SLOVENSKI STANDARD
oSIST prEN 17322:2018

01-november-2018

Trdni matriksi z vidika okolja - Določevanje polikloriranih bifenilov (PCB) s plinsko kromatografijo z masno selektivnim detektorjem (GC/MS) ali s plinsko kromatografijo z detektorjem z zajetjem elektronov (GC/ECD)

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

Schlamm, behandelter Bioabfall, Abfällen und Boden - Bestimmung von polychlorierten Biphenylen (PCB) mittels Gaschromatographie mit Massenspektrometrie-Kopplung (GC-MS) und Gaschromatographie mit Elektroneneinfangdetektion (GC-ECD)

Matrices solides environnementales - Détermination des biphényles polychlorés (PCB) par chromatographie en phase gazeuse-spectrométrie de masse (CG-SM) ou chromatographie en phase gazeuse avec détection par capture d'électrons (CG-DCE)

Ta slovenski standard je istoveten z: **prEN 17322**

ICS:

13.030.10	Trdni odpadki	Solid wastes
13.080.10	Kemijske značilnosti tal	Chemical characteristics of soils
71.040.50	Fizikalnokemijske analitske metode	Physicochemical methods of analysis

oSIST prEN 17322:2018 **en,fr,de**

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

DRAFT
prEN 17322

November 2018

ICS 13.030.10; 13.030.20; 13.080.10

Will supersede EN 15308:2016, EN 16167:2018

English Version

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

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This draft European Standard is submitted to CEN members for enquiry. It has been drawn up by the Technical Committee CEN/TC 444.

If this draft becomes a European Standard, CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

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Recipients of this draft are invited to submit, with their comments, notification of any relevant patent rights of which they are aware and to provide supporting documentation.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

CEN-CENELEC Management Centre: Rue de la Science 23, B-1040 Brussels

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European foreword

This document (prEN 17322:2018) has been prepared by Technical Committee CEN/TC 444 "Test methods for environmental characterization of solid matrices", the secretariat of which is held by NEN.

This document is currently submitted to the CEN Enquiry.

This document is the result of the merging of EN 16167:2018 and EN 15308:2016, with minor technical modifications. This document will supersede EN 16167 and EN 15308 after publication.

The preparation of this document by CEN is based on a mandate by the European Commission (Mandate M/330), which assigned the development of standards on sampling and analytical methods for hygienic and biological parameters as well as inorganic and organic determinants, aiming to make these standards applicable to sludge, sediment, treated biowaste, waste and soil as far as this is technically feasible.

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 European Standard 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 European Standard 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 15527). It has been tested for ruggedness.

This European Standard 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 European Standard 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 European Standard should be familiar with usual laboratory practice. This European Standard 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 European Standard be carried out by suitably trained staff.

1 Scope

This document specifies a method 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 European Standard

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 European Standard, 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 European Standard contains decision tables based on the properties of the sample and the extraction and clean-up procedure to be used.

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 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.

EN 15002, *Characterization of waste — Preparation of test portions from the laboratory sample*

EN 15934, *Sludge, treated biowaste, soil and waste — Calculation of dry matter fraction after determination of dry residue or water content*

EN 16179, *Sludge, treated biowaste and soil — Guidance for sample pretreatment*

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

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

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

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

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

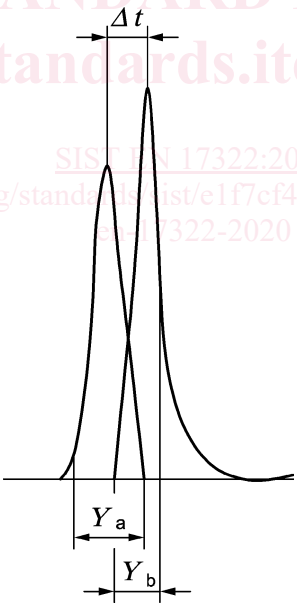
3 Terms and definitions

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

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

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

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



Key

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

$$\boldsymbol{R} = 2 \times \frac{\Delta\ \mathbf{t}}{\boldsymbol{Ya} + \boldsymbol{Yb}} \quad (\mathbf{x})$$

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 European Standard, different procedures for different steps (modules) are allowed. Which modules should be used depends on the sample. A recommendation is given in this European Standard. Performance criteria are described and it is the responsibility of the laboratories applying this European Standard 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 eluate 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 analyzed 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. 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.

— PCB28 – PCB31

— PCB52 – PCB73

— PCB101 – PCB89 / PCB90

— PCB118 – PCB106

— PCB138 – PCB164 / PCB163

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 specialised 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 shall be followed with respect to all hazards associated with this method.

7 Reagents

7.1 General

All reagents shall be of recognised 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 89 °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) 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)

7.3.3.1 Bio-Beads® S-X3.

NOTE Bio-Beads® is an example of a suitable product available commercially. 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 they can be shown to lead to the same results.

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®

NOTE 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 they can be shown to lead to the same results.

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

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 (7.3.5.3).

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.