SLOVENSKI STANDARD
SIST EN 16691:2015

01-december-2015

Kakovost vode - Določevanje policikličnih aromatskih ogljikovodikov (PAH) v celotnem vzorcu vode z ekstrakcijo tekoče-trdno v kombinaciji s plinsko kromatografijo/masno spektrometrijo (GC/MS)

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

Wasserbeschaffenheit - Bestimmung von polycyclischen aromatischen Kohlenwasserstoffen (PAK) in Gesamtwasserproben mittels Flüssig/Fest-Extraktion in Verbindung mit Gaschromatographie-Massenspektrometrie (GC-MS)

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

Ta slovenski standard je istoveten z: **EN 16691:2015**

ICS:

13.060.50	Preiskava vode na kemične snovi	Examination of water for chemical substances

SIST EN 16691:2015 **en,fr,de**

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 16691

September 2015

ICS 13.060.50

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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COMITÉ EUROPÉEN DE NORMALISATION
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Contents

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of an identical text or by endorsement, at the latest by March 2016, and conflicting national standards shall be withdrawn at the latest by March 2016.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 PAH[1], 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)*

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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 ± 2)°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 ± 2)°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-eluents can affect the trueness of the analysis.

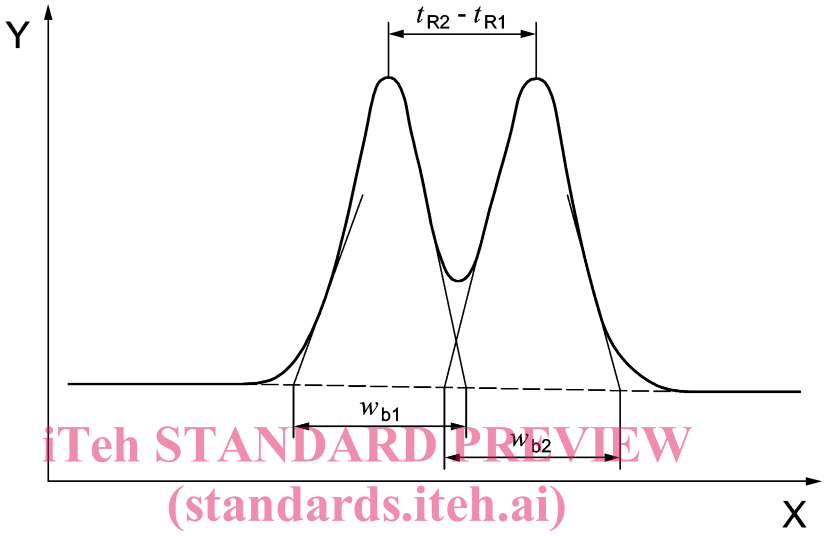
A chromatographic resolution of $R > 0{,}8$ is required for anthracene and phenanthrene (m/z 178) and benzo[*a*]pyrene and benzo[*e*]pyrene (m/z 252) . If the criterion cannot be reached, a suitable capillary column shall be chosen, capable to meet the required resolution.

A chromatographic resolution of $R > 0{,}8$ is required for benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene (*m/z* 252). If the criterion cannot be reached for benzo[*j*]fluoranthene, the sum of the co-eluting PAH shall be given in the test report.

Co-eluting mass fragments of dibenzo[*a,h*]anthracene und dibenzo[*a,c*]anthracene (*m/z* 276) may lead to interferences with indeno[1,2,3-*cd*]pyrene.

The resolution shall be assessed if adjustments in the chromatographic system have been made which may affect the resolution, e. g. shortening of the separation column, installation of a new column.

The chromatographic resolution is calculated according to Figure 1 and Formula (1).



Key:

X	time
Y	intensity
t_{R1}, t_{R2}	retention time of eluting substances 1 and 2 in seconds (s)
w_{b1}, w_{b2}	peak width at the base of each peak in seconds (s)

Figure 1 — Resolution of chromatographic peaks

$$R = 2\frac{(t_{R2} - t_{R1})}{w_{b1} + w_{b2}} \qquad (1)$$

where

R	is the resolution;
t_{R1}, t_{R2}	Retention time of eluting substances 1 and 2 in seconds (s);
w_{b1}, w_{b2}	peak width at the base of each peak in seconds (s).

5 Reagents

The reagents shall be free from impurities possibly interfering with the GC-MS analysis.

Use solvents and reagents of sufficient purity, i.e. with negligibly low impurities compared with the concentration of analytes to be determined. As reagents use, as far as available, “residual grade”, “picograde” or better in order to obtain clean blanks. Check blanks regularly and establish proper charge control. If necessary, apply additional cleaning steps.

5.1 Water, complying to grade 1 according to EN ISO 3696, or equivalent.

5.2 Operating gases for the gas chromatography mass spectrometry, of high purity and according to the manufacturer's specifications.

5.3 Nitrogen of high purity, i.e. minimum 99,996 % by volume, for concentration by evaporation.

5.4 Solvents for extraction, chromatography and preparation of reference solutions.

A variety of solvents may be used depending on the procedural step and the availability of commercial stock solutions, e. g.

- acetone, C_3H_6O, (boiling point: 56 °C);
- dichloromethane, CH_2Cl_2, (boiling point: 39,7 °C);
- toluene, C_7H_8, (boiling point: 111 °C);
- *iso*-hexane, C_6H_{14}, (boiling point: 60 °C).

5.5 Sodium sulfate, Na_2SO_4, anhydrous, pre-cleaned by heating to 500 °C for 4 h or free of interfering compounds. Store the dried sodium sulfate in an Erlenmeyer with a glass stopper (6.12) in the desiccator (6.11). The shelf life is 6 months.

5.6 Silica, average particle size approximately 40 µm, heated at 450 °C for 3 h and stored in a desiccator to ensure maximum activity.

5.7 Stock solutions:

For the shelf life of the stock solutions see analysis certificate of the stock solution.

5.7.1 Stock solution of internal standards (deuterated PAH standards), see Table 2[2].

^{13}C-isotopically labelled PAH standards may also be used as internal standards.

5.7.2 Stock solution of the 7 target substances (native reference PAH standards), see Table 2.

5.7.3 Stock solution injection standard

1,2,3,4-Tetrachloronaphthalene (CAS-RN 20020-02-4) or any other suitable standard: 1 000 mg/l in e. g. dichloromethane.

Some of the stock solutions may crystallize if they are stored for a long period of time in the freezer. In this case bring the solution, before use, to room temperature and place it in an ultrasonic bath for approximately 10 min.

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2) PAH stock solutions are commercially available. Examples are for instance CIL ES-2528 d-PAH cocktail: 100 mg/l in benzene-d6 and NIST SRM 1647e: 1 mg/l to 20 mg/l in acetonitrile. These examples are given only as information for the users of this European Standard and do not constitute an endorsement by CEN of these products.

5.8 Standards:

5.8.1 **Native reference substances** and deuterated internal standards (see Table 2):

For all 7 PAH deuterated internal standards are used. The deuterated internal standards are added to the sample to be extracted and are therefore dissolved in a water soluble solvent e. g. acetone (5.4).

Table 2 — Native and deuterated PAH

Native reference substances	Deuterated internal standard substances	CAS-RN (deuterated substances)
anthracene	anthracene-d10	1719–06–8
fluoranthene	fluoranthene-d10	93951–69–0
benzo[*b*]fluoranthene	benzo[*b*]fluoranthene-d12	93951–98–5
benzo[*k*]fluoranthene	benzo[*k*]fluoranthene-d12	93952–01–3
benzo[*a*]pyrene	benzo[*a*]pyrene-d12	63466–71–7
indeno[1,2,3-*cd*]pyrene	indeno[1,2,3-*cd*]pyrene-d12	203578–33–0
benzo[*g,h,i*]perylene	benzo[*g,h,i*]perylene-d12	93951–66–7

5.8.2 Internal standard

Prepare a solution of deuterated PAH internal standards by diluting the stock solution (5.7.1) in an appropriate solvent with a final mass concentration of 5 µg/ml (see Annex C, Table C.1).

5.8.3 Injection standard

Prepare a solution of 1,2,3,4-tetrachloronapthalene by diluting the stock solution (5.7.3) in toluene (5.4) with a final mass concentration of 10 µg/ml (see Annex C, Table C.2).

This standard is added to a sample before injection into the GC-MS apparatus, to monitor variability of instrument response and to calculate internal standard recovery

5.8.4 Calibration standard

Prepare calibration standard solutions for at least five concentration levels (e. g. CS1 to CS5 as given in Annex C) by diluting the deuterated PAH internal standard solution (5.8.2), the native PAH solution (5.7.2) and the injection standard 1,2,3,4-tetrachloronaphthalene (5.7.3) in toluene (5.4) with final mass concentrations of native PAH from 1 ng/ml to 2 000 ng/ml (see Annex C). These calibration standards are also used for the determination of retention times of the native and deuterated PAH, the Relative Response Factors (*RRF*) and the recovery of the internal standards.

6 Apparatus

Equipment or parts of it which have contact with the water sample or its extract shall be free from residues causing interferences. It is recommended to clean all glassware, for example, by rinsing with detergent and hot water, and drying for about 15 min to 30 min at about 120 °C. After cooling the glassware can be rinsed with acetone (5.4), sealed and stored in a clean environment.

It is preferable not to re-use glassware that has been in contact with samples with high concentration of PAH. Glassware can be re-used as long as an effective method of cleaning has been demonstrated.

6.1 Sample containers, preferably of stainless steel or brown/green glass narrow-necked, flat-bottomed, 1 000 ml, with PTFE cap liner. Avoid plastics and organic materials other than polytetrafluoroethene (PTFE).

6.2 Microlitre syringes, e. g. 10 µl, 100 µl and 1 000 µl.

6.3 Glass autosampler vials, brown glass, capacity e. g. 2 ml, with inert cap and PTFE-coated septum.

6.4 Capillary gas chromatograph with mass spectrometric detector (GC-MS), using EI-ionization mode, gas supply in accordance with the respective manufacturer's instructions.

6.5 Capillary column, high resolution, low bleeding, for gas chromatography (see 4.2 for requirements and Annex A for an example).

6.6 One-mark volumetric flasks, according to EN ISO 1042, class A.

6.7 Pasteur pipettes.

6.8 Molecular sieve beads, pore diameter 0,4 nm.

6.9 Vacuum device for solid-phase extraction, extraction box or automated workstation for solid-phase extraction.

6.10 Solid-phase extraction disk, inner diameter between 40 mm and 60 mm packed with an appropriate reversed phase adsorbent material (see Annex E for examples).

6.11 Desiccator.

6.12 Erlenmeyer with glass stopper.

6.13 Equipment for concentrating the eluates by evaporation, e. g. rotary evaporator, adjustable for constant vacuum and with a temperature-controlled water bath, or stripping equipment using nitrogen gas.

6.14 Glass bottles, brown/green glass, narrow-necked, flat-bottomed, 1 000 ml, with PTFE cap liner.

6.15 Balance, with an accuracy of ± 0,1 g.

6.16 Glass wool, rinsed with *iso*-hexane (5.4).

7 Sampling

For sampling, use thoroughly cleaned, flat bottomed sample containers (6.1).

Preservation and handing of the sample can be found in EN ISO 5667-3 Store the sample at (3 ± 2)°C, protected from light, until the extraction is carried out.

Ensure that the extraction is carried out within the maximum preservation time, as specified in EN ISO 5667-3, to avoid losses. It is generally recommended to carry out the extraction as soon as practicable to minimize potential adsorption to the glass wall which could be a potential interference if glassware is re-used.