

SLOVENSKI STANDARD
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Blato, obdelani biološki odpadki in tla - Določevanje policikličnih aromatskih ogljikovodikov (PAH) s plinsko kromatografijo (GC) in s tekočinsko kromatografijo visoke ločljivosti (HPLC)

Sludge, treated biowaste and soil - Determination of polycyclic aromatic hydrocarbons (PAH) by gas chromatography (GC) and high performance liquid chromatography (HPLC)

Schlamm, behandelter Bioabfall und Boden - Bestimmung von polycyclischen aromatischen Kohlenwasserstoffen (PAK) mittels Gaschromatographie (GC) und Hochleistungs-Flüssigkeitschromatographie (HPLC)

Boue, biodéchet traité et sol - Dosage des hydrocarbures aromatiques polycycliques (HAP) par chromatographie en phase gazeuse et chromatographie liquide à haute performance

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Sludge, treated biowaste and soil - Determination of polycyclic aromatic hydrocarbons (PAH) by gas chromatography (GC) and high performance liquid chromatography (HPLC)

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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 400.

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Foreword

This document (prEN 16181:2010) has been prepared by Technical Committee CEN/TC 400 "Project Committee - Horizontal standards in the fields of sludge, biowaste and soil", the secretariat of which is held by DIN.

This document is currently submitted to the CEN Enquiry.

This European Standard is part of a modular horizontal approach in which this document belongs to the analytical step.

The preparation of this document by CEN is based on a mandate by the European Union (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, treated biowaste and soil as far as this is technically feasible.

Until now, test methods determining properties of materials within the environmental area were prepared in Technical Committees (TCs) working on specific products/matrices (e. g. soil, waste, sludge). However, it is understood that many steps within individual test procedures may also be used for the analysis of various other materials. By careful determination of these steps and selection of specific questions within these steps, elements of the test procedure can be described in a way that can be used for a variety of matrices and materials with certain specifications. This optimization is in line with the development among end-users of standards. A majority of routine environmental analyses are carried out by institutions and laboratories working under a scope that is not limited to one single environmental matrix but covers a wide variety of matrices. Availability of standards covering more matrices contributes to the optimization of laboratory procedures and standard maintenance costs, e. g. costs related to accreditation and recognition.

A horizontal modular approach was developed in the project 'Horizontal'. 'Modular' means that a test standard developed in this approach concerns a specific step in assessing a property and not the whole "chain of measurement" (from sampling to analyses). A beneficial feature of this approach is that individual "modules" can be replaced by improved ones without jeopardizing the standard "chain".

The results of the desk study as well as the evaluation and validation studies have been subject to discussions with all parties concerned in the CEN structure during the development by project 'Horizontal'. The results of these consultations with interested parties in the CEN structure have been presented to and discussed in CEN/TC 400.

Based on data from interlaboratory studies and consultations with interested parties within CEN member bodies, it has been concluded that this draft standard prEN XXXX is acceptable for its intended use and is ready for CEN enquiry.

It is recognized that standardization in the environmental field in most national standardization bodies is organized in national standardization committees that mirror the vertical structure of technical committees in the environmental field in CEN. The present CEN enquiry therefore asks for special attention by the NSBs to assure that the relevant and interested parties are consulted during the CEN enquiry, i. e. to assure that one single consolidated enquiry reply on this draft standard prEN XXXX can be presented by the NSB that covers the entire scope of this draft standard.

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 are 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.

It is to be underlined that the target contamination level of PAH can lie in the range of about 0,01 mg/kg per individual PAH (agricultural soil and sediment) to about 200 mg/kg and higher (e. g. contaminated soil at coking plant sites or waste). The use of internal and injection standards is described in order to have an internal check on execution of the extraction and clean-up procedure. The method is as far as possible in agreement with the method described for PCBs (see prEN WI 00400003).

This document is the result of a desk study "Horizontal European standard for determination of PAH in sludge, soil and biowaste" in the project "Horizontal" and aims at evaluating the latest developments in assessing PAH in sludge, soil, treated biowaste and neighbouring fields. After an evaluation study, in which the ruggedness of the method was studied, a European-wide validation of the draft standard has taken place. The results of the desk studies as well as the evaluation and validation studies have been subject to discussions with all parties concerned in CEN.

This European Standard is (applicable and) validated for several types of matrices as indicated below (see Annex B for the results of the validation):

Table 1 — Matrices for which this European standard is (applicable and) validated

Matrix	Validated for
Sludge	Municipal sludge
Biowaste	Fresh compost

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WARNING — Persons using this European Standard should be familiar with normal 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 European Standard specifies the quantitative determination of 16 polycyclic aromatic hydrocarbons (PAH) (see Table 2) in sludge and treated biowaste using GC/MS and HPLC-UV-DAD/FLD covering a wide range of PAH contamination levels (see also annex A).

When using fluorescence detection acenaphthylene cannot be measured.

**Table 2 — Polycyclic aromatic hydrocarbons
which can be analysed using this European Standard**

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[ah]anthracene	53-70-3
Benzo[ghi]perylene	191-24-2
^a 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.

Typically, a lower limit of application of 0,01 mg/kg (expressed as dry matter) may be ensured for each individual PAH. This depends on instrument and sample.

Sludge and treated biowaste may differ in properties and also in the expected contamination levels of PAHs 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. Two general lines are followed, an agitation procedure (shaking) or use of soxhlet/pressurised liquid extraction.

NOTE Other PAH compounds can also be analysed with this method, provided suitability has been proven.

2 Normative references

The following referenced documents are indispensable for the application 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.

prEN WI00400022, *Sludge, treated biowaste and soil — Guidance for sample pretreatment*

EN 15308, *Characterization of waste — Determination of selected polychlorinated biphenyls (PCB) in solid waste by using capillary gas chromatography with electron capture or mass spectrometric detection*

prEN 15934, *Sludge, treated biowaste, soil and waste — Calculation of dry matter by determination of dry residue or water content*

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

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

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

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

3 Terms and definitions

[SIST-TS CEN/TS 16181:2013](https://standards.iteh.ai/catalog/standards/sist/3dd22326-5883-4188-972d-c5cf8ea32b03/sist-ts-cen-ts-16181-2013)

<https://standards.iteh.ai/catalog/standards/sist/3dd22326-5883-4188-972d-c5cf8ea32b03/sist-ts-cen-ts-16181-2013>

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

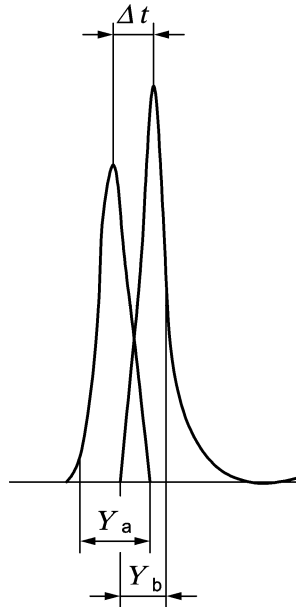
3.1

critical pair

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

[EN 15308:2008]

NOTE see Figure 1.



Key

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

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

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

Figure 1 — Example of a chromatogram of a critical pair

4 Principle

After pretreatment to reduce the moisture content and to increase the homogeneity (see 9.2), the test sample is extracted with a solvent.

The extract is concentrated and interfering compounds are removed by a clean-up method suitable for the specific matrix. The eluate is concentrated. For HPLC analysis the concentrated eluate is taken up in an appropriate less volatile water miscible polar solvent and the non-polar eluate 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 external 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 change 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. Unsymmetrical peaks and peaks being broader than the corresponding peaks of the reference substance suggest interferences.

Chromatographic separation between dibenzo[ah]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, when necessary, corrected. Sufficient resolution (e. g. 0,8) between the peaks of benzo[b]fluoranthene and benzo[k]fluoranthene as well as of benzo[a]pyrene and benzo[e]pyrene shall be set as quality criteria for the capillary column. Benzo[b]fluoranthene and benzo[j]fluoranthene cannot be separated. Triphenylene may not be completely separated from benzo[a]anthracene and chrysene. In this case it shall be stated in the report.

5.3 Interferences with the HPLC

Substances that show either fluorescence or quenching and co-elute with the PAHs to be determined may interfere 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. Unsymmetrical peaks and peaks being broader than the corresponding peaks of the reference substance suggest interferences. This problem may arise for naphthalene and phenanthrene depending on the selectivity of the phases used.

Incomplete removal of the solvents used for sample extraction and clean-up (hexane, acetone, dichloromethane) may lead to poor reproducibility of the retention times and wider peaks or double peaks especially for the 2- and 3-ring PAHs. Extracts shall be diluted sufficiently with acetonitrile for the HPLC-analysis, otherwise the detection of naphthalene and 3-ring PAH can be interfered by a broad toluene peak.

Separation between dibenzo[ah]anthracene and indeno[1,2,3-cd]pyrene can be critical. When incomplete resolution is encountered, peak integration shall be checked and, when necessary, corrected.

Usually perylene is incompletely resolved from benzo[b]fluoranthene, but by choosing a selective wavelength, the perylene peak can be suppressed.

6 Safety remarks

Certain PAH are highly carcinogenic and shall be handled with extreme care. Avoid contact of solid materials, solvent extracts and solutions of standard PAH.

PAH may co-distil with solvent and become deposited outside of stoppered bottles. All containers containing solutions of PAH in solvent shall therefore always be handled using gloves which are solvent resistant and preferably disposable.

PAH contamination of vessels may be detected by irradiation with 366 nm UV-light.

Vessels containing PAH solutions should be stored standing in beakers to contain any spillage in the case of breakage.

Solid PAH are most dangerous and give rise to a dust hazard due to their crystals becoming electrostatically charged. These materials shall only be handled where proper facilities are available (e. g. adequate fume hoods, protective clothing, dust masks). It is strongly advised that standard solutions are prepared centrally in suitably equipped laboratories or are purchased from suppliers specialised in their preparation.

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Solvent solutions containing PAH 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, C_2H_4O .

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

NOTE Hexane-like solvents with a boiling range between 30 °C and 69 °C are allowed.

7.2.3 Toluene, C_7H_8 .

7.2.4 Anhydrous 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, $NaCl$, anhydrous.

7.3 Reagents for clean-up**7.3.1 Clean-up using aluminium oxide**

7.3.1.1 Aluminium oxide, Al_2O_3

Basic or neutral, specific surface 200 m²/g, activity Super I according to Brockmann¹⁾.

7.3.1.2 Deactivated aluminium oxide

Deactivated with 10 % water.

Add 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 of two weeks.

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

1) Brockman Activity Scale : a measure of the percentage of water added to the adsorbent based upon weight/weight relationships between water and the adsorbent. Grade I corresponds to 0 % water added,

H. Brockmann and H. Schrodder; Ber. Deut. Chem. Ges. 74, 73 (1941)

J. W. Hampson, W. F. Bleam, Thermochimica Acta 288 (1996) 179 189