INTERNATIONAL STANDARD

ISO 18475

First edition
2023-10

Environmental solid matrices — Determination of polychlorinated biphenyls (PCB) by gas chromatography - mass selective detection (GC-MS) or electron-capture detection (GC-ECD)

Reference number
ISO 18475:2023(E)

COPYRIGHT PROTECTED DOCUMENT

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO document should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

ISO draws attention to the possibility that the implementation of this document may involve the use of (a) patent(s). ISO takes no position concerning the evidence, validity or applicability of any claimed patent rights in respect thereof. As of the date of publication of this document, ISO had not received notice of (a) patent(s) which may be required to implement this document. However, implementers are cautioned that this may not represent the latest information, which may be obtained from the patent database available at www.iso.org/patents. ISO shall not be held responsible for identifying any or all such patent rights.

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by the European Committee for Standardization (CEN) (as EN 17322:2020) and was adopted, without modification other than those given below, by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical and physical characterization.*

- change of EN ISO 5667-15 reference to ISO 5667-15 reference;
- change of EN ISO 16720 reference to ISO 16720 reference;
- change of EN ISO 22892 reference to ISO 22892 reference;
- change of EN ISO 5667-13 reference to ISO 5667-13 reference;
- change of EN ISO 6468 reference to ISO 6468 reference;
- uniform spelling of sulfate and sulfite;
- editorially revised.

This first edition cancels and replaces ISO 10382:2002 and ISO 13876:2013, which have been technically revised.

The main changes are as follows:

- deletion of OCP analysis (this document specifies methods for quantitative determination of polychlorinated biphenyls);
- addition of GC-MS as a detection method;
- extension of the scope to sludge, sediment, treated biowaste and waste;

- addition of modern extraction techniques and commonly used methods with optimized extraction time, proven clean-up methods and state of the art quantification methods;
- update of normative references.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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 PCB 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, pre-treatment, extraction and 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).

This document was developed by merging of EN 16167:2018, initially elaborated as a CEN Technical Specification in the European project 'HORIZONTAL' and validated by CEN/TC 400 with the support of BAM, with EN 15308, published by CEN/TC 292.

Considered the different matrices and possible interfering compounds, this document does not contain one single possible way of working. Several choices are possible, in particular relating to clean-up. Detection with both MS-detection and ECD-detection is possible. Two different extraction procedures are described and 9 clean-up procedures. 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. The method is as far as possible in agreement with the method described for PAH (EN 16181:2018 and EN 15527:2008). It has been tested for ruggedness.

This document is applicable and validated for several types of matrices as indicated in Table 1 (see also Annex A for the results of the validation).

Table 1 — Matrices for which this document is applicable and validated

Matrix	Materials used for validation
Soil	Sandy soil Mix of soil from the vicinity of Berlin, Germany and PCB-free German reference soil
Sludge	Mix of municipal waste water treatment plant sludge from North Rhine Westphalia, Germany
Biowaste	Mix of compost from the vicinity of Berlin, Germany and sludge from North Rhine Westphalia, Germany
Waste	Contaminated soil, building debris, waste wood, sealant waste, electronic waste, shredder light fraction, cable shredder waste

WARNING — Persons using this document should be familiar with usual laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted according to this document be carried out by suitably trained staff.

Environmental solid matrices — Determination of polychlorinated biphenyls (PCB) by gas chromatography - mass selective detection (GC-MS) or electron-capture detection (GC-ECD)

1 Scope

This document specifies methods for quantitative determination of seven selected polychlorinated biphenyls (PCB28, PCB52, PCB101, PCB118, PCB138, PCB153 and PCB180) in soil, sludge, sediment, treated biowaste, and waste using GC-MS and GC-ECD (see Table 2).

Table 2 — Target analytes of this document

Target analyte		CAS-RN [a]
PCB28	2,4,4'-trichlorobiphenyl	7012–37–5
PCB52	2,2',5,5'-tetrachlorobiphenyl	35693–99–3
PCB101	2,2',4,5,5'-pentachlorobiphenyl	37680–73–2
PCB118	2,3',4,4',5-pentachlorobiphenyl	31508–00–6
PCB138	2,2',3,4,4',5'-hexachlorobiphenyl	35065–28–2
PCB153	2,2',4,4',5,5'-hexachlorobiphenyl	35065–27–1
PCB180	2,2',3,4,4',5,5'-heptachlorobiphenyl	35065–29–3

[a] CAS-RN Chemical Abstracts Service Registry Number.

The limit of detection depends on the determinants, the equipment used, the quality of chemicals used for the extraction of the sample and the clean-up of the extract.

Under the conditions specified in this document, lower limit of application from 1 µg/kg (expressed as dry matter) for soils, sludge and biowaste to 10 µg/kg (expressed as dry matter) for solid waste can be achieved. For some specific samples the limit of 10 µg/kg cannot be reached.

Sludge, waste and treated biowaste may differ in properties, as well as in the expected contamination levels of PCB and presence of interfering substances. These differences make it impossible to describe one general procedure. This document contains decision tables based on the properties of the sample and the extraction and clean-up procedure to be used.

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

The method can be applied to the analysis of other PCB congeners not specified in the scope, provided suitability is proven by proper in-house validation experiments.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 5667-15, *Water quality — Sampling — Part 15: Guidance on the preservation and handling of sludge and sediment samples*

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods — Part 1: Linear calibration function*

ISO 16720, *Soil quality — Pretreatment of samples by freeze-drying for subsequent analysis*

ISO 18512, *Soil quality — Guidance on long and short term storage of soil samples*

ISO 22892, *Soil quality — Guidelines for the identification of target compounds by gas chromatography and mass spectrometry*

3 Terms and definitions

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

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at https://www.electropedia.org/

3.1

critical pair

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

$$R = 2 \times \frac{\Delta t}{Ya + Yb} \ (x) \qquad (1)$$

where

R resolution

Δt difference in retention times of the two peaks a and b in seconds (s)

Y_a peak width at the base of peak a in seconds (s)

Y_b peak width at the base of peak b in seconds (s)

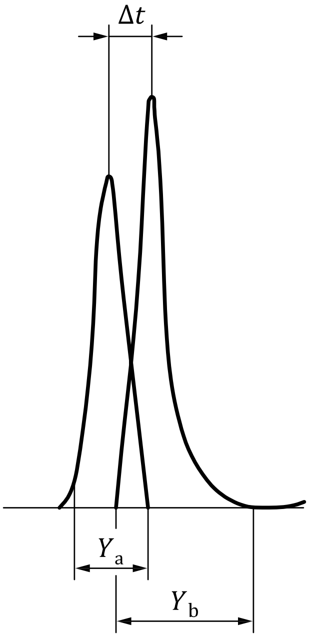

Figure 1 — Example of a chromatogram of a critical pair

3.2
congener
member of the same kind, class or group of chemicals, e.g. anyone of the two hundred and nine individual PCB

Note 1 to entry: The IUPAC congener numbers are for easy identification; they do not represent the order of chromatographic elution.

3.3
injection standard
$^{13}C_{12}$-labelled PCB or other PCB that is unlikely to be present in 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

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

3.5
polychlorinated biphenyl
PCB
biphenyl substituted with one to ten chlorine atoms

3.6
sediment
solid material, both mineral and organic, deposited in the bottom of a water body

[SOURCE: ISO 5667-12:2017]

4 Principle

Due to the multi-matrix character of this document, different procedures for different steps (modules) are allowed. Which modules should be used depends on the sample. A recommendation is given in this document. Performance criteria are described and it is the responsibility of the laboratories applying this document to show that these criteria are met. Using of spiking standards (internal standards) allows an overall check on the efficiency of a specific combination of modules for a specific sample. But it does not necessarily give the information regarding the extensive extraction efficiency of the native PCB bonded to the matrix.

After pre-treatment, the sample is extracted with a suitable solvent.

The extract is concentrated by evaporation. If necessary, interfering compounds are removed by a clean-up method suitable for the specific matrix, before the concentration step.

The extract is analysed by gas chromatography. The various compounds are separated using a capillary column with a stationary phase of low polarity. Detection occurs by mass spectrometry (MS) or an electron capture detector (ECD).

PCB are identified and quantified by comparison of relative retention times and relative peak heights (or peak areas) with respect to internal standards added. The efficiency of the procedure depends on the composition of the matrix that is investigated.

5 Interferences

5.1 Interference with sampling and extraction

Use sampling containers of materials (preferably of steel, aluminium or glass) that do not affect the sample during the contact time. Avoid plastics and other organic materials during sampling, sample storage or extraction. Keep the samples from direct sunlight and prolonged exposure to light.

During storage of the samples, losses of PCB may occur due to adsorption on the walls of the containers. The extent of the losses depends on the storage time.

5.2 Interference with GC

Substances that co-elute with the target PCB may interfere with the determination. These interferences may lead to incompletely resolved signals and may, depending on their magnitude, affect accuracy and precision of the analytical results. Peak overlap does not allow an interpretation of the result. Asymmetric peaks and peaks being broader than the corresponding peaks of the reference substance suggest interferences.

Chromatographic separation between the following pairs can be critical.

- PCB28 – PCB31
- PCB52 – PCB73
- PCB101 – PCB89 / PCB90
- PCB118 – PCB106
- PCB138 – PCB164 / PCB163

The critical pair PCB28 and PCB31 is used for selection of the capillary column (see 8.2.2). If molecular mass differences are present, quantification can be made by mass selective detection. If not or using ECD, the specific PCB is reported as the sum of all PCBs present in the peak. Typically, the concentrations of the co-eluting congeners compared to those of the target congeners are low. When incomplete resolution is encountered, peak integration shall be checked and, when necessary, corrected.

Presence of tetrachlorobenzyltoluene (TCBT)-mixtures or sulfur can disturb the determination of the PCB with GC-ECD.

High mineral oil content can also disturb the determination of PCB with GC-MS.

6 Safety remarks

PCBs are highly toxic and shall be handled with extreme care. Avoid contact with solid materials, solvent extracts and solutions of standard PCB. Contact of solutions of standard with the body should be prevented. It is strongly advised that standard solutions are prepared centrally in suitably equipped laboratories or are purchased from suppliers specialized in their preparation.

Solvent solutions containing PCB and samples shall be disposed of in a manner approved for disposal of toxic wastes.

For the handling of hexane precautions shall be taken because of its neurotoxic properties.

National regulations enforcing locally stricter requirements are used with respect to all hazards associated with this method.

7 Reagents

7.1 General

All reagents shall be of recognized analytical grade. The purity of the reagents used shall be checked by running a blank test as described in 10.1 The blank shall be less than 50 % of the lowest reporting limit.

7.2 Reagents for extraction

7.2.1 Acetone (2-propanone), $(CH_3)_2$ CO.

7.2.2 *n*-heptane, C_7H_{16}.

7.2.3 Petroleum ether, boiling range 40 °C to 60 °C.

Hexane-like solvents with a boiling range between 30 °C and 98 °C are allowed.

7.2.4 Sodium sulfate, Na_2SO_4. The anhydrous sodium sulfate shall be kept carefully sealed.

7.2.5 Distilled water or water of equivalent quality, H_2O.

7.2.6 Sodium chloride, NaCl,

7.2.7 Keeper substance. High boiling compound, i.e. octane, nonane.

7.3 Reagents for clean-up

7.3.1 Clean-up A using aluminium oxide

7.3.1.1 Aluminium oxide, Al_2O_3

Basic or neutral, specific surface 200 m^2/g, activity Super I[13].

7.3.1.2 Deactivated aluminium oxide

Deactivated with approximately 10 % water.

Add approximately 10 g of water (7.2.5) to 90 g of aluminium oxide (7.3.1.1). Shake until all lumps have disappeared. Allow the aluminium oxide to condition before use for some 16 h, sealed from the air, use it for maximum two weeks.

NOTE 1 The activity depends on the water content. It can be necessary to adjust the water content.

NOTE 2 Commercially available aluminium oxides with 10 % mass fraction water can also be used.

7.3.2 Clean-up B using silica gel 60 for column chromatography

7.3.2.1 Silica gel 60, particle size 63 µm to 200 µm.

7.3.2.2 Silica gel 60, water content: mass fraction $w(H_2O) = 10\ \%$.

Silica gel 60 (7.3.2.1), heated for at least 3 h at 450 °C, cooled down and stored in a desiccator containing magnesium perchlorate or a suitable drying agent. Before use heat at least for 5 h at 130 °C in a drying oven. Then allow cooling in a desiccator and add 10 % water (mass fraction) (7.2.5) in a flask. Shake for 5 min intensively by hand until all lumps have disappeared and then for 2 h in a shaking device. Store the deactivated silica gel in the absence of air, use it for maximum of two weeks.

7.3.3 Clean-up C using gel permeation chromatography (GPC)[1]

7.3.3.1 Bio-Beads®[2] S-X3.

7.3.3.2 Ethyl acetate, $C_4H_8O_2$.

7.3.3.3 Cyclohexane, C_6H_{12}.

Preparation of GPC, for example: put 50 g Bio-Beads® S-X3 (7.3.3.1) into a 500 ml Erlenmeyer flask and add 300 ml elution mixture made up of cyclohexane (7.3.3.3) and ethyl acetate (7.3.3.2) 1:1 (volume fraction) in order to allow the beads to swell; after swirling for a short time until no lumps are left, maintain the flask closed for 24 h. Drain the slurry into the chromatography tube for GPC. After approximately three days, push in the plungers of the column so that a filling level of approximately 35 cm is obtained. To further compress the gel, pump approximately 2 l of elution mixture through the column at a flow rate of 5 ml · min^{-1} and push in the plungers to obtain a filling level of approximately 33 cm.

7.3.4 Clean-up D using Florisil®[3]

7.3.4.1 Florisil®, baked 2 h at 600 °C. Particle size 150 µm to 750 µm.

7.3.4.2 Iso-octane, C_8H_{18}.

7.3.4.3 Toluene, C_7H_8.

7.3.4.4 Iso-octane/Toluene 95/5 volumetric fraction

---

[1] GPC is also known as SEC (size exclusion chromatography).

[2] Bio-Beads® is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product. Equivalent products can be used if they can be shown to lead to the same results.

[3] 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 document and does not constitute an endorsement by ISO of this product. Equivalent products can be used if they can be shown to lead to the same results.

7.3.5 Clean-up E using silica H_2SO_4/silica NaOH

7.3.5.1 Silica, SiO_2, particle size 70 µm to 230 µm, baked at 180 °C for a minimum of 1 h, and stored in a pre-cleaned glass bottle with screw cap that prevents moisture from entering.

7.3.5.2 Sulfuric acid H_2SO_4 95 – 97 % percent mass fraction

7.3.5.3 Silica, treated with sulfuric acid.

Mix 56 g silica (7.3.5.1) and 44 g sulfuric acid (7.3.5.2).

7.3.5.4 Sodium hydroxide solution, c(NaOH) = 1 mol/l.

7.3.5.5 Silica, treated with sodium hydroxide.

Mix 33 g silica (7.3.5.1) and 17 g sodium hydroxide (7.3.5.4).

7.3.5.6 *n*-hexane, C_6H_{14}

7.3.6 Clean-up F using benzenesulfonic acid/sulfuric acid

7.3.6.1 silica gel with particle size between 40 µm to 200 µm.

7.3.6.2 benzenesulfonic acid $C_6H_6O_3S > 98$ % percent mass fraction

Mix 500 mg of silica gel with sulfuric acid (7.3.5.2) or benzenesulfonic acid (7.3.6.2) and add it into a 3 ml column

7.3.7 Clean-up G using TBA sulfite reagent

7.3.7.1 Tetrabutylammonium reagent (TBA sulfite reagent) 97 % percent mass fraction

7.3.7.2 2-Propanol, C_3H_8O.

7.3.7.3 Sodium sulfite, $Na_2SO_3 > 98$ % percent mass fraction

Saturate a solution of tetrabutylammonium hydrogen sulphate in a mixture of equal volume of water and 2-propanol, $c((C_4H_9)_4NHSO_4) = 0{,}1$ mol/l, with sodium sulphite.

NOTE 25 g of sodium sulphite might be sufficient for 100 ml of solution.

7.3.8 Clean-up H using pyrogenic copper

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

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

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

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

7.3.8.4 Anionic detergent aqueous solution (e.g. 35 g/100 ml, n-dodecane-1-sulfonic acid sodium salt ($CH_3(CH_2)_{11}SO_3Na$).

NOTE Other commercially available detergents can also be suitable.

7.3.8.5 Deoxygenated water

7.3.8.6 Pyrogenic copper

Dissolve 45 g copper(II)-sulfate pentahydrate (7.3.8.1) in 480 ml water containing 20 ml hydrochloric acid (7.3.8.2) in a 1 000 ml beaker.

Take 15 g of zinc granules size (7.3.8.3) add 25 ml water and one drop of anionic detergent solution (7.3.8.4) in another 1 000 ml beaker.

Stir with a magnetic stirrer at a high speed to form a slurry. Then whilst 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 (7.3.8.5) three times, to eliminate residual salts.

Then the water is carefully replaced with 250 ml acetone (7.2.1) (whilst continuously stirring the mixture). This operation is repeated twice more to ensure elimination of water.

Then the above procedure is repeated three times with 250 ml *n*-hexane (7.3.5.6), to ensure elimination of the acetone.

Carefully transfer the copper with hexane into an Erlenmeyer flask and store under hexane. The flask shall be sealed to prevent ingress of air and stored in an explosion-proof refrigerator 2 °C to 8 °C.

The shelf life of the pyrogenic copper is at least two months. The clean-up efficiency then declines. The copper changes colour as the clean-up efficiency decreases.

NOTE Granulated copper activated with HCL is commercially available and can be used.

7.3.9 Clean-up I using silica/silver nitrate

7.3.9.1 Silver nitrate, $AgNO_3$.

7.3.9.2 Silver nitrate/silica adsorbent

Dissolve 10 g of $AgNO_3$ (7.3.9.1) in 40 ml water (7.2.5) and add this mixture in portions to 90 g of silica (7.3.5.1). Shake the mixture until it is homogenous and leave it for 30 min. Put the mixture into a drying oven at (70 ± 5) °C. Within 5 h regular increase the temperature from 70 °C to 125 °C. Activate the mixture for 15 h at 125 °C. Store the mixture in brown glass bottles.

NOTE Commercial pre-packed columns could also be used if performance has been demonstrated

7.4 Gas chromatographic analysis

Operating gases for GC/ECD, resp GC-MS, of high purity and in accordance with the manufacturer's specifications

7.5 Standards

7.5.1 General

Choose the internal standards substances whose physical and chemical properties (such as extraction behaviour, retention time) are similar to those of the compounds to be analysed. $^{13}C_{12}$-PCBs should be used as internal standards for the GC-MS method for evaluation of results.

7.5.2 Calibration standards

The calibration standard should contain the following compounds:

PCB28	2,4,4'-trichlorobiphenyl	(CAS-RN 7012-37-5)
PCB52	2,2',5,5'-tetrachlorobiphenyl	(CAS-RN 35693-99-3)
PCB101	2,2',4,5,5'-pentachlorobiphenyl	(CAS-RN 37680-73-2)
PCB118	2,3',4,4',5-pentachlorobiphenyl	(CAS-RN 31508-00-6)
PCB138	2,2',3,4,4',5'-hexachlorobiphenyl	(CAS-RN 35065-28-2)
PCB153	2,2',4,4',5,5'-hexachlorobiphenyl	(CAS-RN 35065-27-1)
PCB180	2,2',3,4,4',5,5'-heptachlorobiphenyl	(CAS-RN 35065-29-3)

The numbers 28, 52 etc. correspond to the sequential numbers of chlorobiphenyls according to the IUPAC rules for the nomenclature of organic compounds.

7.5.3 Internal and injection standards

7.5.3.1 General

The PCB congeners to be considered as internal and injection standards are listed below. The internal standard shall be added to the sample. For MS-detection labelled PCB congeners are highly recommended.

When highly contaminated samples are analysed, an aliquot of the extract is often used for further clean-up. This makes the costs of analyses caused by the use of labelled standard very high. In these cases, it is allowed to add the internal standard in two steps. Step 1 addition of unlabelled internal standards to the sample. Step 2 addition of labelled congeners to the aliquot of the extract used for clean-up.

At least three congeners, covering the chromatogram shall be used as internal standard.

Other PCB not present in the sample, or $^{13}C_{12}$-labelled PCBs not used as internal standard, can be used as injection standard. Injection standards are useful for investigation of any disturbance in the chromatographic process.

NOTE Some PCB mixtures contain up to 2,5 % of PCB155 as an impurity.

PCB30, PCB143 and PCB207 are also recommended as internal standards as they are rarely found in real samples.

PCB198 or PCB209 are recommended as injection standards for ECD-detection because of less interferences.

7.5.3.2 Labelled PCB congeners

PCB28	$^{13}C_{12}$-2,4,4’-trichlorobiphenyl	(CAS-RN 208263-76-7)
PCB52	$^{13}C_{12}$-2,2‘,5,5‘-tetrachlorobiphenyl	(CAS-RN 208263-80-3)
PCB101	$^{13}C_{12}$-2,2‘,4,5,5‘-pentachlorobiphenyl	(CAS-RN 104130-39-4)
PCB118	$^{13}C_{12}$-2,3‘,4,4‘,5-pentachlorobiphenyl	(CAS-RN 104130-40-7)
PCB138	$^{13}C_{12}$-2,2‘,3,4,4‘,5‘-hexachlorobiphenyl	(CAS-RN 208263-66-5)
PCB153	$^{13}C_{12}$-2,2‘,4,4‘,5,5‘-hexachlorobiphenyl	(CAS-RN 185376-58-3)
PCB180	$^{13}C_{12}$-2,2‘,3,4,4‘,5,5‘-heptachlorobiphenyl	(CAS-RN 208263-72-3)

7.5.3.3 Non-labelled PCB congeners

PCB29	2,4,5-trichlorobiphenyl	(CAS-RN 15862-07-4)
PCB30	2,4,6-trichlorobiphenyl	(CAS-RN 35693-92-6)
PCB143	2,2',3,4,5,6'-hexachlorobiphenyl	(CAS-RN 68194-15-0)
PCB155	2,2',4,4',6,6'-hexachlorobiphenyl	(CAS-RN 33979-03-2)
PCB198	2,2',3,3',4,5,5’,6-octachlorobiphenyl	(CAS-RN 68194-17-2)
PCB207	2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl	(CAS-RN 52663-79-3)
PCB209	2,2',3,3',4,4',5,5’,6,6'-decachlorobiphenyl	(CAS-RN 2051-24-3)

7.5.3.4 PCB congeners for resolution check

PCB28	2,4,4'-trichlorobiphenyl	(CAS-RN 7012-37-5)
PCB 31	2,4',5-trichlorobiphenyl	(CAS-RN 16606-02-3)

7.6 Preparation of standard solutions

7.6.1 Preparation of calibration standard solutions of PCBs

Prepare individual concentrated primary standard solutions of about 0,4 mg/ml in *n*-heptane (7.2.2) by weighing approximately 10 mg of each of the calibration standards (7.5.2) to the nearest 0,1 mg and dissolving them in 25 ml of *n*-heptane.

Combine small quantities (2 ml to 10 ml) of these individual primary standard solutions into a mixed standard solution of PCB.

NOTE Because of the dangerous nature of the substances to be used, commercially available - preferably certified standard solutions or mixed standard solutions are preferred. It is essential to avoid skin contact.

The working standard solutions shall be in the same solvent as the extract.

Store the primary and diluted standard solutions in a dark place at a temperature of (5 ± 3) °C. The solutions are stable for at least one year, provided that evaporation of solvent is negligible.

Components present in mixed standard solutions should be completely separated by the gas chromatographic columns used.

7.6.2 Preparation of internal standard solution

Prepare a concentrated primary internal standard solution, containing at least three different components (7.5.3), of about 0,4 mg/ml in one of the solvent used for extraction (Table 4 specifies the adequate solvents); by weighing approximately 10 mg of each of the chosen internal standards to the nearest 0,1 mg and dissolving them in 25 ml of solvent. Prepare from this a secondary internal solution with such a concentration that the added amount gives a peak with measurable peak area or peak height in the chromatogram (at least 10 times the detection limit).

If the two-step procedure for GC-MS is used, make two different internal standard solutions, one containing the non-labelled compounds. At least two unlabelled congeners shall be used in the first internal standard solution and at least three labelled congeners in the second solution.

Internal standard solutions have to be stored at (5 ± 3) °C.

7.6.3 Preparation of injection standard solution

Prepare a concentrated primary injection standard solution, containing at least two different components (7.5.3), of about 0,4 mg/ml in an appropriate solvent as the one used for the extract, by weighing approximately 10 mg of each of the chosen injection standards to the nearest 0,1 mg and dissolving them in 25 ml. Prepare from this a secondary internal solution which such a concentration that the added amount gives a peak with measurable peak area or peak surface in the chromatogram (at least 10 times the detection limit).

Injection standard solutions have to be stored at (5 ± 3) °C.

8 Apparatus

8.1 Extraction and clean-up procedures

Usual laboratory glassware.

All glassware and material that comes into contact with the sample or extract shall be thoroughly cleaned.

8.1.1 Sample bottles, made of glass, stainless steel or aluminium, with glass stopper or screw top and polytetrafluoroethylene (PTFE) seal of appropriate volume.

Glass is not appropriate for sludge samples.

WARNING — For safety reasons, biologically active sludge samples shall not be stored in a sealed container.

8.1.2 Shaking device, with horizontal movement (200 strokes to 300 strokes per min) or an end-over-end shaking device.

8.1.3 Water bath, adjustable up to 100 °C.

8.1.4 Separating funnels of appropriate volume.

8.1.5 Conical flasks of appropriate volume.

8.1.6 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, heating device.

8.1.7 Ultrasonic bath

8.1.8 Pressurized liquid extraction apparatus, combining elevated temperature and pressure with liquid solvents to achieve extraction of the analytes from the solid matrix.

8.1.9 Concentrator, Kuderna Danish type.

Other evaporators, e.g. a rotary evaporator, may be used if found to be equally suitable.

8.1.10 Boiling chips, glass or porcelain beads.

8.1.11 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.

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

8.1.13 Chromatography tubes. Chromatography column of glass, 5 mm to 10 mm inside diameter, length e.g. 600 mm.

8.2 Gas chromatograph

8.2.1 General

Gas chromatograph equipped with a capillary column, mass spectrometric detection (MS) or electron capture detector (ECD) based on 63Ni.

NOTE Working with an encapsulated radioactive source as present in an ECD requires a licence in line with the appropriate national regulations.

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.

8.2.2 Capillary columns, each comprising a 5 % phenyl-methyl silicone stationary phase coated onto fused silica capillary column or an equivalent chemically bonded phase column. The chromatographic peaks of PCB28 and PCB31 shall be resolved sufficiently (resolution at least 0,5) for integrating the PCB28 peak. In general, column length is typically 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 second column, coated with a moderate polar phase (e.g. CP-Sil 19, OV 1701[4]), etc.), shall be used to confirm the result obtained.

NOTE The retention times for the PCB on different capillary columns are given in Annex B.

9 Sample storage and preservation

9.1 Sample storage

The samples shall be analysed as soon as possible after sampling. This applies in particular to the examination of microbiologically active solids.

If necessary, sludge samples shall be stored according to ISO 5667-15.

---

4) CP-Sil 19, OV 1701 are examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products. Equivalent products may be used if they can be shown to lead to the same results.

Dried samples can be stored at room temperature in a dark place up to one month. Soil samples shall be stored according to ISO 18512.

9.2 Sample pre-treatment

Suitable pre-treatment of samples accordingly to EN 16179 (sludge, biowaste and soil) or EN 15002 (waste), if not otherwise specified, and considering the specific drying procedures as specified in Table 3 to obtain a test sample.

If the quantification of PAH is intended on the same sample, drying in a ventilated oven at 40 °C shall not be used.

Complete drying of the sample is essential if Soxhlet is used for extraction. Complete drying is also recommended if the sample shall be stored for a long period.

Table 3 — Drying techniques for samples of different matrices for subsequent analyses of PCB

Matrix	Drying technique			
	Air drying or Ventilated drying oven at 40 °C	Freeze drying (ISO 16720)	Na_2SO_4 [a]	No drying
Sludge	x	x	x [a]	
Biowaste (compost, mixed waste)		x	x	x
Waste	x	x	x	x
Soil Sediment	x	x	x	x

[a] Na_2SO_4 can be used for preservation.

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.

10 Procedure

10.1 Blank test

Perform a blank test following the applied procedure (selected extraction and clean-up procedure) using the same amount of reagents that are used for the pre-treatment, extraction, clean-up and analysis of a sample. Analyse the blank immediately prior to analysis of each series of samples to demonstrate sufficient freedom from contamination. The blank shall be less than 50 % of the lowest reporting limit.

10.2 Extraction

10.2.1 General

Depending on the sample (matrix and moisture content), choose a suitable extraction method (see Table 4). Extraction method 1 (10.2.2) or 3 (10.2.4) are recommended if it is important to break up aggregates in the sample to access the PCBs. With wet samples, these methods shall be applied in order to eliminate the presence of water. If dissolving of the PCBs is the most important step (waste and organic rich materials) and the sample is dry, extraction method 2 (10.2.3) using Soxhlet is recommended.

For sludge, it has been shown that Soxhlet is applicable. In presence of plastics, use of acetone shall be avoided, because the use of acetone leads to a high amount of co-extractives. However, a general rule cannot be given, because samples may contain all: aggregates, organic matter and (plastic) waste.

Other extraction procedures, e.g. ultrasonic extraction, microwave or high-pressure liquid extraction may be used provided:

— the laboratory can show that the extraction efficiency is equivalent to one of the extraction procedures 1, 2 or 3 as described in this document, or

— the sample requires another approach as shown by the laboratory and the results of the procedures are congruent with the performance criteria as described in 10.7.5 and 10.8.6.

NOTE For application of this document for some types of waste, the addition of acetone with Soxhlet extraction has been shown to be effective.

Extraction procedures described in this document are suitable to extract up to 20 g of dry sample. If the sample has a low density (i.e. some wastes) or the sample is homogeneous, depending on the expected PCB content and on the homogeneity of the sample, less sample can be used. In general, the following amounts of dry sample can be used: 2 g to 10 g of sewage sludge, 10 g to 25 g of waste, 5 g to 20 g of compost or 2 g to 20 g of biowaste, 2 g to 20 g of soil or sediment. The amount of sample shall be weighed with an accuracy of at least 1 %.

Table 4 — Extraction procedures to be used for different matrices

Moisture status of the sample	Matrix	Extraction solvent	Extraction technique	Extraction procedure	Remark
Dry	Soil, sediment, sludge, biowaste, compost	Acetone/ petroleum ether or hexane-like solvent	Agitation, end-over-end shaking, sonication	Extraction procedure 1 (see 10.2.2)	
	Plastic-rich waste	Petroleum ether or hexane-like solvent	Agitation, end-over-end shaking, sonication	Extraction procedure 1 (see 10.2.2)	
	Soil, sediment, Sludge, biowaste, compost, waste	Petroleum ether or hexane-like solvent	Soxhlet, pressurized liquid extraction	Extraction procedure 2 (see 10.2.3)	
Wet	Soil, sediment, biowaste, waste, compost	Acetone/ petroleum ether or hexane-like solvent	Agitation, end-over-end shaking, sonication	Extraction procedure 1 (see 10.2.2)	Also applicable for field moist samples with dry matter content > 75 %
	Soil, sediment, biowaste, compost	Acetone/ petroleum ether or hexane-like solvent /NaCl	Agitation	Extraction procedure 3 (see 10.2.4)	

10.2.2 Extraction procedure 1: Samples using acetone/petroleum ether or hexane-like solvent and agitation or sonication

Place the sample in a bottle (8.1.1). Add a definite volume of the secondary internal standard solution (7.5.3). Add 50 ml of acetone (7.2.1) to the sample and extract by shaking or sonication, thoroughly to break up aggregates for 30 min. Then add 50 ml of petroleum ether or hexane-like solvent (7.2.3) and shake again or sonicate thoroughly during at least 1 h. Use a horizontal shaking device or an end-over-end shaking device (8.1.2) and have the solvent movement in the sample bottle as long as possible (horizontal position). After the solids have been settled, decant the supernatant. Wash the solid phase with 50 ml of petroleum ether or hexane-like solvent (7.2.3) and decant again. Collect the extracts in a separating funnel (8.1.4) and remove the acetone by shaking twice with 400 ml of water (7.2.5). Dry the extract over sodium sulfate (7.2.4). Rinse the sodium sulfate with petroleum ether or hexane-like solvent (7.2.3) and add the rinsing to the extract.

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 petroleum ether or hexane-like solvent (7.2.3).

NOTE 1 Tap water has shown to be applicable for removal of the acetone, because target compounds are not present.

If the sample contains water up to 25 %, the same procedure can be used. If the water content of the sample is greater than 25 % this procedure is less effective and the amount of acetone shall be increased. The ratio acetone: water should be at least 9:1. The ratio acetone : petroleum ether or hexane-like solvent should be kept constant to 1:2.

The definite amount of the internal standard added in all extraction methods shall have such a quantity that their concentrations in the final extract are within the working range of the measurement method. Typically, the concentration of the individual internal standards in the final extract is 0,1 µg/ml. To 'wet' the complete sample, a minimum amount of 100 µl of internal standard is recommended.

NOTE 2 In matrices with a high organic matter content (e.g. some sludge) longer extraction procedures can be necessary. Extraction procedure 2 (see 10.2.3) can be preferred for these samples.

10.2.3 Extraction procedure 2: Samples using Soxhlet or pressurized liquid extraction

Place the sample in the extraction thimble (8.1.6). Add the definite amount of the secondary internal standard solution (7.5.3) and approximately 70 ml of the extraction solvent (7.2.2 or 7.2.3) to the extraction vessel. Extract the sample with the Soxhlet extraction apparatus (8.1.6). The duration of the extraction should be calculated with a minimum of 100 extraction cycles.

NOTE If the sample is hygroscopic and is not dried just before analysis, it is advised to add Na_2SO_4 to the sample to get a free-flowing material.

Pressurized liquid extraction (PLE) (8.1.8) may also be used.

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 concentration of co-extractives. In these cases, extraction should only be performed with 50 ml of petroleum ether or hexane-like solvent (7.2.3). PLE is not recommended in this case.

10.2.4 Extraction procedure 3: Samples using acetone/petroleum ether or hexane-like solvent/sodium chloride and agitation

Take an amount of sample and put it into a 1 l sample bottle (8.1.1). Add the definite amount of the secondary internal standard solution (7.5.3). If the sample is dry, add 50 ml water. For moist samples, the water quantity to be added is calculated using Formula (1):

$$m_w = 50 - \frac{m_E \cdot m_{H_2O}}{100} \tag{1}$$

where

m_w is the mass of water to be added, expressed in grams (g);

m_E is the mass of the sifted sample, expressed in grams (g);

$m_{\mathrm{H_2O}}$ is the water content of the sample, determined according to EN 15934, expressed in percent (%).

Add 40 g sodium chloride (7.2.6), 100 ml acetone (7.2.1) and 50 ml petroleum ether or hexane-like solvent (7.2.3) to the moistened preparations, close the sample bottle and shake it with a shaking device (8.1.2) for at least 12 h.

The organic phase shall be separated, if necessary, using a centrifuge with sealable centrifuge cups. Collect the extract in a separating funnel of 1 l capacity. Dry the extract over sodium sulfate (7.2.4) and transfer the dried extract to the concentrator (8.1.9). Rinse the sodium sulfate with petroleum ether or hexane-like solvent (7.2.3) and add the rinsing to the extract.

10.3 Concentration

If necessary, add a boiling chip (8.1.10) to the extract and concentrate the extract to approximately 10 ml by evaporation using a concentrator (8.1.9). Transfer the concentrated extract to a calibrated test tube (8.1.12) and concentrate to 1 ml using a gentle stream of nitrogen or another inert gas at room temperature. If necessary, fill up to the 1ml. If clean-up method H is used, concentration is not necessary. Record the final volume of the extract.

In heavily contaminated samples, an aliquot is used for further clean-up. Establish the fraction f of the extract used for further clean-up. If non-labelled congeners have been used as internal standard added to the sample, add a definite amount of the secondary internal standard solution containing $^{13}C_{12}$-congeners.

To prevent losses of the most volatile PCBs it is not allowed to evaporate till complete dryness. It is advisable to add a small amount (one drop) of keeper substance (7.2.7).

10.4 Clean-up of the extract

10.4.1 General

Clean-up shall be used if compounds are 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 chromatographic system). If no or negligible interfering substances are present, no clean-up is necessary. Depending on the substances to be removed, Table 5 shall be used. If polar compounds shall be removed take special care on the recoveries of the low chlorinated PCBs.

Table 5 — Clean-up methods

Method	Clean-up	For removal of	Suitable for	Remarks
Clean-up A	Aluminium oxide	Polar compounds	MS and ECD	Difficult to adjust water content and keep it constant
Clean-up B	Silica	Polar compounds		Attention: some charges of silica can contain low concentrations of PCBs
Clean-up C	Gel permeation	High molecular compounds, lipids	MS	
Clean-up D	Florisil®	Polar compounds		Analysis of pesticides is possible after this clean-up
Clean-up E	H_2SO_4/Silica NaOH	Polar compounds, PAH, lipids		Especially suitable for lipid containing samples
Clean-up F	Benzenesulfonic acid/ sulfuric acid	Polar compounds, (poly) aromatics, bases, hetero compounds, oil	MS and ECD	Especially suitable for samples containing high concentration of mineral oil
Clean-up G	TBA	Sulfur	ECD	
Clean-up H	Cu	Sulfur	ECD	

Table 5 *(continued)*

Method	Clean-up	For removal of	Suitable for	Remarks
Clean-up I	$AgNO_3$/Silica	Sulfur + polar compounds	MS and ECD	Also applicable for MS

NOTE Different materials such as modified silica gel or Polymer-Based Solid-Phase extraction can be used if performance is proven.

Other clean-up procedures may also be used, provided they remove the interfering peaks in the chromatogram and recoveries after use of the clean-up are at least 80 % for all relevant congeners (including internal standards).

The extract obtained in 10.3 or in a previous clean-up step shall be quantitatively transferred to the clean-up system; alternatively, an aliquot may be used.

10.4.2 Clean-up A – Aluminium oxide

Prepare an adsorption column by placing a small plug of quartz wool (8.1.11) in the chromatography tube (8.1.13) and packing it dry with (2,0 ± 0,1) g of aluminium oxide (7.3.1.1). If necessary, add a layer of sodium sulfate (7.2.4)

Apply the extract to the dry packed adsorption column. Rinse the test tube twice with 1 ml of petroleum ether or hexane-like solvent (7.2.3) and quantitatively transfer the rinsings to the column as soon as the liquid level reaches the upper side of the column packing. Elute with approximately 20 ml of petroleum ether or hexane-like solvent. Collect the entire eluate.

Keeper substance (7.2.7) is added to the eluate, and then the eluate is reduced to the desired volume (see 10.3).

If a new batch of aluminium oxide is used, the solvent volume to eluate the specified PCB congeners completely from the column shall be determined using a proper PCB standard solution.

NOTE Commercially available disposable aluminium oxide cartridges can be used as an alternative if found suitable. A column is suitable if the performance of the method is in agreement with 5.2, 10.7.5 and 10.8.6.

10.4.3 Clean-up B – Silica gel

Put glass wool (8.1.11) and 10 g silica gel (7.3.2.2) into the chromatographic tube (8.1.13). Then add a layer of sodium sulfate (7.2.4) and condition with 20 ml petroleum ether or hexane-like solvent (7.2.3). Apply the extract to the column when the level of the solvent mixture is drained to approximately 0,5 cm above the column packing.

Elution is performed using a total of 10 ml petroleum ether or hexane-like solvent (7.2.3). Keeper substance (7.2.7) is added to the eluate, and then the eluate is reduced to the desired volume (see 10.3).

10.4.4 Clean-up C – Gel permeation chromatography

The extract is carefully reduced under a gentle nitrogen flow. The residue is immediately dissolved in 5 ml solvent mixture [(ethyl acetate (7.3.3.2) and cyclohexane (7.3.3.3) (1:1 volume fraction)] and is then put into the GPC column.

The solvent mixture for GPC is used for elution.

The GPC system-settings should be:

- Flow rate: 5 ml/min;
- Volume of the sample loop: 5 ml;
- First fraction: 120 ml (24 min);
- PCB elution: 155 ml (31 min);
- Last fraction: 20 ml (4 min).

The elution volumes of the first fraction, eluate and last fraction shall be considered recommended values and shall be regularly verified by means of the multi-component PCB-standard solution.

Keeper substance (7.2.7) is added to the eluate, and then the eluate is reduced to the desired volume (see 10.3)

NOTE During use of the gel permeation column a small shift in volume to be collected can occur. This is visible in a decrease of recoveries of the internal standards. If this occurs, readjustment of the sampled volume can be necessary.

10.4.5 Clean-up D – Florisil®

Add into a chromatographic tube (8.1.13) 5 mm sodium sulfate (7.2.4), 1,5 g Florisil (7.3.4.1), and again 5 mm sodium sulfate (7.2.4). To fix the mixture, place glass wool (8.1.11) on the top. Rinse the column with approximately 50 ml isooctane (7.3.4.2). Apply the extract to the column. Rinse the extraction tube/vessel for two times with 1 ml isooctane/toluene (95/5 volume fraction in percent) (7.3.4.4). and quantitatively transfer it onto the column. Afterwards elute with 7 ml isooctane /toluene (7.3.4.4). One drop of keeper substance (7.2.7) is added to the eluate, and then the eluate is reduced to the desired volume (see 10.3).

Alternatively, empty SPE-cartridges filled with a minimum of 2 g of Florisil (7.3.4.1) can be used instead of chromatographic tubes (8.1.13). For pre-conditioning, 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.

10.4.6 Clean-up E – Silica H_2SO_4/silica NaOH

The combined silica H_2SO_4/silica NaOH phase is effective in the removal of polar compounds, polycyclic aromatic compounds and triglycerides.

Prepare an adsorption column by pouring consecutively 1 g silica NaOH (7.3.5.4), 5 g silica H2SO4 (7.3.5.2) and 2 g sodium sulfate (7.2.4) in a clean chromatography column (8.1.13). Add a sufficient amount of n-hexane (7.3.5.6) and elute until the top of the n-hexane phase reaches the top of the sodium sulfate layer. Apply the extract to the top of the sodium sulfate layer and ensure it passes through the column. Elute with about 60 ml of n-hexane and collect the entire n-hexane fraction. One drop of keeper substance (7.2.7) is added to the eluate, and then the eluate is reduced to the desired volume (see 10.3).

10.4.7 Clean-up F – Benzenesulfonic acid/sulfuric acid

Benzenesulfonic acid/sulfuric acid pre-treatment is effective if the sample contains large amounts of oil.

Condition the silica cartridges by eluting three times with 2 ml portions of n-hexane (7.3.5.6). 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 × 1 ml n-hexane like solvent (7.2.3 or 7.3.5.6) to the column and wait once again for 30 s. Elute the PCB from the column with 3 × 0,5 ml of n-hexane like solvent (7.2.3 or 7.3.5.6). Collect the entire eluate. Keeper substance (7.2.7) is added to the eluate, and then the eluate is reduced to the desired volume (see 10.3).

10.4.8 Clean-up G – TBA sulfite reagent

Add 2 ml of TBA sulfite reagent (7.3.7.1) to 1 ml of concentrated extract and shake for 1 min. Add 10 ml of water (7.2.5) and shake again for 1 min. Separate the organic phase from the water with a Pasteur pipette and add a few crystals of sodium sulfate (7.2.4) to remove the remaining traces of water.

10.4.9 Clean-up H – Clean-up using pyrogenic copper to remove elemental sulfur and some other organic sulfur compounds

Add 1 ml of the extract (in petroleum ether or hexane-like solvent (7.2.3)) to a centrifuge tube. Add 100 mg pyrogenic copper powder (prepared according to procedure given in 7.3.8.6). Centrifuge the tube more than 5 min at approximately 3 500 r/min (ensure that there is no visible turbidity). Remove the extract and if necessary, clean-up further using column chromatography (8.1.13).

10.4.10 Clean up I – $AgNO_3$/silica

Add into a chromatographic tube (8.1.13) sodium sulfate (7.2.4) e.g. 5 mm high, 2 g of the AgNO3/silica mixture (7.3.9.2) and again 5 mm high sodium sulfate (7.2.4). Rinse the column with approximately 50 ml *n*-hexane (7.3.5.6) or petroleum ether or hexane-like solvent (7.2.3). Apply the extract to the filled column. Rinse the extraction vessel for three times with 2 ml n-hexane or petroleum ether or hexane-like solvent and quantitatively transfer it onto the column, when the meniscus of the extract riches the surface of the sodium sulfate (7.2.4). Add in the same manner 40 ml of hexane (7.3.5.6) or petroleum ether or hexane-like solvent (7.2.3) onto the column. Keeper substance (7.2.7) is added to the eluate, and then the eluate is reduced to the desired volume (see 10.3).

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

10.5 Addition of the injection standard

If addition of an injection standard is necessary, add an appropriate amount of the secondary injection standard (7.6.3) to the extract obtained after clean-up (this amount shall be in line with the concentration of the calibration standard). Record the final volume V.

10.6 Gas chromatographic analysis (GC)

10.6.1 General

Both MS and ECD detectors are allowed, but in special cases only one gives the proper results. In general MS is recommended. In the following cases ECD-detection may be preferred:

- Presence of mineral oil. Removal of mineral oil may be difficult, because the polarity of these compounds can be comparable to PCBs. An ECD-detector is not sensitive for mineral oil and no clean-up or a less effective clean-up is possible.
- Using an ECD-detector, the pattern of the PCBs is more easily recognized.
- An ECD-detector can be used for a first screening to select the samples having PCB-concentrations higher than the minimum reporting value. For samples with PCB-concentrations lower than this value further identification is not necessary.

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

10.6.2 Setting the gas chromatograph

Set the gas chromatograph (8.2) in such a way that sufficient separation of the PCBs is achieved (see 5.2). Annex B gives an example of conditions for the gas chromatograph and the elution order of the target PCBs as can be expected on two different columns.

10.7 Mass spectrometry (MS)

10.7.1 Mass spectrometric conditions

Tune the mass spectrometer 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 6. For each native congener, two ions making part of the chlorine isotope cluster of the molecular ion and one specific fragment ion are chosen.

Table 6 — Diagnostic ions for PCBs to be used with MS detection

Compound	Diagnostic Ion 1 *m/z*	Diagnostic Ion 2 *m/z*	Diagnostic Ion 3 *m/z*
PCB28	256 (100)	258 (74)	186 (82)
$^{13}C_{12}$-PCB28	268	270	
PCB52	292 (100)	294 (49) or 290 (77)	220 (95)
$^{13}C_{12}$-PCB52	304	302 or 306	
PCB101	326 (100)	328 (65)	256 (62)
$^{13}C_{12}$-PCB101	338	340	
PCB118	326 (100)	328 (62)	254 (57) or 256 (62)
$^{13}C_{12}$-PCB118	338	340	
PCB138	360 (100)	362 (92) or 358 (42)	290 (106)
$^{13}C_{12}$-PCB138	372	374	
PCB153	360 (100)	362 (92) or 358 (42)	290 (73)
$^{13}C_{12}$-PCB153	372	374	
PCB180	394 (100)	396 (96)	324 (84)
$^{13}C_{12}$-PCB180	406	408	

m – mass of ion

z – charge number of ion

Brackets values are abundance values which are normalized to the diagnostic ion 1. Values for diagnostic ions 2 and 3 may depend on the MS-system and its actual condition. Presented values should be considered indications.

10.7.2 Calibration of the method using an internal standard

10.7.2.1 General

This is an independent method for the determination of the mass concentrations and is not influenced by injection errors, the volume of water present in the sample or matrix effects in the sample, provided that recovery of the compounds to be analysed is about equal to that of the internal standard.

Add a specific mass of the internal standard and injection standard (7.5.3) to dilutions of the mixed calibration solution (7.5.2). The mass concentration of both standards shall be the same for all calibration solutions and comparable with the concentration of both standards in the final extract. Run the GC-MS analysis with the calibration solutions, prepared as described in 7.5.2. Calculate the relative response ratio for the native PCB and the $^{13}C_{12}$-PCB 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 (2):

$$\frac{A_\text{n}}{A_\text{C13}} = s \cdot \frac{\rho_\text{n}}{\rho_\text{C13}} + b \tag{2}$$

where

A_n	is the measured response of the native PCB, e.g. peak area;
A_{C13}	is the measured response of the $^{13}C_{12}$-labelled PCB internal standard, e.g. peak area;
s	is the slope of the calibration function;
ρ_n	is the mass concentration of the native PCB in the calibration solution, expressed in micrograms per litre (µg/l);
ρ_{C13}	is the mass concentration of the $^{13}C_{12}$-labelled PCB internal standard in the calibration solution, expressed in micrograms per litre (µg/l);
b	is the intercept of the calibration curve with the ordinate.

Two types of calibration are distinguished: the initial calibration (10.7.2.2) and the daily calibration (validity check of the initial calibration); the last one is called calibration verification (10.7.2.3).

Nonlinear calibration methods may be applied.

10.7.2.2 Initial calibration

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.

Take a gas chromatogram of a series of at least five standard solutions with equidistant concentrations, including the solvent blank. Identify the peaks, using MS or the gas chromatograms of the individual compounds. Prepare a calibration graph for each compound.

Check for linearity according to ISO 8466-1.

Nonlinear calibration using all five standards is allowed. In that case, the same five standards shall be used for re-calibration.

10.7.2.3 Calibration verification

The calibration verification checks the validity of the linear working range of the initial calibration curve and is performed at the beginning of each series of samples.

For every series of samples, inject at least two calibration standards with concentrations of (20 ± 10) % and (80 ± 10) % of the established linear range and calculate the straight line from these measurements. If the straight line falls within ±10 % of the reference values of the initial calibration line, the initial calibration line is assumed to be valid. If not, a new calibration line shall be established according to 10.7.2.2.

10.7.3 Measurement

Analyse the extracts according to 10.6, followed by 10.7, resp. 10.8, depending on the decision of the laboratory. With the aid of the absolute retention times, identify the peaks to be used to calculate the relative retention times. Use the internal standard or injection standard as close as possible to the PCB-peak to be quantified. For the other relevant peaks in the gas chromatograms, determine the relative retention times.

If the concentration is above the level for proper identification or quantification, a diluted extract shall be injected for proper identification or quantification of the relevant PCBs or re-extract the sample using a lower amount of sample.

If as a result of dilution, the internal standard is outside the linear range, Formula (4) in 10.7.5 does not give the proper quantification and the deviation from linearity shall be taken into account.

10.7.4 Identification

Apply ISO 22892 for the identification of the PCBs. In ISO 22892, the chromatographic criteria and MS-criteria are described, necessary for proper identification. Use the diagnostic ions as given in Table 6.

10.7.5 Check on method performance

Because this document allows using different modules, comparing the measured response of the internal standards and injection standards in both the injected performance standard solution and the injected sample is a check on the performance of the total procedure.

Use for this analysis:

- the same final volume,
- the same definite volume of internal standard, and
- the same definite volume of injection standard,

as used for the samples.

This is the performance standard.

The performance standard may be one of the calibration standards, provided that the ratio of the volumes (internal standard/injection standard) used is the same.

Calculate for each internal standard the ratio between sample and performance standard solution using the closest injection standard with Formula (3):

$$U = \frac{A_1(S)}{A_2(S)} \times \frac{A_2(ps)}{A_1(ps)} \times 100 \tag{3}$$

where

U is the recovery rate, expressed in percent (%);

A_1 is the measured response of the $^{13}C_{12}$-labelled PCB internal standard, e.g. peak area;

A_2 is the measured response of the $^{13}C_{12}$-labelled PCB injection standard, e.g. peak area;

ps is the performance standard;

S is the sample.

The recovery of the internal standard shall be at least 50 %.

If the two-step procedure for addition of the internal standard has been used, calculate the extraction ratio between the non-labelled PCB added to the sample and the labelled PCB to the extract using Formula (4):

$$E = \frac{A_{1,\text{mean}}(S) \times f}{A_3(S)} \times \frac{A_3(ps)}{A_{1,\text{mean}}(ps)} \times 100 \tag{4}$$

where

E	is the extraction recovery rate in percent (%);
$A_{1,\text{mean}}$	is the average measured response of the $^{13}C_{12}$-labelled PCB internal standard, e.g. peak area;
A_3	is the measured response of the non-labelled PCB internal standard, e.g. peak area;
f	is the fraction of the original extract used for clean-up;
ps	is the performance standard;
S	is the sample.

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 fulfil the requirement described before. In other cases, the values should be reported as indicative.

10.7.6 Calculation

Calculate the mass content of the individual PCB from the multipoint calibration of the total method by using Formula (5).

$$w_n = \frac{(A_n / A_{c13}) - b}{s.m.d_s} \cdot p_{C13} \cdot f_e \cdot f_t \cdot V \times 100 \tag{5}$$

where

w_n	is the content of the individual PCB found in the sample, expressed in milligrams per kilogram (mg/kg) on the basis of the dry matter;
A_{C13}	is the measured response of the $^{13}C_{12}$-labelled PCB internal standard in the sample extract;
A_n	is the measured response of the native PCB in the sample extract;
ρ_{C13}	is the mass of the $^{13}C_{12}$-labelled PCB internal standard added to the sample, expressed in micrograms per litre (µg/l);
m	is the mass of the sample used for extraction, expressed in grams (g);
d_s	is the dry matter fraction in the field moist sample, determined according to EN 15934, expressed in percent mass fraction;
f_e	is the ratio of the total organic solvent volume used for extraction to that of the aliquot used for the analysis; $f = 1$ if the whole extract is used;
f_t	is the addition factor;
V	is the volume of the final solution, expressed in millilitres (ml);
s	is the slope of the recalibration function;
b	is the intercept of the recalibration curve with the ordinate.

The result shall be expressed in milligrams per kilogram (mg/kg) dry matter and rounded to two significant figures. If necessary, Annex C could be used to provide the calculation of the total content of PCB.

10.8 Electron capture detection (ECD)

10.8.1 General

Using ECD, the same procedure as for MS can be followed, except the points described below for all specific steps in the measurement. For ECD, the same order in paragraphs has been used as in 10.7 (MS-detection). Only differences are described.

NOTE It is essential that the analyst pays attention to the presence of sulfur in the extract and uses the suitable clean-up before injection.

10.8.2 ECD conditions

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 selected to give the best sensitivity to PCB.

10.8.3 Calibration of the method using internal standards

Using an ECD, internal and injection standards are not $^{13}C_{12}$-PCBs but standards described in 7.5.3.3. Replace $^{13}C_{12}$-labelled PCB by used internal standard in Formula (2).

Formula (2) shall be used replacing A_{C13} by $A_{IS,i}$ and ρ_{C13} by $\rho_{IS,i}$ with:

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

$\rho_{IS,i}$ is the mass concentration of internal standard i in the calibration solution, in micrograms per litre (µg/l).

10.8.4 Measurement

Refer to 10.7.3.

10.8.5 Identification

Check the presence of any assigned compound by repeating the gas chromatographic analysis from 10.8.1, using GC-MS (see above) or using a column with a moderate polar phase (8.2.2) in combination with ECD. According to ISO 22892, three identification points shall be obtained. Measuring only with ECD, at least check the results with another column and recognition of the PCB-pattern are necessary. The results using the second column should be within 10 %. If both are correct, the three identification points (ISO 22892) for identification are obtained. If one is missing, only indication can be reported.

10.8.6 Check on ECD method performance

Mistakes are probable when a peak of an interfering compound appears at the same position in the chromatogram as that of the internal standard. Therefore, the following procedure is used to check if interfering compounds are present.

The presence or absence of interfering compounds is determined from the measured responses of the injection standards. When no interfering compounds are present in the extract, the ratio between the responses of the injection standards in the extracts is equal to that ratio in the standard solutions. The quotient of these ratios is called the relative response ratio, *RRR*. When no interfering compounds are present in the extract the value of *RRR* is in principle 1,00. In this document, it is assumed that no interfering compounds are present in the extract when *RRR* = (1,00 ± 0,05).

When the value of *RRR* deviates from (1,00 ± 0,05), it is assumed that the response of one of the injection standards is influenced by an interfering compound present in the extract. In this case the performance of the method is calculated using the undisturbed injection standard.

Verify the correctness of the response of the injection standards as follows:

Calculate the relative response ratio *RRR* for the PCB injection standards by using Formula (6):

$$RRR = \frac{R_{e,198}}{R_{e,2}} \times \frac{R_{s,2}}{R_{s,209}} \qquad (6)$$

where

RRR	is the relative response ratio;
$R_{e,198}$	is the response of PCB198 in the extract;
$R_{e,2}$	is the response of the selected second internal standard in the extract;
$R_{s,209}$	is the response of PCB209 in the working standard solution;
$R_{s,2}$	is the response of the selected second injection standard in the working standard solution.

PCB198 or PCB209 are recommended as injection standards for ECD-detection because of fewer interferences, other internal standards could be used.

The theoretical value of the relative response ratio *RRR* is 1,00. If *RRR* = (1,00 ± 0,05), regard the injection standards as correctly quantified and enter the value 1,00 for *RRR* in Formula (6). If *RRR* < 0,95 or *RRR* > 1,05, the gas chromatogram shall be checked for correct quantification of both injection standards. Take particular note of the peak shapes and peak widths. If the quantification has been correctly carried out, use both standards if *RRR* = (1,00 ± 0,05). Use only the injection standard PCB198 if *RRR* < 1,05 and use only PCB209 if *RRR* > 1,05.

Calculate the ratio between sample and performance standard solution for each internal standard using the closest injection standard according to Formula (3) (see 10.7.5).

If multiple clean-up is necessary, lower ratios can be found, because with each clean-up step losses are accepted by this document. Lower ratios are acceptable if this can be explained by the accepted losses in each clean-up step. The minimum recovery of internal standards shall be 50 %.

10.8.7 Calculation

Internal and injection standards are not $^{13}C_{12}$-labelled-PCB standards but standards as described in 7.5.3.3. Replace $^{13}C_{12}$-labelled PCB internal standard by the applied internal standards (7.5.3.3) in Formula (5).

If necessary, Annex C could be used to provide the calculation of the total content of PCB.

11 Performance characteristics

The method is “performance based”. It is permitted to modify the method to overcome interferences not specified in this document, provided that the performance criteria are met (10.7.5 or 10.8.6). Internal standards shall be used to check the pre-treatment, extraction and clean-up procedures.

Some samples may require multiple clean-up in case of lower recoveries.

12 Precision

The performance characteristics of the method data have been evaluated (see Annex A and [12]).

13 Test report

The test report shall contain at least the following information:

a) a reference to this document ;

b) complete identification of the sample;

c) the extraction procedure, clean-up procedure and detection procedure used for the analysis;

d) the results of the determination according to 10.7 (GC-MS) and 10.8 (GC-ECD);

e) any details not specified in this document or which are optional, as well as any factor which may have affected the results.

The summary of extraction, clean-up and detection procedures used for the analysis shall be documented by the laboratory and shall be made available on request.

Annex A
(informative)

Repeatability and reproducibility data

A.1 Materials used in the inter-laboratory comparison study

The inter-laboratory comparison for the determination of polychlorinated biphenyls (PCB) by GC-MS and GC-ECD in sludge, treated biowaste and soil was carried out by 9 laboratories using GC-ECD and 17 laboratories using GC-MS on three materials listed in Table A.1. Mixing of different materials had to be applied to obtain the desired concentration levels. Detailed information can be found on the inter-laboratory comparison study, in the publication of Kalbe et al.; 2019[12].

Table A.1 — Materials tested in the interlaboratory comparison for the determination of PCB by GC-MS and GC-ECD in soil, sludge, and treated biowaste

Sample	Grain size	Material tested
Soil	< 2,0 mm	Mix of soil from the vicinity of Berlin, Germany and PCB-free German reference soil
Sludge (<0,5 mm)	< 0,5 mm	Mix of municipal waste water treatment plant sludges from North Rhine Westphalia, Germany
Compost	< 0,25 mm	Mix of compost from the vicinity of Berlin, Germany and sludge from North Rhine Westphalia, Germany

A separate inter-laboratory comparison was carried out on waste of various origins and industrially contaminated soil. Table A.2 describes the test materials.

Table A.2 — Materials tested in the inter-laboratory comparison for the determination of PCB by GC-MS and GC-ECD in contaminated soil and waste

Sample	Grain size	Material tested
Contaminated Soil	< 1 mm	The sample was taken from an old industrial site. 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.
Building debris	< 1 mm	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.
Waste wood	< 1 mm	After grinding using a cutting mill two subsequent milling processes with sieves of 2 mm and 1 mm were performed to obtain visually homogenous material. 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.
Sealant waste	< 1 mm	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 polyacrylic 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.

Table A.2 *(continued)*

Sample	Grain size	Material tested
Electronic waste	< 0,75 mm	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.
Shredder light fraction	< 1 mm	This material is a fraction of waste from used devices and vehicles. Typically, it consists of 25 % to 35 % mass fraction plastics, 20 % to 30 % mass fraction elastomers, 10 % to 16 % mass fraction glass, 3 % to 5 % mass fraction lacquers, 3 % to 6 % mass fraction textiles, 3 % to 6 % mass fraction wood/fibrous materials, 0,5 % to 4 % mass fraction alumina, 1 % to 3 % mass fraction copper, 3 % to 13 %mass fraction iron, 10 % to 20 % mass fraction 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.
Cable shredder fraction	< 2 mm	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.
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.2 Inter-laboratory comparison results

The statistical evaluation was conducted according to ISO 5725-2. The average values, the repeatability standard deviation (sr) and the reproducibility standard deviation (sR) were obtained (Tables A.3 and A.4).

Table A.3 — Results of the inter-laboratory comparison studies of the determination of polychlorinated biphenyls (PCB) by GC-MS and GC-ECD in soil, sludge, and treated biowaste

Parameter	Matrix	l_o	L	n_o	n	$\bar{x}$ mg/kg	s_R mg/kg	CV_R %	s_r mg/kg	CV_r %
PCB 28	Soil	27	24	81	72	0,073	0,015	21,12	0,004	6,04
	Compost	27	22	81	66	0,755	0,242	32,10	0,027	3,52
	Sludge	27	26	81	78	0,761	0,213	28,02	0,065	8,59
PCB 52	Soil	27	27	81	81	0,733	0,188	25,70	0,041	5,62
	Compost	27	24	81	72	0,352	0,100	28,33	0,013	3,75
	Sludge	27	26	81	78	0,347	0,137	39,49	0,027	7,81
PCB 101	Soil	27	27	81	81	0,764	0,192	25,18	0,048	6,33
	Compost	27	21	81	63	0,375	0,063	16,77	0,011	3,03
	Sludge	27	27	81	81	0,381	0,105	27,54	0,030	7,89
PCB 118	Soil	27	26	81	78	0,650	0,164	25,29	0,034	5,30
	Compost	27	24	81	72	0,219	0,070	31,84	0,008	3,80
	Sludge	27	27	81	81	0,234	0,067	28,63	0,020	8,62
PCB 138	Soil	27	26	81	78	0,472	0,120	25,51	0,034	7,15
	Compost	27	24	81	72	0,425	0,105	24,66	0,026	6,16
	Sludge	27	24	81	72	0,453	0,161	35,49	0,026	5,66

Table A.3 *(continued)*

Parameter	**Matrix**	l_o	L	n_o	n	$\overline{x}$ mg/kg	s_R mg/kg	CV_R %	s_r mg/kg	CV_r %
PCB 153	Soil	27	26	81	78	0,342	0,075	22,01	0,021	6,25
	Compost	27	25	81	74	0,414	0,097	23,34	0,017	4,14
	Sludge	27	27	81	80	0,444	0,126	28,42	0,032	7,19
PCB 180	Soil	27	27	81	81	0,098	0,022	22,68	0,007	6,81
	Compost	27	25	81	74	0,249	0,063	25,26	0,015	6,10
	Sludge	27	25	81	75	0,266	0,093	34,92	0,017	6,27
SUM7 PCB	Soil	27	27	81	81	3,14	0,641	20,41	0,185	5,89
	Compost	27	25	81	75	2,81	0,545	19,42	0,120	4,28
	Sludge	27	26	81	78	2,91	0,666	22,89	0,178	6,13

Key

l_o	Number of participating laboratories
l	Number of laboratories after elimination of outliers
n_o	Number of single measurement values
n	Number of single measurement values without outliers
$\overline{x}$	Total mean (without outliers)
s_R	Reproducibility standard deviation
CV_R	Coefficient of variation of reproducibility
s_r	Repeatability standard deviation
CV_r	Coefficient of variation of repeatability

Table A.4 — Results of the inter-laboratory comparison studies of the determination of polychlorinated biphenyls (PCB) by GC-MS and GC-ECD in waste and contaminated soil

Sample	**Analyte**	***o*** %	***p***	***n***	**Outliers**	***x*** mg/kg	s_R mg/kg	CV_R %	s_r mg/kg	CV_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
	Sum PCB_7	14,3	14	30	2	4,659	1,17	25,1	0,131	2,8

Table A.4 *(continued)*

Sample	**Analyte**	o %	p	n	**Outliers**	x mg/kg	s_R mg/kg	CV_R %	s_r mg/kg	CV_r %
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
	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

Table A.4 *(continued)*

Sample	Analyte	o %	p	n	Outliers	x mg/kg	s_R mg/kg	CV_R %	s_r mg/kg	CV_r %
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
CV_R	Coefficient of variation of reproducibility
s_r	Estimate of the repeatability standard deviation
CV_r	Coefficient of variation of repeatability

Annex B
(informative)

Examples for gas chromatographic conditions and retention times of PCBs

Optimized for the gas chromatograph could be the following:

- Separation column: Capillary column (see 8.2.2);
- Oven temperature program: 60 °C, 2 min;

30 °C/min to 120 °C;

5 °C/min to 300 °C;

300 °C, 15 min;

- Injector temperature: 260 °C;
- Splitless injection: 1 µl, keep the split 1,8 min closed;
- Carrier gas: Helium 0,8 ml/min to 1 ml/min.

Table B.1 shows examples for retentions times of the target PCBs determined on different columns.

Table B.1 — Examples for retention times of PCBs for two different capillary columns

Component	Retention time min	
	A [a]	**B** [b]
PCB28	33,32	32,98
PCB52	34,85	34,54
PCB101	38,71	38,27
PCB118	41,89	41,61
PCB138	45,00	44,54
PCB153	43,18	42,49
PCB180	50,41	49,47

NOTE Depending upon the column used the co-elution of the stated PCBs with other congeners is possible. For the co-elution information please consult the column specification or column procedures.

[a] 50 m CP-Sil 8[c]; internal diameter 0,22 mm; film layer 0,12 µm

[b] 50 m CP-Sil 19[2]; internal diameter 0,22 mm; film layer 0,12 µm

[c] CP-Sil 8, CP-Sil 19 are examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products. Equivalent products may be used if they can be shown to lead to the same results.