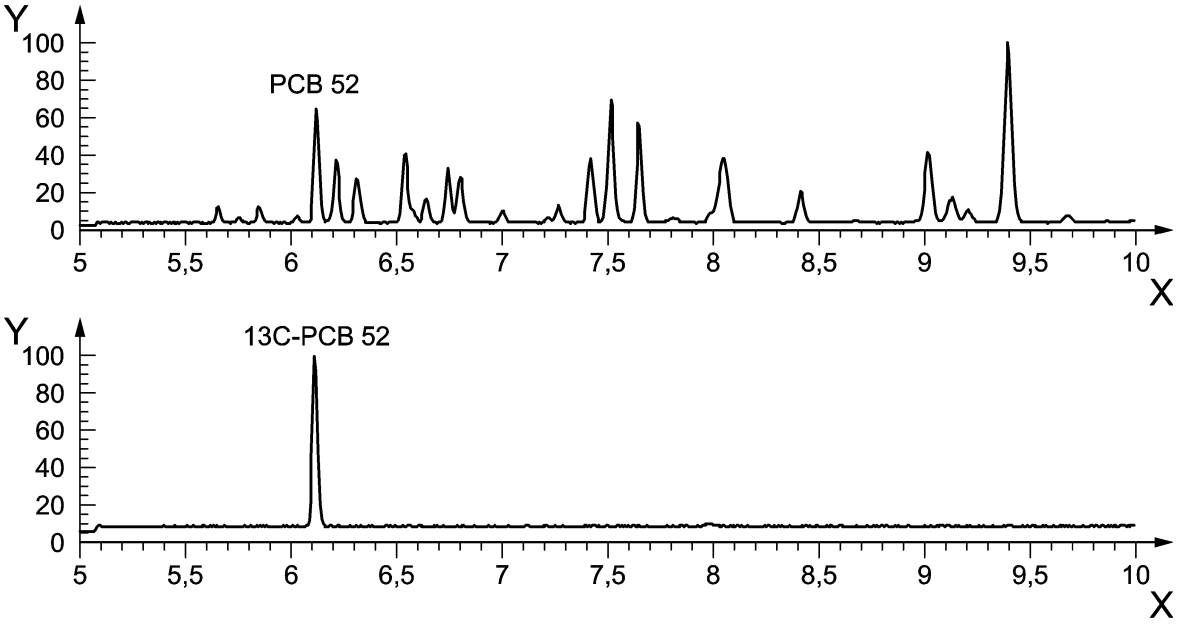
Y relative abundance in per cent

Figure B.2 — Selected ion chromatograms for PCB-28 and ^{13}C-PCB-28, for a calibration solution and a contaminated soil extract

Examples of selected ion chromatograms for PCB-52 and 13C-PCB-52 are presented in Figure B.3 for a calibration solution and for a contaminated soil extract.



a)



b)

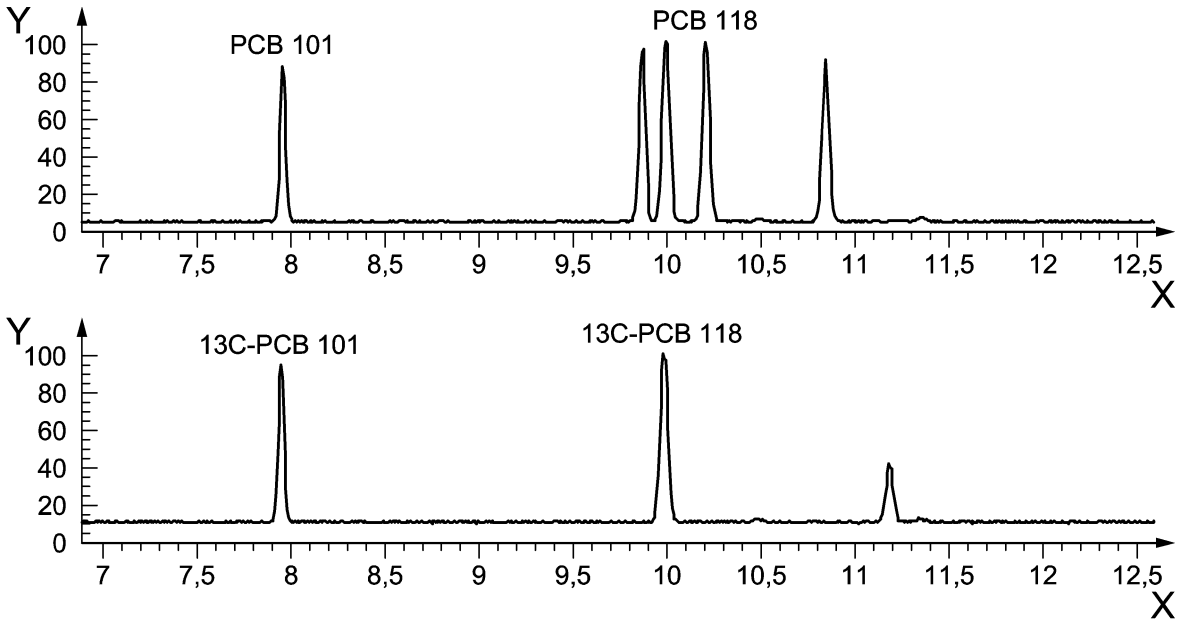
Key

X time in min

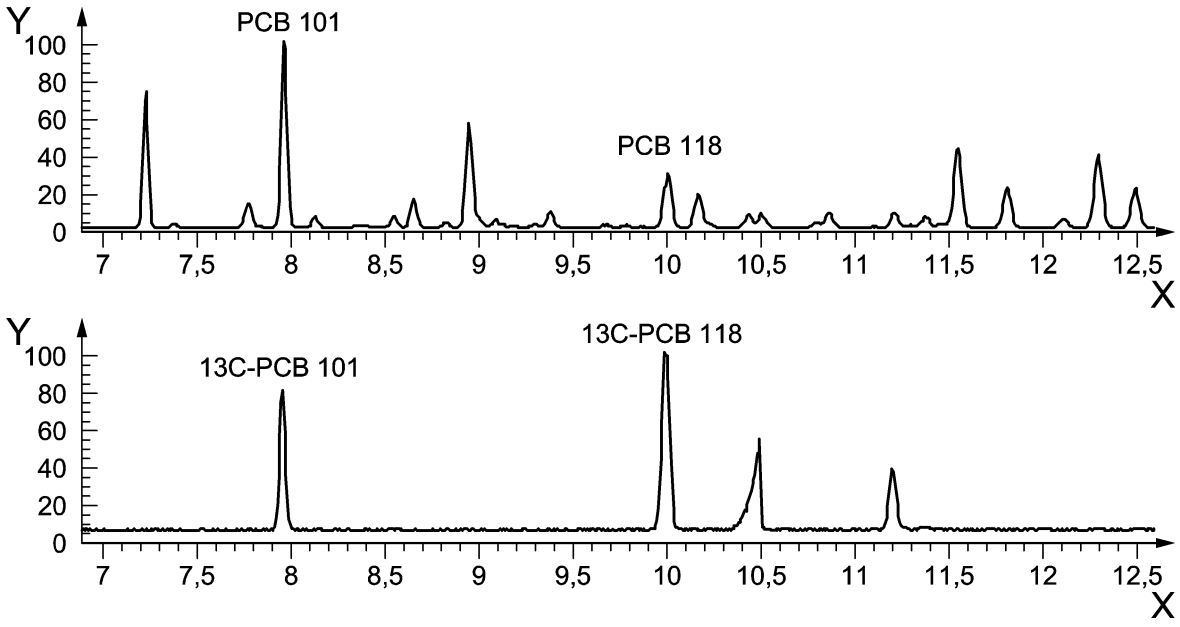
Y relative abundance in per cent

Figure B.3 — Selected ion chromatograms for PCB-52 and ^{13}C-PCB-52, for a calibration solution and a contaminated soil extract

Examples of selected ion chromatograms for PCB-101, PCB-118 and 13C-PCB-101, 13C-PCB-118 are presented in Figure B.4 for a calibration solution and for a contaminated soil extract.



a)



b)

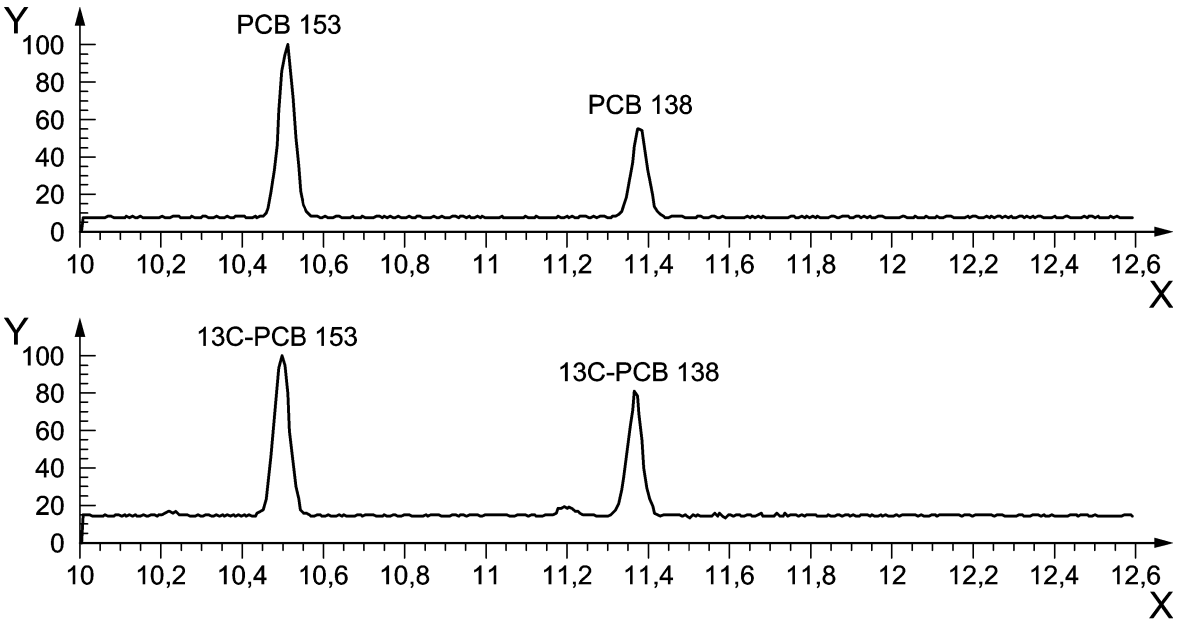
Key

X time in min

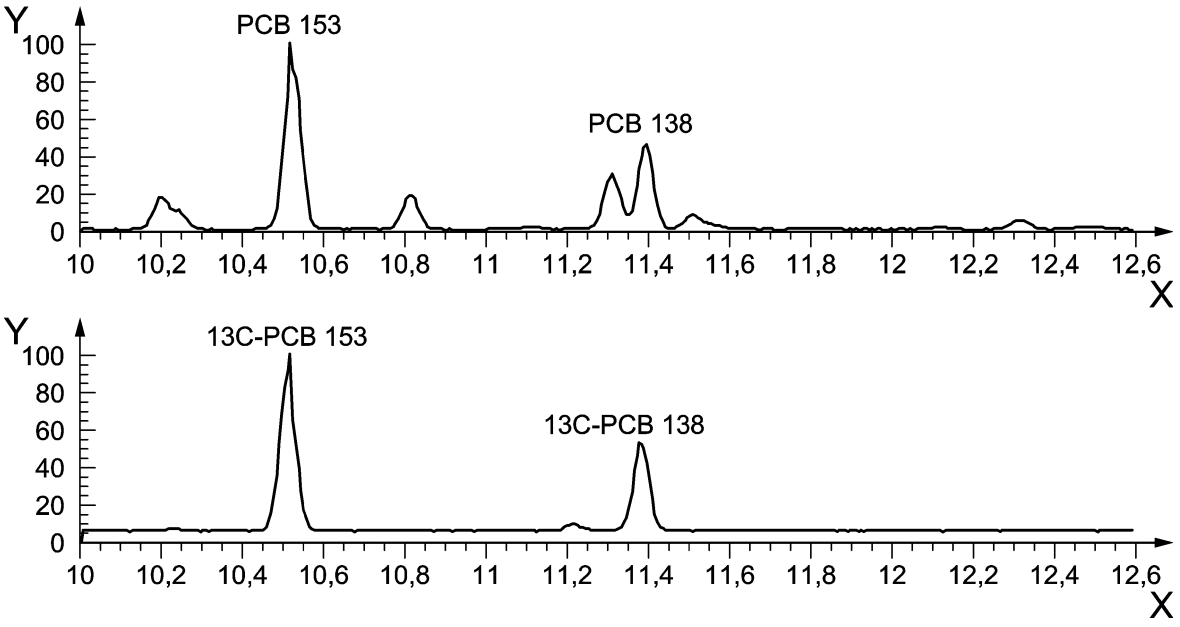
Y relative abundance in per cent

Figure B.4 — Selected ion chromatograms for PCB-118 and ^{13}C-PCB-118, for a calibration solution and a contaminated soil extract

Examples of selected ion chromatograms for PCB-153, PCB-138 and ^{13}C-PCB-153, ^{13}C-PCB-138 are presented in Figure B.5 for a calibration solution and for a contaminated soil extract.



a)



b)

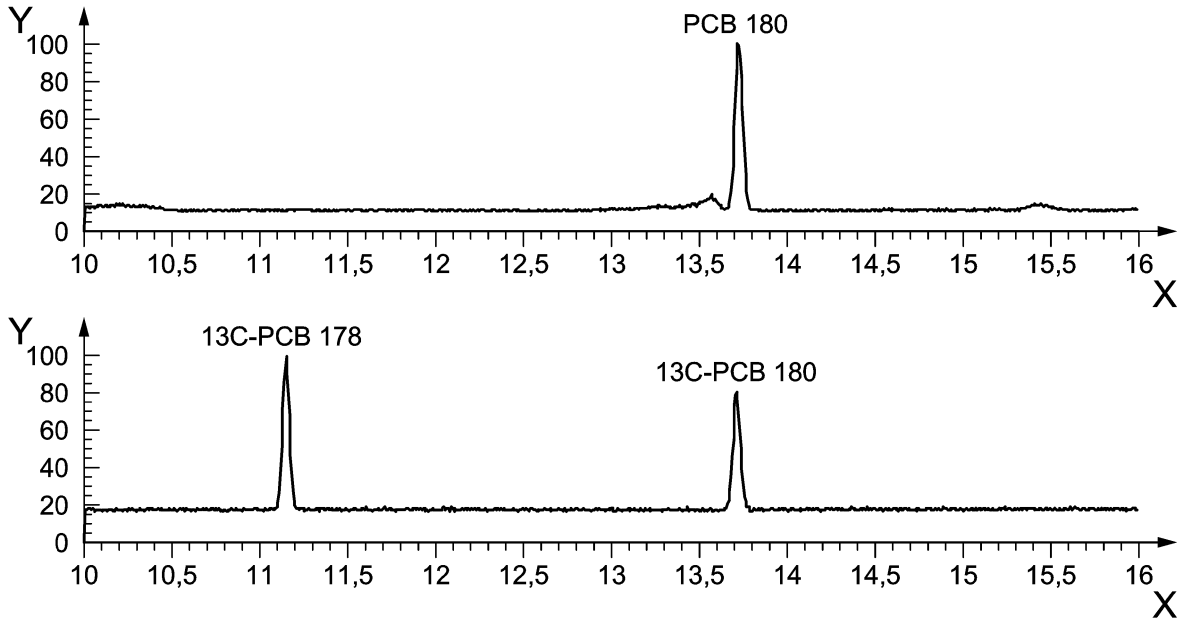
Key

X time in min

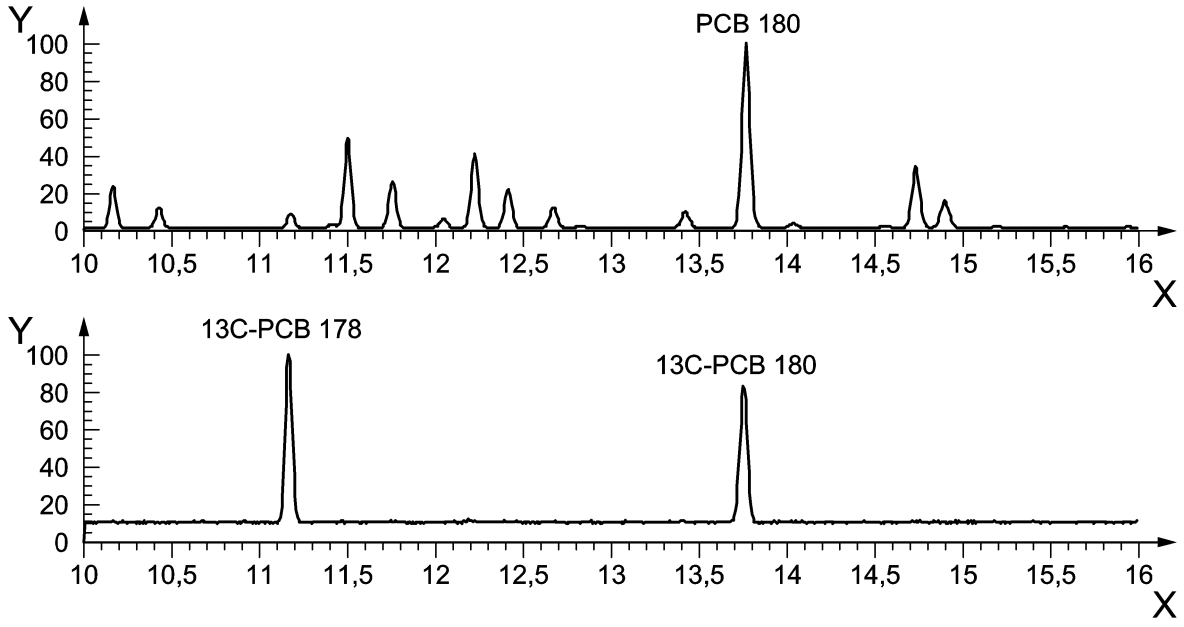
Y relative abundance in per cent

Figure B.5 — Selected ion chromatograms for PCB-138, PCB-153, ^{13}C-PCB-138 and ^{13}C-PCB-153, for a calibration solution and a contaminated soil extract

Examples of selected ion chromatograms for PCB-180 and ^{13}C-PCB-180 are presented in Figure B.6 for a calibration solution and for a contaminated soil extract



a)



b)

Key

X time in min

Y relative abundance in per cent

Figure B.6 — Selected ion chromatograms for PCB-180 and ^{13}C-PCB-180, for a calibration solution and a contaminated soil extract

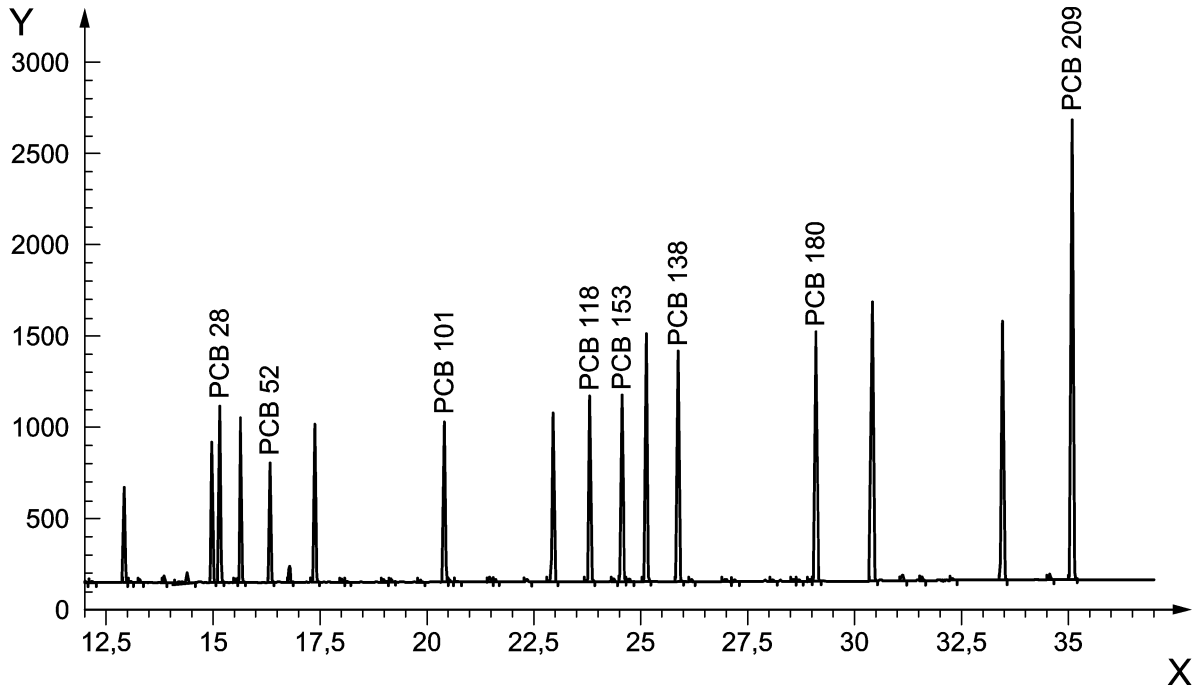
Annex C
(informative)

Examples of GC-ECD chromatograms of a calibration standard solution and a cable shredder sample

GC-μECD chromatograms were recorded under the conditions given below.

GC:	HP 6890 with μECD
Capillary column:	HT-8, 50 m x 0,22 mm x 0,25 μm
Oven temperature programme:	50 °C, 2 min
	50 °C/min to 168 °C
	4 °C/min to 310 °C
	310 °C, 20 min
Split/splitless injection:	1,0 μl
Injector temperature:	250 °C
Carrier gas:	Hydrogen, 2,0 ml/min

Examples of gas chromatograms obtained by GC-μECD, for a PCB standard solution of 15 congeners and for a cable shredder extract contaminated with PCB are presented respectively in Figure C.1 and Figure C.2.

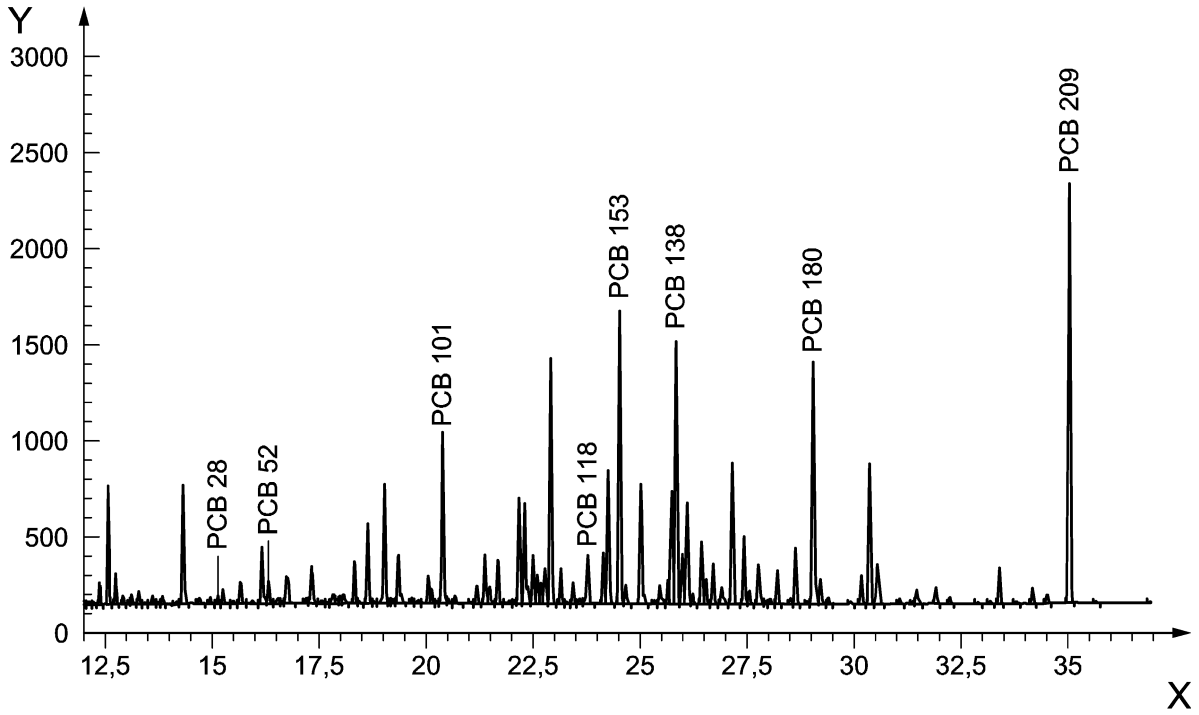


Key

X time in min

Y relative abundance

Figure C.1 — Gas chromatogram of PCB standard solution (15 congeners) in cyclohexane, Promochem NE-USL 100 (concentration 25 pg/µl) analysed by GC-µECD on a HT-8 capillary column



Key

X time in min

Y relative abundance

Figure C.2 — Gas chromatogram of a cable shredder extract contaminated with PCB at a level of approximately 22 mg/kg (sum of seven congeners) analysed by GC-μECD on a HT-8 capillary column

Annex D
(normative)

Calculation method for the estimation of total PCB content

The PCBs represent 209 chemical compounds with a basic structure constituted by two aromatic rings and between 1 and 10 chlorine atoms in substitution to the hydrogen atoms of the rings. According to the number of chlorine atoms and their position around the rings, 209 possible combinations exist and the different compounds are named congeners. Ballschmiter and Zell (1987, [9]) attributed codification numbers to each congener; the codification is detailed in Table D.1 below.

Table D.1 — Codification of PCB congeners

CASRN	Congener Number	IUPAC Name
1336-36-3		Polychlorinated biphenyl (PCB)
2051-60-7	1	2-Chlorobiphenyl
2051-61-8	2	3-Chlorobiphenyl
2051-62-9	3	4-Chlorobiphenyl
13029-08-8	4	2,2'-Dichlorobiphenyl
16605-91-7	5	2,3-Dichlorobiphenyl
25569-80-6	6	2,3'-Dichlorobiphenyl
33284-50-3	7	2,4-Dichlorobiphenyl
34883-43-7	8	2,4'-Dichlorobiphenyl
34883-39-1	9	2,5-Dichlorobiphenyl
33146-45-1	10	2,6-Dichlorobiphenyl
2050-67-1	11	3,3'-Dichlorobiphenyl
2974-92-7	12	3,4-Dichlorobiphenyl
2974-90-5	13	3,4'-Dichlorobiphenyl
34883-41-5	14	3,5-Dichlorobiphenyl
2050-68-2	15	4,4'-Dichlorobiphenyl
38444-78-9	16	2,2',3-Trichlorobiphenyl
37680-66-3	17	2,2',4-Trichlorobiphenyl
37680-65-2	18	2,2',5-Trichlorobiphenyl
38444-73-4	19	2,2',6-Trichlorobiphenyl
38444-84-7	20	2,3,3'-Trichlorobiphenyl
55702-46-0	21	2,3,4-Trichlorobiphenyl

38444-85-8	22	2,3,4'-Trichlorobiphenyl
55720-44-0	23	2,3,5-Trichlorobiphenyl
55702-45-9	24	2,3,6-Trichlorobiphenyl
55712-37-3	25	2,3',4-Trichlorobiphenyl
38444-81-4	26	2,3',5-Trichlorobiphenyl
38444-76-7	27	2,3',6-Trichlorobiphenyl
7012-37-5	28	2,4,4'-Trichlorobiphenyl
15862-07-4	29	2,4,5-Trichlorobiphenyl
35693-92-6	30	2,4,6-Trichlorobiphenyl
16606-02-3	31	2,4',5-Trichlorobiphenyl
38444-77-8	32	2,4',6-Trichlorobiphenyl
38444-86-9	33	2,3',4'-Trichlorobiphenyl
37680-68-5	34	2,3',5'-Trichlorobiphenyl
37680-69-6	35	3,3',4-Trichlorobiphenyl
38444-87-0	36	3,3',5-Trichlorobiphenyl
38444-90-5	37	3,4,4'-Trichlorobiphenyl
53555-66-1	38	3,4,5-Trichlorobiphenyl
38444-88-1	39	3,4',5-Trichlorobiphenyl
38444-93-8	40	2,2',3,3'-Tetrachlorobiphenyl
52663-59-9	41	2,2',3,4-Tetrachlorobiphenyl
36559-22-5	42	2,2',3,4'-Tetrachlorobiphenyl
70362-46-8	43	2,2',3,5-Tetrachlorobiphenyl
41464-39-5	44	2,2',3,5'-Tetrachlorobiphenyl
70362-45-7	45	2,2',3,6-Tetrachlorobiphenyl
41464-47-5	46	2,2',3,6'-Tetrachlorobiphenyl
2437-79-8	47	2,2',4,4'-Tetrachlorobiphenyl
70362-47-9	48	2,2',4,5-Tetrachlorobiphenyl
41464-40-8	49	2,2',4,5'-Tetrachlorobiphenyl
62796-65-0	50	2,2',4,6-Tetrachlorobiphenyl
68194-04-7	51	2,2',4,6'-Tetrachlorobiphenyl
35693-99-3	52	2,2',5,5'-Tetrachlorobiphenyl
41464-41-9	53	2,2',5,6'-Tetrachlorobiphenyl
15968-05-5	54	2,2',6,6'-Tetrachlorobiphenyl
74338-24-2	55	2,3,3',4-Tetrachlorobiphenyl

41464-43-1	56	2,3,3',4'-Tetrachlorobiphenyl
70424-67-8	57	2,3,3',5-Tetrachlorobiphenyl
41464-49-7	58	2,3,3',5'-Tetrachlorobiphenyl
74472-33-6	59	2,3,3',6-Tetrachlorobiphenyl
33025-41-1	60	2,3,4,4'-Tetrachlorobiphenyl
33284-53-6	61	2,3,4,5-Tetrachlorobiphenyl
54230-22-7	62	2,3,4,6-Tetrachlorobiphenyl
74472-34-7	63	2,3,4',5-Tetrachlorobiphenyl
52663-58-8	64	2,3,4',6-Tetrachlorobiphenyl
33284-54-7	65	2,3,5,6-Tetrachlorobiphenyl
32598-10-0	66	2,3',4,4'-Tetrachlorobiphenyl
73575-53-8	67	2,3',4,5-Tetrachlorobiphenyl
73575-52-7	68	2,3',4,5'-Tetrachlorobiphenyl
60233-24-1	69	2,3',4,6-Tetrachlorobiphenyl
32598-11-1	70	2,3',4',5-Tetrachlorobiphenyl
41464-46-4	71	2,3',4',6-Tetrachlorobiphenyl
41464-42-0	72	2,3',5,5'-Tetrachlorobiphenyl
74338-23-1	73	2,3',5',6-Tetrachlorobiphenyl
32690-93-0	74	2,4,4',5-Tetrachlorobiphenyl
32598-12-2	75	2,4,4',6-Tetrachlorobiphenyl
70362-48-0	76	2,3',4',5'-Tetrachlorobiphenyl
32598-13-3	77	3,3',4,4'-Tetrachlorobiphenyl
70362-49-1	78	3,3',4,5-Tetrachlorobiphenyl
41464-48-6	79	3,3',4,5'-Tetrachlorobiphenyl
33284-52-5	80	3,3',5,5'-Tetrachlorobiphenyl
70362-50-4	81	3,4,4',5-Tetrachlorobiphenyl
52663-62-4	82	2,2',3,3',4-Pentachlorobiphenyl
60145-20-2	83	2,2',3,3',5-Pentachlorobiphenyl
52663-60-2	84	2,2',3,3',6-Pentachlorobiphenyl
65510-45-4	85	2,2',3,4,4'-Pentachlorobiphenyl
55312-69-1	86	2,2',3,4,5-Pentachlorobiphenyl
38380-02-8	87	2,2',3,4,5'-Pentachlorobiphenyl
55215-17-3	88	2,2',3,4,6-Pentachlorobiphenyl
73575-57-2	89	2,2',3,4,6'-Pentachlorobiphenyl
68194-07-0	90	2,2',3,4',5-Pentachlorobiphenyl

68194-05-8	91	2,2',3,4',6-Pentachlorobiphenyl
52663-61-3	92	2,2',3,5,5'-Pentachlorobiphenyl
73575-56-1	93	2,2',3,5,6-Pentachlorobiphenyl
73575-55-0	94	2,2',3,5,6'-Pentachlorobiphenyl
38379-99-6	95	2,2',3,5',6-Pentachlorobiphenyl
73575-54-9	96	2,2',3,6,6'-Pentachlorobiphenyl
41464-51-1	97	2,2',3,4',5'-Pentachlorobiphenyl
60233-25-2	98	2,2',3,4',6'-Pentachlorobiphenyl
38380-01-7	99	2,2',4,4',5-Pentachlorobiphenyl
39485-83-1	100	2,2',4,4',6-Pentachlorobiphenyl
37680-73-2	101	2,2',4,5,5'-Pentachlorobiphenyl
68194-06-9	102	2,2',4,5,6'-Pentachlorobiphenyl
60145-21-3	103	2,2',4,5',6-Pentachlorobiphenyl
56558-16-8	104	2,2',4,6,6'-Pentachlorobiphenyl
32598-14-4	105	2,3,3',4,4'-Pentachlorobiphenyl
70424-69-0	106	2,3,3',4,5-Pentachlorobiphenyl
70424-68-9	107	2,3,3',4',5-Pentachlorobiphenyl
70362-41-3	108	2,3,3',4,5'-Pentachlorobiphenyl
74472-35-8	109	2,3,3',4,6-Pentachlorobiphenyl
38380-03-9	110	2,3,3',4',6-Pentachlorobiphenyl
39635-32-0	111	2,3,3',5,5'-Pentachlorobiphenyl
74472-36-9	112	2,3,3',5,6-Pentachlorobiphenyl
68194-10-5	113	2,3,3',5',6-Pentachlorobiphenyl
74472-37-0	114	2,3,4,4',5-Pentachlorobiphenyl
74472-38-1	115	2,3,4,4',6-Pentachlorobiphenyl
18259-05-7	116	2,3,4,5,6-Pentachlorobiphenyl
68194-11-6	117	2,3,4',5,6-Pentachlorobiphenyl
31508-00-6	118	2,3',4,4',5-Pentachlorobiphenyl
56558-17-9	119	2,3',4,4',6-Pentachlorobiphenyl
68194-12-7	120	2,3',4,5,5'-Pentachlorobiphenyl
56558-18-0	121	2,3',4,5',6-Pentachlorobiphenyl
76842-07-4	122	2,3,3',4',5'-Pentachlorobiphenyl
65510-44-3	123	2,3',4,4',5'-Pentachlorobiphenyl
70424-70-3	124	2,3',4',5,5'-Pentachlorobiphenyl
74472-39-2	125	2,3',4',5',6-Pentachlorobiphenyl

57465-28-8	126	3,3',4,4',5-Pentachlorobiphenyl
39635-33-1	127	3,3',4,5,5'-Pentachlorobiphenyl
38380-07-3	128	2,2',3,3',4,4'-Hexachlorobiphenyl
55215-18-4	129	2,2',3,3',4,5-Hexachlorobiphenyl
52663-66-8	130	2,2',3,3',4,5'-Hexachlorobiphenyl
61798-70-7	131	2,2',3,3',4,6-Hexachlorobiphenyl
38380-05-1	132	2,2',3,3',4,6'-Hexachlorobiphenyl
35694-04-3	133	2,2',3,3',5,5'-Hexachlorobiphenyl
52704-70-8	134	2,2',3,3',5,6-Hexachlorobiphenyl
52744-13-5	135	2,2',3,3',5,6'-Hexachlorobiphenyl
38411-22-2	136	2,2',3,3',6,6'-Hexachlorobiphenyl
35694-06-5	137	2,2',3,4,4',5-Hexachlorobiphenyl
35065-28-2	138	2,2',3,4,4',5'-Hexachlorobiphenyl
56030-56-9	139	2,2',3,4,4',6-Hexachlorobiphenyl
59291-64-4	140	2,2',3,4,4',6'-Hexachlorobiphenyl
52712-04-6	141	2,2',3,4,5,5'-Hexachlorobiphenyl
41411-61-4	142	2,2',3,4,5,6-Hexachlorobiphenyl
68194-15-0	143	2,2',3,4,5,6'-Hexachlorobiphenyl
68194-14-9	144	2,2',3,4,5',6-Hexachlorobiphenyl
74472-40-5	145	2,2',3,4,6,6'-Hexachlorobiphenyl
51908-16-8	146	2,2',3,4',5,5'-Hexachlorobiphenyl
68194-13-8	147	2,2',3,4',5,6-Hexachlorobiphenyl
74472-41-6	148	2,2',3,4',5,6'-Hexachlorobiphenyl
38380-04-0	149	2,2',3,4',5',6-Hexachlorobiphenyl
68194-08-1	150	2,2',3,4',6,6'-Hexachlorobiphenyl
52663-63-5	151	2,2',3,5,5',6-Hexachlorobiphenyl
68194-09-2	152	2,2',3,5,6,6'-Hexachlorobiphenyl
35065-27-1	153	2,2',4,4',5,5'-Hexachlorobiphenyl
60145-22-4	154	2,2',4,4',5,6'-Hexachlorobiphenyl
33979-03-2	155	2,2',4,4',6,6'-Hexachlorobiphenyl
38380-08-4	156	2,3,3',4,4',5-Hexachlorobiphenyl
69782-90-7	157	2,3,3',4,4',5'-Hexachlorobiphenyl
74472-42-7	158	2,3,3',4,4',6-Hexachlorobiphenyl
39635-35-3	159	2,3,3',4,5,5'-Hexachlorobiphenyl
41411-62-5	160	2,3,3',4,5,6-Hexachlorobiphenyl

74472-43-8	161	2,3,3',4,5',6-Hexachlorobiphenyl
39635-34-2	162	2,3,3',4',5,5'-Hexachlorobiphenyl
74472-44-9	163	2,3,3',4',5,6-Hexachlorobiphenyl
74472-45-0	164	2,3,3',4',5',6-Hexachlorobiphenyl
74472-46-1	165	2,3,3',5,5',6-Hexachlorobiphenyl
41411-63-6	166	2,3,4,4',5,6-Hexachlorobiphenyl
52663-72-6	167	2,3',4,4',5,5'-Hexachlorobiphenyl
59291-65-5	168	2,3',4,4',5',6-Hexachlorobiphenyl
32774-16-6	169	3,3',4,4',5,5'-Hexachlorobiphenyl
35065-30-6	170	2,2',3,3',4,4',5-Heptachlorobiphenyl
52663-71-5	171	2,2',3,3',4,4',6-Heptachlorobiphenyl
52663-74-8	172	2,2',3,3',4,5,5'-Heptachlorobiphenyl
68194-16-1	173	2,2',3,3',4,5,6-Heptachlorobiphenyl
38411-25-5	174	2,2',3,3',4,5,6'-Heptachlorobiphenyl
40186-70-7	175	2,2',3,3',4,5',6-Heptachlorobiphenyl
52663-65-7	176	2,2',3,3',4,6,6'-Heptachlorobiphenyl
52663-70-4	177	2,2',3,3',4,5',6'-Heptachlorobiphenyl
52663-67-9	178	2,2',3,3',5,5',6-Heptachlorobiphenyl
52663-64-6	179	2,2',3,3',5,6,6'-Heptachlorobiphenyl
35065-29-3	180	2,2',3,4,4',5,5'-Heptachlorobiphenyl
74472-47-2	181	2,2',3,4,4',5,6-Heptachlorobiphenyl
60145-23-5	182	2,2',3,4,4',5,6'-Heptachlorobiphenyl
52663-69-1	183	2,2',3,4,4',5',6-Heptachlorobiphenyl
74472-48-3	184	2,2',3,4,4',6,6'-Heptachlorobiphenyl
52712-05-7	185	2,2',3,4,5,5',6-Heptachlorobiphenyl
74472-49-4	186	2,2',3,4,5,6,6'-Heptachlorobiphenyl
52663-68-0	187	2,2',3,4',5,5',6-Heptachlorobiphenyl
74487-85-7	188	2,2',3,4',5,6,6'-Heptachlorobiphenyl
39635-31-9	189	2,3,3',4,4',5,5'-Heptachlorobiphenyl
41411-64-7	190	2,3,3',4,4',5,6-Heptachlorobiphenyl
74472-50-7	191	2,3,3',4,4',5',6-Heptachlorobiphenyl
74472-51-8	192	2,3,3',4,5,5',6-Heptachlorobiphenyl
69782-91-8	193	2,3,3',4',5,5',6-Heptachlorobiphenyl
35694-08-7	194	2,2',3,3',4,4',5,5'-Octachlorobiphenyl
52663-78-2	195	2,2',3,3',4,4',5,6-Octachlorobiphenyl

42740-50-1	196	2,2',3,3',4,4',5,6'-Octachlorobiphenyl
33091-17-7	197	2,2',3,3',4,4',6,6'-Octachlorobiphenyl
68194-17-2	198	2,2',3,3',4,5,5',6-Octachlorobiphenyl
52663-75-9	199	2,2',3,3',4,5,5',6'-Octachlorobiphenyl
52663-73-7	200	2,2',3,3',4,5,6,6'-Octachlorobiphenyl
40186-71-8	201	2,2',3,3',4,5',6,6'-Octachlorobiphenyl
2136-99-4	202	2,2',3,3',5,5',6,6'-Octachlorobiphenyl
52663-76-0	203	2,2',3,4,4',5,5',6-Octachlorobiphenyl
74472-52-9	204	2,2',3,4,4',5,6,6'-Octachlorobiphenyl
74472-53-0	205	2,3,3',4,4',5,5',6-Octachlorobiphenyl
40186-72-9	206	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl
52663-79-3	207	2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl
52663-77-1	208	2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl
2051-24-3	209	Decachlorobiphenyl

NOTE 1 This table is proposed by EPA for PCB species by congener numbers (EPA Nov.2003).

NOTE 2 The numbers established by Ballschmiter et al. [9] vary from IUPAC rules as indicated below:

- 199 (Ballschmiter) = 200 (IUPAC);
- 200 (Ballschmiter) = 201 (IUPAC);
- 201 (Ballschmiter) = 199 (IUPAC).

The PCBs have been synthetized for industrial applications and due to their thermal and chemical stability, especially for transformer oil and paint pigments. They have always been used in commercial mixtures which names vary according to the producers. A non-exhaustive list is given below (see Table D.2).

Table D.2 — List of commercial mixtures of PCBs by producers and commercial names

Producer	Country	Commercial name of mixtures
Monsanto	USA and United Kingdom	Aroclor®
Bayer	Germany	Clophen®
Prodelec	France	Phenclor® and Pyralène®
Kanegafuchi	Japan	Santotherm®
Mitsubishi	Japan	Santotherm®
Caffaro	Italy	Fenclor® / Apirolio®

As PCBs are classified as Persistent Organic Pollutants by the Commission Regulation 850/2004/EC on the environment and its amendment 756/2010/EC, for their treatment and elimination (Annex IV of CR 850/2004/EC and Annexes IV and V for CR 756/2010/EC) with a threshold at 50 mg/kg on the total content of PCBs in waste, a calculation method is needed to estimate the total PCB content on the basis of the analytical results obtained for the 7 congeners included in this standard.

For the determination of PCBs and related compounds in petroleum products and used oils, two EN standards exist: EN 12766-1 deals with the separation and determination of selected PCB congeners, EN 12766-2 describes methods for the calculation of the total PCB content. One method uses six congeners (see Table D.3 below), among the 209 possible compounds. These two standards are cited as references in European regulation for PCB elimination.

Table D.3 — Identification of the 6 congeners concerned in EN 12766–1 and EN 12766–2 standards

Congener n°	Weight fraction of each congener mg/kg
28	W_1
52	W_2
101	W_3
153	W_4
138	W_5
180	W_6

In order to obtain the total content of PCBs, the sum of the mass contents of the 6 individual PCB congeners is multiplied by a factor 5 and the result is rounded to the nearest 0,1 mg/kg.

$$\omega(PCB) = \sum_{i=1}^{i=6} W_i x 5 \qquad \text{(D.1)}$$

Considering the 6 congeners for the estimation of the total PCB content (according to EN 12766-2), the sum of the 6 congeners represents between 13 % and 30 % of the total PCB content, depending on the commercial mixtures considered (see Table D.4). Considering the mean value of the sum, the 6 PCB

congeners represent 20 % of the total content, justifying the factor 5 used in the calculation formula of EN 12766-2.

Table D.4 — Mass proportions represented by the sum of the mass concentrations of different PCB congeners in commercial mixtures

	Arochlor® 1242		**Arochlor® 1248**		**Arochlor® 1254**		**Arochlor® 1260**		**Mixture of 4 Arochlors®**	
Sum (% m/m)	*x*	s	*x*	S	*x*	S	*x*	S	*x*	s
Σ6 PCB	12,9	0,6	13,8	1,4	23,4	3,0	29,8	7,2	20,0	8,1

x Mean value

s Standard deviation

Σ6 PCB Sum of the weight percent of congeners 28–52–101–138–153–180.

Annex E
(informative)

Summary of general requirements and recommendations

Purpose of this summary is to support the organization of sampling and sample pretreatment processes. The information given should be helpful for preparing a sampling plan.

Requirements (Table E.1) not mentioned in the normative part of this document should be considered as recommendations.

Table E.1 — General requirements and recommendations

Matrix restrictions	Solid waste
Typical working range	Above 0,1 mg/kg
Sampling instrument	Stainless steel equipment; avoid contact to plastics
Pretreatment of sample container	Clean and dry
Material of sample container	Glass, stainless steel
Transport conditions	Ambient temperature or lower
Preservation	No
Storage conditions	About 20 °C (ambient temperature) or lower
Drying procedure	Air drying at maximum 40 °C or freeze drying (depending on material)
Particle size reduction	Crushing, cutting, grinding (depending of material)
Particle size	Less than 2 mm recommended (plastics: 0,5 mm)
Laboratory sample	About 1 kg depending on homogeneity and particle size of material
Test portion	About 20 g

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[1] EN 15002, *Characterization of waste - Preparation of test portions from the laboratory sample*

[2] EN 61619, *Insulating liquids - Contamination by polychlorinated biphenyls (PCBs) - Method of determination by capillary column gas chromatography*

[3] EN ISO 6468, *Water quality - Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes - Gas chromatographic method after liquid-liquid extraction (ISO 6468)*

[4] EN ISO 22892, *Soil quality - Guidelines for the identification of target compounds by gas chromatography and mass spectrometry (ISO 22892:2006)*

[5] ISO 11464, *Soil quality — Pretreatment of samples for physico-chemical analysis*

[6] ISO 14507, *Soil quality — Pretreatment of samples for determination of organic contaminants*

[7] SCHULZ D.E., PETRICK G., DUINKER J.C. Complete characterization of polychlorinated biphenyl congeners in commercial arochlor and chlophen mixtures by multidimensional gas chromatography-electron capture detection. *Environ. Sci. Technol.* 1989, **23** (7) pp. 852–859

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