

VEE KVALITEET. MITMETE POLÜTSÜKLILISTE
AROMAATSETE SÜSIVESINIKE (PAH) MÄÄRAMINE VEE
KOGUPROOVIDES, KASUTADES TAHKE FAASI
EKSTRAKTSIOONI (SPE) JA GAASIKROMATOGRAAFIAT
MASSISPEKTROMEETRILISE DETEKTEERIMISEGA
(GC-MS)

Water quality - Determination of selected polycyclic
aromatic hydrocarbons (PAH) in whole water samples -
Method using solid phase extraction (SPE) with
SPE-disks combined with gas chromatography mass
spectrometry (GC-MS)

EESTI STANDARDI EESSÕNA

NATIONAL FOREWORD

See Eesti standard EVS-EN 16691:2015 sisaldab Euroopa standardi EN 16691:2015 ingliskeelset teksti.	This Estonian standard EVS-EN 16691:2015 consists of the English text of the European standard EN 16691:2015.
Standard on jõustunud sellekohase teate avaldamisega EVS Teatajas.	This standard has been endorsed with a notification published in the official bulletin of the Estonian Centre for Standardisation.
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English Version

Water quality - Determination of selected polycyclic aromatic hydrocarbons (PAH) in whole water samples - Method using solid phase extraction (SPE) with SPE-disks combined with gas chromatography mass spectrometry (GC-MS)

Qualité de l'eau - Dosage des hydrocarbures aromatiques polycycliques (HAP) sélectionnés dans des échantillons d'eau totale - Méthode par extraction en phase solide (SPE) avec disques SPE, avec couplage chromatographie en phase gazeuse-spectrométrie de masse (CG-SM)

Wasserbeschaffenheit - Bestimmung von ausgewählten polycyclischen aromatischen Kohlenwasserstoffen (PAK) in Gesamtwasserproben - Verfahren mittels Festphasenextraktion (SPE) mit SPE-Disks in Verbindung mit Gaschromatographie Massenspektrometrie (GC-MS)

This European Standard was approved by CEN on 27 June 2015.

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European foreword

This document (EN 16691:2015) has been prepared by Technical Committee CEN/TC 230 “Water analysis”, the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by March 2016, and conflicting national standards shall be withdrawn at the latest by March 2016.

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

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Introduction

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.

Polycyclic aromatic hydrocarbons (PAH) are priority substances listed in Annex X of the EU Water Framework Directive (WFD, Directive 2000/60/EC) for which environmental quality standards (EQS) have been set at EU level for inland as well as other surface waters to protect the aquatic environment against chemical pollution (Directive 2008/105/EC). With the exception of metals, the EQSs are expressed as total concentrations in the whole water sample. Furthermore, analytical methods used in WFD monitoring need to meet certain requirements as regards the minimum limit of quantification and the maximum tolerable measurement uncertainty (Directive 2009/90/EC). So far, there is no standardized method available for the determination of PAH in whole water samples fulfilling those requirements. Hence, the European Commission mandated CEN to develop or improve standards in support of the implementation of the monitoring requirements of WFD.

Directive 2008/105/EC has been amended by Directive 2013/39/EU, however, this standard has been developed for the analysis of PAH as listed in Annex A of Directive 2008/105/EC.

Organic compounds as specified in the WFD occur in nearly all types of water. These substances are adsorbed on solids (sediments, suspended matter) as well as dissolved in the liquid phase. A large group of these compounds are polycyclic aromatic hydrocarbons (PAH). There are further standards for the analytical determination of PAH in water and waste water:

- EN ISO 17993 describes a method for the determination of 15 PAH by high performance liquid chromatography/UV detection in drinking water, ground water and surface water;
- ISO 7981-1 and ISO 7981-2 describe methods for the determination of 6 PAH by high performance thin layer chromatography or by high performance liquid chromatography in drinking water and ground water;
- ISO 28540 describes a method for at least 16 PAH using gas chromatography with mass spectrometric detection (GC-MS) in drinking water, ground water and surface water;
- ISO/TS 28581 describes a method for the determination of polycyclic hydrocarbons and pesticide residues in drinking water, ground water surface water and waste water.

1 Scope

This European Standard specifies a method for the determination of 7 polycyclic aromatic hydrocarbons (PAH) in whole water samples listed in Table 1. The method uses solid-phase disk extraction with SPE-disks followed by gas chromatography-mass spectrometry (GC-MS). It is applicable to the analysis of PAHs in surface water containing suspended particulate matter (SPM) up to 500 mg/l (whole water samples), drinking water and groundwater.

The lower and upper limit of the working range depends on the matrix, on the specific compound to be analyzed and on the sensitivity of the mass spectrometric detection unit. The limit of quantification (LOQ) determined in the validation is given in Table 1. The upper limit of the working range is approximately 2 000 ng/l.

This method is, with some modifications suitable for the analysis of waste water. This method is applicable to other PAH¹⁾, provided the method is validated for each PAH.

Table 1 — Polycyclic aromatic hydrocarbons (PAH) determined by this method

Substance	Molecular formula	Molar mass g/mol	EC number ^a	CAS-RN ^b	LOQ ^c ng/l
anthracene	C ₁₄ H ₁₀	178,23	204-371-1	120-12-7	0,24
fluoranthene	C ₁₆ H ₁₀	202,26	205-912-4	206-44-0	2,1
benzo[b]fluoranthene	C ₂₀ H ₁₂	252,32	205-911-9	205-99-2	0,56
benzo[k]fluoranthene	C ₂₀ H ₁₂	252,32	205-916-6	207-08-9	0,44
benzo[a]pyrene	C ₂₀ H ₁₂	252,32	200-028-5	50-32-8	0,33
benzo[ghi]perylene	C ₂₂ H ₁₂	276,34	205-883-8	191-24-2	0,44
indeno[1,2,3-cd]pyrene	C ₂₂ H ₁₂	276,34	205-893-2	193-39-5	0,42
^a EC Number: European inventory of existing commercial substances (EINECS) or European list of notified chemical substances (ELINCS). ^b CAS-RN: Chemical Abstracts Service Registry Number. ^c For the determination of the LOQ the procedure given in NEN 7777+C1:2012 [12] was used.					

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 ISO 1042, *Laboratory glassware - One-mark volumetric flasks (ISO 1042)*

EN ISO 3696, *Water for analytical laboratory use - Specification and test methods (ISO 3696)*

EN ISO 5667-1, *Water quality - Sampling - Part 1: Guidance on the design of sampling programmes and sampling techniques (ISO 5667-1)*

1) During the inter-laboratory validation trial the method was tested for all 16 EPA PAH (see Annex B).

EN ISO 5667-3, *Water quality - Sampling - Part 3: Preservation and handling of water samples (ISO 5667-3)*

3 Principle

PAH (see Table 1) present in the whole water sample are extracted by liquid-solid extraction using an adsorption disk. An internal standard mixture is added to the sample prior to extraction. The extract is concentrated by evaporation, and the residue is dissolved in a solvent appropriate for clean-up or GC-analysis. The extract is analyzed by gas chromatography separation with a low resolution mass spectrometry detection using electron impact (EI) ionization mode (6.4). The concentration of the component is calculated using calibration lines (see Clause 9) and internal standards added before extraction with a correction for recovery, final volume and detector response.

If necessary, extracts (of surface water samples) can be cleaned by column chromatography prior to analysis. (see Annex D). Prior to injection, an injection standard is added to each extract, and an aliquot of the extract is injected into the gas chromatograph.

PAH are separated on a suitable fused silica capillary column (6.5) with an efficient separation e. g. coated with a film of cross-linked non-polar polysiloxane or slightly polar modified polysiloxane. The column shall be suitable for separating benzo[a]pyrene and benzo[e]pyrene. Identification and quantification is performed by means of mass spectrometry using electron impact ionization (EI) (6.4).

4 Interferences

4.1 Interferences with sampling, extraction and concentration

Use sampling containers of materials (6.1) that do not affect the analyte content during the contact time, preferably of stainless steel or glass. Avoid plastics and organic materials other than polytetrafluoroethene (PTFE) during sampling, sample storage at $(3 \pm 2)^{\circ}\text{C}$ or extraction.

If automatic samplers are used, avoid the use of silicone or rubber material for the tubes. If these materials are present, ensure that the contact time is minimized. Rinse the sampling line with the water to be sampled before taking the test sample. EN ISO 5667-1 and EN ISO 5667-3 provide guidance. Storage temperature is at $(3 \pm 2)^{\circ}\text{C}$. For sampling and sample preservation see Clause 7. During storage of the test samples, losses of components may occur due to adsorption on the walls of the containers. The extent of the losses may depend on the storage time.

Commercially available solid-phase extraction disks (SPE-disks) differ frequently in quality. Variations in the selectivity of the materials also frequently occur from batch to batch, thus possibly causing significant deviations in extraction yield. This does not basically impair their suitability, apart from a resulting higher detection limit for individual substances. To ensure that the measuring results show high trueness and precision, use materials of one batch for both measurement and calibration. Avoid major fluctuations in the extraction times and elution procedures within one sample sequence when analysing the samples.

4.2 Interferences with GC

Substances with similar retention times and masses as the target PAH may lead to interferences and overlapping or incompletely resolved peaks in the chromatogram. Depending on their intensity those co-elutents can affect the trueness of the analysis.

A chromatographic resolution of $R > 0,8$ is required for anthracene and phenanthrene (m/z 178) and benzo[a]pyrene and benzo[e]pyrene (m/z 252). If the criterion cannot be reached, a suitable capillary column shall be chosen, capable to meet the required resolution.