
**Water quality — Determination of
16 polycyclic aromatic hydrocarbons
(PAH) in water — Method using gas
chromatography with mass spectrometric
detection (GC-MS)**

*Qualité de l'eau — Détermination de 16 hydrocarbures aromatiques
polycycliques (HAP) dans l'eau — Méthode par chromatographie en
phase gazeuse avec détection par spectrométrie de masse (CG-SM)*
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Published in Switzerland

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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

ISO 28540 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

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Introduction

Polycyclic aromatic hydrocarbons (PAH) occur in nearly all types of water, these substances are adsorbed on solids (sediments, suspended matter) as well as dissolved in the liquid phase.

ISO 17993^[7] specifies methods for the determination of 15 PAH by high performance liquid chromatography in drinking water, ground water, and surface water.

ISO 7981-1^[3] and ISO 7981-2^[4] specify 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.

This International Standard 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.

Some PAH are known or suspected to cause cancer. Maximum acceptable levels have been set in a number of countries. For instance, the European Council Directive 98/83/EC on the quality of water intended for human consumption (Reference [10]) set the maximum acceptable level for benzo[*a*]pyrene at 0,010 µg/l, and for the sum of four specified PAH (benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*ghi*]perylene, indeno[1,2,3-*cd*]pyrene) at 0,100 µg/l.

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Water quality — Determination of 16 polycyclic aromatic hydrocarbons (PAH) in water — Method using gas chromatography with mass spectrometric detection (GC-MS)

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This 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 International Standard be carried out by suitably trained staff.

1 Scope

This International Standard specifies a method for the determination of at least 16 selected PAH (see Table 1) in drinking water and ground water in mass concentrations above 0,005 µg/l and in surface water in mass concentrations above 0,01 µg/l (for each individual compound).

This International Standard can be used for samples containing up to 150 mg/l of suspended matter.

This method is, with some modification, also suitable for the analysis of waste water. It is possible that this method is applicable to other PAH, provided the method is validated for each case.

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.

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

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

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*

3 Terms and definitions

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

3.1

analyte

substance to be determined

[ISO 15089:2000^[5], 3.2]

NOTE Substances determinable by this International Standard are listed in Table 1.

3.2 calibration solution
solution prepared from a secondary standard and/or stock solutions and used to calibrate the response of the instrument with respect to analyte concentration

[ISO 18073:2004^[8], 3.1.2]

3.3 GC-MS determination diagnostic ion
selected fragment or molecular ion of the target compound with the highest possible specificity

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

NOTE In this International Standard, the injection standard mixture contains an isotopically labelled PAH.

3.5 internal standard
isotopically labelled PAH or PAH unlikely to be present in the sample, added to samples prior to extraction, against which the concentrations of native substances are calculated

3.6 selected ion monitoring/recording mode SIM/SIR
measuring the intensity of selected diagnostic ions only

NOTE Adapted from ISO 22892:2006^[9], 3.8.

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4 Principle

The PAH (see Table 1) present in the aqueous sample are extracted from the water sample by liquid-liquid extraction with hexane. An internal standard mixture is added to the sample prior to extraction. The extract is concentrated by evaporation, and the residue taken up in a solvent appropriate for clean-up or GC analysis.

NOTE 1 Other volatile solvents can be used as well if it is proven that there is equal or better recovery (recovery mass fraction between 70 % and 110 %).

The liquid-liquid extraction method shall not be used with samples containing more than 150 mg/l of suspended matter.


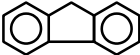


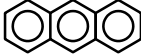
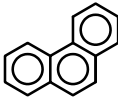

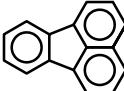
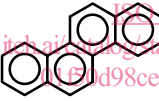
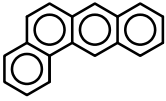
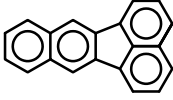
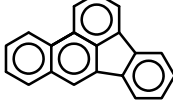
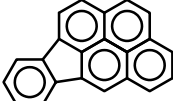
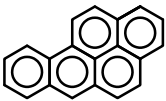

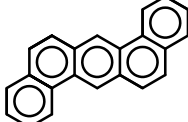
WARNING — The use of this International Standard may involve hazardous materials, operations and equipment. This International Standard does not purport to address all the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

NOTE 2 For samples that contain more than 150 mg/l suspended matter the procedure described in ISO 17858:2007^[6], 4.1, 4.2 and 4.3, can be used.

If necessary, extracts of surface water samples can be cleaned by column chromatography prior to analysis. Prior to injection, injection standards are 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, coated with a film of cross-linked non-polar polysiloxane or slightly polar modified polysiloxane with an efficient separation. 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).

Table 1 — Polycyclic aromatic hydrocarbons determinable by this International Standard

Name Chemical formula Molar mass % carbon CAS number	Structure	Name Chemical formula Molar mass % carbon CAS number	Structure
Naphthalene C ₁₀ H ₈ 128,17 g/mol 93,75 % C 91-20-3		Fluorene C ₁₃ H ₁₀ 166,22 g/mol 93,59 % C 86-73-7	
Acenaphthylene C ₁₂ H ₈ 152,20 g/mol 94,6 % C 208-96-8		Acenaphthene C ₁₂ H ₁₀ 154,21 g/mol 93,05 % C 83-32-9	
Anthracene C ₁₄ H ₁₀ 178,23 g/mol 94,05 % C 120-12-7		Phenanthrene C ₁₄ H ₁₀ 178,23 g/mol 94,05 % C 85-01-8	
Pyrene C ₁₆ H ₁₀ 202,26 g/mol 95,0 % C 129-00-0		Fluoranthene C ₁₆ H ₁₀ 202,26 g/mol 95,0 % C 206-44-0	
Chrysene C ₁₈ H ₁₂ 228,29 g/mol 94,45 % C 218-01-9		Benzo[a]anthracene C ₁₈ H ₁₂ 228,29 g/mol 94,45 % C 56-55-3	
Benzo[k]fluoranthene ^a C ₂₀ H ₁₂ 252,32 g/mol 95,2 % C 207-08-9		Benzo[b]fluoranthene ^a C ₂₀ H ₁₂ 252,32 g/mol 95,2 % C 205-99-2	
Indeno[1,2,3-cd]pyrene ^a C ₂₂ H ₁₂ 276,34 g/mol 95,6 % C 193-39-5		Benzo[a]pyrene ^a C ₂₀ H ₁₂ 252,32 g/mol 95,2 % C 50-32-8	
Benzo[ghi]perylene ^a C ₂₂ H ₁₂ 276,34 g/mol 95,6 % C 191-24-2		Dibenzo[a,h]anthracene ^a C ₂₂ H ₁₄ 278,35 g/mol 94,7 % C 53-70-3	

^a Compound specified by Council Directive 98/93/EC (Reference [10]).

5 Interferences

5.1 Interferences with sampling, extraction, and concentration

Use sampling containers of materials that do not affect the analyte content during the contact time (preferably of stainless steel or glass). Avoid plastics and other organic materials during sampling, sample storage or extraction. Care should be taken when using surfactants for cleaning sample containers, because they may lead to the formation of emulsions during liquid-liquid 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. Use ISO 5667-1 and ISO 5667-3 for guidance.

Keep the test samples away from direct sunlight and prolonged exposure to light. Store the samples in amber containers. Clear glass bottles are suitable as well, but then the samples shall be kept in a dark place.

During storage of the test samples, losses of PAH may occur due to adsorption on to the walls of the containers. The extent of the losses may depend on the storage time.

5.2 Interferences 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. Non-symmetrical peaks and peaks broader than the corresponding peaks of the reference substance suggest interferences.

Chromatographic separation between dibenzo[*a,h*]anthracene and indeno[1,2,3-*cd*]pyrene is most 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, the baseline corrected. Sufficient resolution (e.g. not less than $R = 0,8$) between the peaks of benzo[*b*]fluoranthene and benzo[*k*]fluoranthene as well as of benzo[*a*]pyrene and benzo[*e*]pyrene is to be set as quality criterion for the capillary column. Benzo[*j*]fluoranthene cannot be separated from benzo[*k*]fluoranthene and benzo[*b*]fluoranthene. It is possible that triphenylene is not completely separated from benzo[*a*]anthracene and chrysene. If this is the case, state this fact in the test report.

NOTE Benzo[*j*]fluoranthene, benzo[*e*]pyrene, and triphenylene are not part of the 16 target analytes.

6 Reagents

WARNING — The use of this International Standard may involve hazardous materials, operations and equipment. This International Standard does not purport to address all the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade, “for residue analysis” or “for GC analysis”, where appropriate, and distilled or demineralized water or water of equivalent purity. Otherwise, pay extra attention that each batch of solvents does not contain blank concentrations affecting the results.

6.1 Sodium thiosulfate pentahydrate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, for dechlorination.

6.2 Solvents.

6.2.1 Hexane, C_6H_{14} .

6.2.2 Acetonitrile, CH_3CN .

6.2.3 Acetone, C_3H_6O .

6.2.4 Decane, $C_{10}H_{22}$.

6.2.5 Isooctane, C_8H_{18} .

6.2.6 Dichloromethane, CH_2Cl_2 .

6.3 Sodium sulfate, Na_2SO_4 , anhydrous, precleaned by heating to 500 °C for 4 h or free of interfering compounds.

6.4 Gases.

6.4.1 Nitrogen, 99,999 % volume fraction, for the purpose of evaporating the extracts.

6.4.2 Helium, 99,999 % volume fraction, for gas chromatography.

6.5 Standards.

6.5.1 Reference substances (see Table 2) and internal standards.

Choose internal standards with physical and chemical properties (such as extraction behaviour, retention time) that are similar to those of the compounds to be analysed.

Use a minimum of three internal standards, e.g. three deuterated PAH, for evaluation of results (see Clauses 11 and 12). Verify the stability of the internal standards regularly. Table 2 contains native PAH and a number of deuterated PAH that can be used. The internal standards are added to the sample to be extracted and are therefore dissolved in a water-soluble solvent.

NOTE 1 ^{13}C isotopically labelled PAH standards can also be used as internal standards.

NOTE 2 Certified solutions of PAH and single solid PAH substances with certified purity are available from a limited number of suppliers¹⁾ or from other commercial providers.

Because of the dangerous nature of these substances, commercially available, preferably certified, standard solutions should be used. Skin contact should be avoided.

6.5.2 Injection standard.

Add an isotopically labelled non-polar substance to the final extract and to the calibration solutions (6.8) before GC-MS injection to check the recovery of the internal standards.

Prepare a stock solution of the injection standard in an appropriate solvent of mass concentration $\rho \approx 10 \mu\text{g/ml}$.

6.6 Single substance stock solutions.

Prepare solutions of the single substances (see Table 1) in an appropriate solvent, e.g. hexane (6.2.1) or acetonitrile (6.2.2), with mass concentration $\rho \approx 200 \mu\text{g/ml}$.

These solutions can be used for confirmation and identification of single PAH in the chromatogram.

1) The Institute for Reference Materials and Measurements (IRMM), Geel, Belgium, the National Institute of Science and Technology (NIST), Washington DC, USA, and the Cambridge Isotope Laboratory (CIL), Andover, MA, USA, are examples of suitable product suppliers. This information is given for the convenience of users of this International Standard and does not constitute an endorsement of these suppliers by ISO.

6.7 Multiple substance stock solution.

Dilute a sufficient volume (e.g. 5 ml) of the single substance stock solutions (6.6) in a one-mark volumetric flask (7.14, e.g. 100 ml) with an appropriate solvent, e.g. hexane (6.2.1) or acetonitrile (6.2.2), to prepare a solution of mass concentration $\rho \approx 10 \mu\text{g/ml}$.

Alternative commercially available (certified) combined and mixed solutions containing only one or some of the reference substances (see Table 1) at an appropriate mass concentration of the relevant single substance, e.g. 10 $\mu\text{g/ml}$ in an appropriate solvent, such as acetonitrile (6.2.2) or hexane (6.2.1), may be used.

The solutions 6.5 to 6.7 are stable for at least 1 year when stored in the dark at room temperature and protected from evaporation. Check the stability of the standard solution regularly. For that purpose, independent solutions for quality control shall be available within a laboratory.

Table 2 — Native PAH and deuterated PAH

PAH reference substances	Labelled internal standard substances deuterated PAH
Naphthalene (CAS No. 91-20-3)	Naphthalene-d8 (CAS No. 1146-65-2)
Acenaphthene (CAS No. 83-32-9)	Acenaphthene-d10 (CAS No. 15067-26-2)
Acenaphthylene (CAS No. 208-96-8)	Acenaphthylene-d8 (CAS No. 93951-97-4)
Fluorene (CAS No. 86-73-7)	Fluorene-d10 (CAS No. 81103-79-9)
Anthracene (CAS No. 120-12-7)	Anthracene-d10 (CAS No. 1719-06-8)
Phenanthrene (CAS No. 85-01-8)	Phenanthrene-d10 (CAS No. 1517-22-2)
Fluoranthene (CAS No. 206-44-0)	Fluoranthene-d10 (CAS No. 93951-69-0)
Pyrene (CAS No. 129-00-0)	Pyrene-d10 (CAS No. 1718-52-1)
Benzo[a]anthracene (CAS No. 56-55-3)	Benzo[a]anthracene-d12 (CAS No. 1718-53-2)
Chrysene (CAS.No. 218-01-9)	Chrysene-d12 (CAS No. 1719-03-5)
Benzo[b]fluoranthene (CAS No. 205-99-2)	Benzo[b]fluoranthene-d12 (CAS No. 93951-98-5)
Benzo[j]fluoranthene ^a (CAS No. 205-82-3)	
Triphenylene ^a (CAS No 217-59-4)	
Benzo[k]fluoranthene (CAS No. 207-08-9)	Benzo[k]fluoranthene-d12 (CAS No. 93952-01-3)
Benzo[a]pyrene (CAS No. 50-32-8)	Benzo[a]pyrene-d12 (CAS No. 63466-71-7)
Benzo[e]pyrene ^a (CAS No. 192-97-2)	
Indeno[1,2,3-cd]pyrene (CAS No. 193-39-5)	Indeno[1,2,3-cd]pyrene-d12 (CAS No. 203578-33-0)
Dibenzo[a,h]anthracene (CAS No. 53-70-3)	Dibenzo[a,h]anthracene-d14 (CAS No. 13250-98-1)
Benzo[ghi]perylene (CAS No. 191-24-2)	Benzo[ghi]perylene-d12 (CAS No. 93951-66-7)

^a Not one of the 16 target analytes; used only to check that resolution is sufficient.