Literaturhinweise

[1] EN 16181:2018, *Boden, behandelter Bioabfall und Schlamm — Bestimmung von polycyclischen aromatischen Kohlenwasserstoffen (PAK) mittels Gaschromatographie (GC) und Hochleistungs-Flüssigkeitschromatographie (HPLC)*

[2] EN 15527:2008, *Charakterisierung von Abfällen — Bestimmung von polycyclischen aromatischen Kohlenwasserstoffen (PAK) in Abfall mittels Gaschromatographie-Massenspektrometrie (GC/MS)*

[3] ISO 18287, *Soil quality — Determination of polycyclic aromatic hydrocarbons (PAH) — Gas chromatographic method with mass spectrometric detection (GC-MS)*

[4] ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

[5] EN ISO 5667-12, *Wasserbeschaffenheit — Probenahme — Teil 12: Anleitung zur Probenahme von Sedimenten* (ISO 5667-12)

[6] EN ISO 5667-13, *Wasserbeschaffenheit — Probenahme — Teil 13: Anleitung zur Probenahme von Schlämmen* (ISO 5667-13)

[7] EN 15002, *Charakterisierung von Abfällen — Herstellung von Prüfmengen aus der Laborprobe*

[8] EN 15934, *Schlamm, behandelter Bioabfall, Boden und Abfall — Berechnung des Trockenmassenanteils nach Bestimmung des Trockenrückstands oder des Wassergehalts*

[9] EN 16179, *Schlamm, behandelter Bioabfall und Boden — Anleitung zur Probenvorbehandlung*

[10] KALBE U., LEHNIK-HABRINK P., BANDOW N., SAUER A., Validation of European horizontal methods for the analysis of PAH, PCB and dioxins in sludge, treated biowaste and soil. *Environ. Sci. (Ruse)*. 2019, **31** S. 29

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– *Entwurf* –

EUROPEAN STANDARD

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DRAFT
prEN 17503

May 2020

ICS 13.030.01; 13.080.10

Will supersede EN 15527:2008, EN 16181:2018

English Version

Environmental solid matrices - Determination of polycyclic aromatic hydrocarbons (PAH) by gas chromatography (GC) and high performance liquid chromatography (HPLC)

Matrices solides environnnementales ¿ Determination des hydrocarbures aromatiques polycycliques (HAP)par chromatographie en phase gazeuse (GC) et chromatographie liquid a haute performance (HPLC)

Umweltrelevante feste Matrizes ¿ Bestimmung von polycyclischen aromatischen Kohlenwasserstoffen (PAK) mittels Gaschromatograpie (GC) und Hochleistungs-Flüssigkeitschromatographie (HPLC)

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.

This draft European Standard was established by CEN in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN-CENELEC Management Centre has the same status as the official versions.

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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

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Contents

European foreword

This document (prEN 17503:2020) 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 will supersede EN 15527:2008 and EN 16181:2018.

Introduction

Polycyclic aromatic hydrocarbons (PAH) are ubiquitous because they are released in appreciable quantities every year into the environment through the combustion of organic matters such as coal, fuel oils, petrol, wood, refuse and plant materials. Since some of these PAH compounds are carcinogenic or mutagenic, their presence in the environment (air, water, soil, sediment and waste) is regularly monitored and controlled. At present determination of PAH is carried out in these matrices in most of the routine laboratories following the preceding steps for sampling, pre-treatment, extraction, clean-up by measurement of specific PAH by means of gas chromatography in combination with mass spectrometric detection (GC-MS) or by high performance liquid chromatography (HPLC) in combination with UV-DAD- or fluorescence-detection (HPLC-UV-DAD/FLD). Both the GC-MS and the HPLC methods are included in this horizontal standard.

This document was developed by merging of EN 16181:2018 [1], initially elaborated as a CEN Technical Specification in the European project 'HORIZONTAL' and validated by CEN/TC400 with the support of BAM, with EN 15527 [2], published by CEN/TC292.

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. Quantification with both GC-MS-detection and HPLC-DAD-UV/FLD is possible. Four different extraction procedures are described and three 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 PCB (EN17322). 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 an industrial area in Brandenburg, Germany and PCB-free German reference soil
Sludge	Mix of municipal waste water treatment plant sludge from the vicinity of Berlin, Germany
Biowaste	Mix of compost from the vicinity of Berlin, Germany
Waste	Contaminated soil, building debris, waste wood, roofing tar, shredder light fraction

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.

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

1 Scope

This document specifies different methods for quantitative determination of 16 polycyclic aromatic hydrocarbons (PAH) (see Table 2) in soil, sludge, sediment, treated biowaste, and waste, using GC-MS or HPLC-UV-DAD/FLD covering a wide range of PAH contamination levels (see Table 2).

When using fluorescence detection, acenaphthylene cannot be measured.

Table 2 —Target analytes of this document

Target analyte	CAS-RN[a]
Naphthalene	91–20–3
Acenaphthene	83–32–9
Acenaphthylene	208–96–8
Fluorene	86–73–7
Anthracene	120–12–7
Phenanthrene	85–01–8
Fluoranthene	206–44–0
Pyrene	129–00–0
Benz[*a*]anthracene	56–55–3
Chrysene	218–01–9
Benzo[*b*]fluoranthene	205–99–2
Benzo[*k*]fluoranthene	207–08–9
Benzo[*a*]pyrene	50–32–8
Indeno[*1,2,3-cd*]pyrene	193–39–5
Dibenz[*a,h*]anthracene	53–70–3
Benzo[*ghi*]perylene	191–24–2

[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 10 µg/kg (expressed as dry matter) for soils, sludge and biowaste to 100 µg/kg (expressed as dry matter) for solid waste can be achieved. For some specific samples (e.g. bitumen) the limit of 100 µg/kg cannot be reached.

Sludge, waste and treated biowaste may differ in properties as well as in the expected contamination levels of PAH 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.

The method can be applied to the analysis of other PAH 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 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

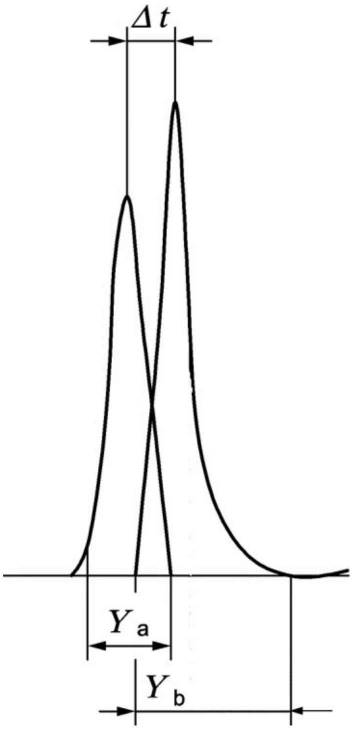
For the purposes of this document, the following terms and definitions apply.

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



$$R = 2 \times \frac{\Delta t}{Y_a + Y_b} \quad (1)$$

Where:

R	peak separation
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
internal standard

isotopically labelled mostly deuterated PAH or native PAH unlikely to be present in the sample, added to samples before extraction and used for quantification of the PAH content

3.3
injection standard

PAH 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
extraction standard

PAH that is unlikely to be present in samples added to the sample prior to extraction. Used for checking the extraction efficiency and not used for quantification purposes

3.5
sediment

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

[SOURCE: ISO 5667-12:2017 definition 3.5]

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 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 PAH 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.

If a solvent exchange for HPLC analysis is necessary, the concentrated extract is taken up in an appropriate less volatile water miscible polar solvent and the non-polar extract residue is removed.

The extract is analysed by GC-MS using a capillary column with a stationary phase of low polarity or by HPLC-UV-DAD/FLD with an appropriate reversed phase column.

PAH are identified and quantified with GC-MS by comparison of relative retention times and relative peak heights (or peak areas) with respect to internal standards added, and with HPLC by using the corresponding variables of the extraction standard solutions. 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 PAH 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-MS

Substances that co-elute with the target PAH 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. Asymmetrical peaks and peaks broader than the corresponding peaks of the reference substance suggest interferences.

Chromatographic separation between dibenz[*a,h*]anthracene and indeno[*1,2,3-cd*]pyrene are mostly critical. Due to their molecular mass differences, quantification can be made by mass selective detection. When incomplete resolution is encountered, peak integration shall be checked and, if necessary, corrected.