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**Blato, obdelani biološki odpadki in tla – Določevanje policikličnih aromatskih ogljikovodikov (PAO) 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)

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

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

## NACIONALNI UVOD

Tehnična specifikacija SIST-TS CEN/TS 16181 ((sl),en), Blato, obdelani biološki odpadki in tla – Določevanje policikličnih aromatskih ogljikovodikov (PAO) s plinsko kromatografijo (GC) in s tekočinsko kromatografijo visoke ločljivosti (HPLC), 2013, ima status slovenske tehnične specifikacije in je istovetna z evropsko tehnično specifikacijo CEN/TS 16181, Sludge, treated biowaste and soil – Determination of polycyclic aromatic hydrocarbons (PAH) by gas chromatography (GC) and high performance liquid chromatography (HPLC), 2013.

## NACIONALNI PREDGOVOR

Evropsko tehnično specifikacijo CEN/TS 16181:2013 je pripravil tehnični odbor Evropskega komiteja za standardizacijo CEN/TC 400 Horizontalni standardi na področju blata, obdelanih bioloških odpadkov in tal, katerega sekretariat vodi DIN.

CEN je pripravil ta dokument na podlagi mandata M/330 Evropske komisije in Evropskega združenja za prosto trgovino, ki narekuje pripravo standardov za vzorčenje in analizne metode za higienske in biološke kakor tudi za anorganske in organske parametre, ki bi bili primerni za blata, obdelane biološke odpadke in tla, kolikor je to tehnično izvedljivo.

Odločitev za privzem te tehnične specifikacije je dne 25. septembra 2013 sprejel tehnični odbor SIST/TC KAT Kakovost tal.

## ZVEZE S STANDARDI

S privzemom te evropske tehnične specifikacije veljajo za omenjeni namen referenčnih standardov vsi standardi, navedeni v izvirniku, razen tistih, ki so že sprejeti v nacionalno standardizacijo:

SIST EN 15934 (en)	Blato, obdelani biološki odpadki, tla in odpadki – Izračun suhe snovi z določevanjem suhega ostanka ali vsebnosti vode
SIST EN 16179 (en)	Blato, obdelani biološki odpadki in tla – Navodilo za pripravo vzorcev
SIST EN ISO 5667-15 (en)	Kakovost vode – Vzorčenje – 15. del: Navodilo za konzerviranje in ravnanje z blatom in vzorci sedimenta (ISO 5667-15)
SIST EN ISO 16720 (en)	Kakovost tal – Priprava vzorcev za analizo z liofilizacijo (ISO 16720)
SIST EN ISO 22892 (en)	Kakovost tal – Smernice za identifikacijo ciljnih spojin s plinsko kromatografijo in masno spektrometrijo (ISO 22892)
SIST ISO 8466-1 (en)	Kakovost vode – Umerjanje in vrednotenje analitskih metod in določitev delovnih karakteristik – 1. del: Statistično vrednotenje linearne umerjalne funkcije

## IZRAZI IN DEFINICIJE

V tem dokumentu se uporabljajo naslednji izrazi in definicije:

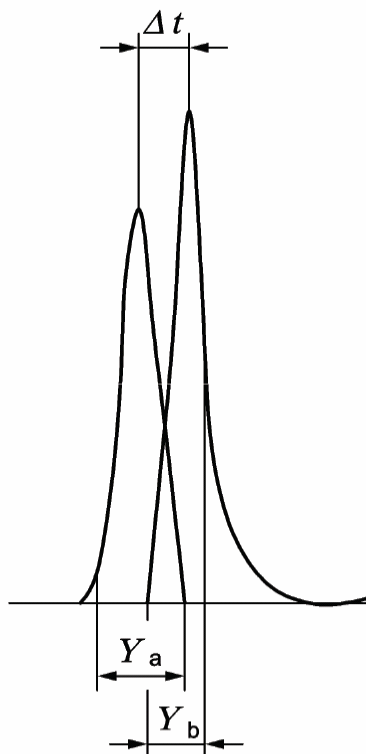
### 3.1

#### kritični par

par kongenerjev, ki bodo ločeni po vnaprej določeni stopnji (npr.  $R = 0,5$ ), s čimer se zagotovi, da kromatografsko ločevanje izpolnjuje minimalna merila kakovosti

[VIR: EN 15308:2008, 3.6]

OPOMBA 1: Glej sliko 1.



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**Legenda:**

$\Delta t$  razlika v retenzijskem času dveh vrhov a in b v sekundah (s)

$Y_a$  širina vrha na bazni liniji vrha a v sekundah (s)

$Y_b$  širina vrha na bazni liniji vrha b v sekundah (s)

**Slika 1: Primer kromatograma za kritični par**

Naslednji definiciji sta opisani v SIST EN 16167, Blato, obdelani biološki odpadki in tla – Določevanje polikloriranih bifenilov (PCB) s plinsko kromatografijo z masno selektivno detekcijo (GC/MS) in s plinsko kromatografijo z detekcijo z zajetjem elektronov (GC/ECD):

**3.2**

**kongener**

element iste vrste, razreda ali skupine kemikalij, na primer vsak od 209 predstavnikov PCB

OPOMBA: Številke kongenerjev po IUPAC so za lažjo identifikacijo in ne predstavljajo zaporedja kromatografskih eluatov.

[VIR: EN 15308:2008, 3.2]

**3.3**

**poliklorirani bifeniil**

**PCB**

bifeniil, substituiran z enim do desetimi atomi klora

[VIR: EN 15308:2008, 3.1]

**OSNOVA ZA IZDAJO TEHNIČNE SPECIFIKACIJE**

- privzem tehnične specifikacije CEN/TS 16181:2013

**OPOMBE**

- Povsod, kjer se v besedilu tehnične specifikacije uporablja izraz “evropska tehnična specifikacija”, v SIST-TS CEN/TS 16181:2013 to pomeni “slovenska tehnična specifikacija”.
- Nacionalni uvod in nacionalni predgovor nista sestavni del te tehnične specifikacije.
- Ta nacionalni dokument je istoveten s CEN/TS 16181:2013 in je objavljen z dovoljenjem

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English Version

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This Technical Specification (CEN/TS) was approved by CEN on 16 July 2012 for provisional application.

The period of validity of this CEN/TS is limited initially to three years. After two years the members of CEN will be requested to submit their comments, particularly on the question whether the CEN/TS can be converted into a European Standard.

CEN members are required to announce the existence of this CEN/TS in the same way as for an EN and to make the CEN/TS available promptly at national level in an appropriate form. It is permissible to keep conflicting national standards in force (in parallel to the CEN/TS) until the final decision about the possible conversion of the CEN/TS into an EN is reached.

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

**CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels**

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## **Foreword**

This document (CEN/TS 16181:2013) 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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association.

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, treated biowaste and soil as far as this is technically feasible.

According to the CEN-CENELEC Internal Regulations, the national standards organisations of the following countries are bound to announce this Technical Specification: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

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## 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, pretreatment, 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 EN 16167).

This document is the result of a desk study "Horizontal Technical Specification 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 Technical Specification is applicable and validated for several types of matrices as indicated in Table 1 (see also Annex A for the results of the validation).

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**Table 1 — Matrices for which this Technical Specification is applicable and validated**

Matrix	Materials used for validation
Sludge	Municipal sludge
Biowaste	Fresh compost

**WARNING —** Persons using this Technical Specification should be familiar with usual laboratory practice. This Technical Specification 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 Technical Specification be carried out by suitably trained staff.

## 1 Scope

This Technical Specification specifies the quantitative determination of 16 polycyclic aromatic hydrocarbons (PAH) (see Table 2) in sludge, soil and treated biowaste using GC-MS and HPLC-UV-DAD/FLD covering a wide range of PAH contamination levels (see also Annex B).

When using fluorescence detection, acenaphthylene cannot be measured.

**Table 2 — Polycyclic aromatic hydrocarbons  
which can be analysed using this Technical Specification**

Target analyte	CAS-RN <sup>a</sup>
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

<sup>a</sup> 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.

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

EN 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.

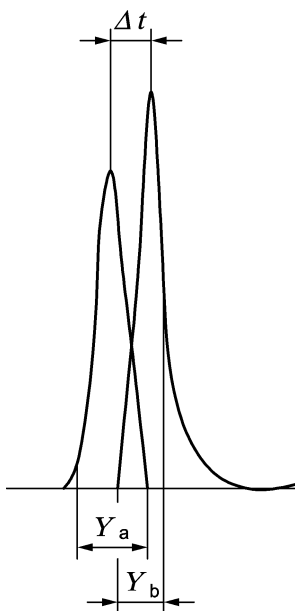
### 3.1

#### critical pair

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

[SOURCE: EN 15308:2008, 3.6]

Note 1 to entry: See Figure 1.



### Key

$\Delta t$  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

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## 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 incomplete 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 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. 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 benz(*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 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 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 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 with by a broad toluene peak.

Separation between dibenz(*a,h*)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 with 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 the 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.

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

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