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**Kakovost vode - Določevanje organoklornih pesticidov (OCP) v celotnem vzorcu vode z ekstrakcijo na trdni fazi (SPE) s SPE-diski v kombinaciji s plinsko kromatografijo/masno spektrometrijo (GC/MS)**

Water quality - Determination of organochlorine pesticides (OCP) in whole water samples using solid phase extraction (SPE) with SPE-disks combined with gas chromatography mass spectrometry (GC-MS)

Wasserbeschaffenheit - Bestimmung von Organochlorpestiziden (OCP) in Gesamtwasserproben mittels Festphasenextraktion (SPE) mit SPE-Scheiben in Verbindung mit Gaschromatographie-Massenspektrometrie (GC-MS)

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Qualité de l'eau - Dosage des pesticides organochlorés (POC) dans la totalité de l'échantillon d'eau par extraction en phase solide (EPS) avec disques EPS, avec couplage chromatographie en phase gazeuse-spectrométrie de masse (CG-SM)

**Ta slovenski standard je istoveten z: EN 16693:2015**

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

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## Water quality - Determination of organochlorine pesticides (OCP) 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 pesticides organochlorés (POC) dans la totalité de l'échantillon d'eau - Méthode par extraction en phase solide (SPE) avec disques SPE, avec couplage chromatographie en phase gazeuse - spectrométrie de masse (CG-SM)

Wasserbeschaffenheit - Bestimmung von Organochlorpestiziden (OCP) 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 16693:2015) 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of an identical text or by endorsement, at the latest by March 2016, and conflicting national standards shall be withdrawn at the latest by March 2016.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.

Organochlorine pesticides (OCP) 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 waters 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 European-wide standardized method available for the determination of OCP 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 OCP as listed in Annex A of Directive 2008/105/EC.

The priority substances list in Annex X of the WFD includes various OCPs such as alachlor, endosulfan, hexachlorobenzene, hexachlorocyclohexane isomers, pentachlorobenzene, aldrin, dieldrin, endrin, isodrin, DDT and its metabolites. Annual average environmental quality standards (AA-EQS) values for individual OCP range from 0,000 5 µg/l to 0,3 µg/l and are defined for the concentration in the whole water sample, including suspended particulate matter (SPM) present in the sample. As long as compounds such as OCP, in particular the larger molecular weight ones, sorb strongly to environmental solids, the fraction bound to particles may be substantial. Therefore it is important to be able to handle whole water samples within the analytical process. Identification and quantification of OCP at trace level concentrations often require both high sensitive chromatographic equipment and effective enrichment steps.

## 1 Scope

This European Standard specifies a method for the determination of selected organochlorine pesticides (OCP) (see Table 1), in water samples. The method uses solid-phase extraction with SPE-disks followed by gas chromatography-mass spectrometry (GC-MS). It is applicable to the analysis of OCPs in surface water containing suspended particulate matter (SPM) up to 500 mg/l (whole water samples), drinking water and groundwater. The lower 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. For compounds listed in Table 1 the limit of determination (LOQ) is at least 30 % of the corresponding AA-EQS value (0,000 15 µg/l to 0,1 µg/l) according to the requirements of the European Quality Standards Directive (Directive 2008/105/EC) for both inland surface waters and other surface waters.

This method may be used for the analysis of other OCPs not listed in Table 1 or other types of water. However, it is important to verify its applicability before use.

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Table 1 — Organochlorine pesticides (OCP) determined by this method

Substance	Molecular formula	Molar mass g/mol	EC Number <sup>a</sup>	CAS RN <sup>b</sup>
Alachlor	C <sub>14</sub> H <sub>20</sub> ClNO <sub>2</sub>	269,77	240-110-8	15972-60-8
<u>Cyclodiene pesticides:</u>				
Aldrin	C <sub>12</sub> H <sub>8</sub> Cl <sub>6</sub>	364,91	206-215-8	309-00-2
Dieldrin	C <sub>12</sub> H <sub>8</sub> Cl <sub>6</sub> O	380,91	200-484-5	60-57-1
Endrin	C <sub>12</sub> H <sub>8</sub> Cl <sub>6</sub> O	380,91	200-775-7	72-20-8
Isodrin	C <sub>12</sub> H <sub>8</sub> Cl <sub>6</sub>	364,91	207-366-2	465-73-6
<u>DDT-total:</u>				
op'-DDT	C <sub>14</sub> H <sub>9</sub> Cl <sub>5</sub>	354,49	212-332-5	789-02-6
pp'-DDT	C <sub>14</sub> H <sub>9</sub> Cl <sub>5</sub>	354,49	200-024-3	50-29-3
pp'-DDD	C <sub>14</sub> H <sub>9</sub> Cl <sub>4</sub>	320,04	200-783-0	72-54-8
pp'-DDE	C <sub>14</sub> H <sub>9</sub> Cl <sub>4</sub>	318,03	200-784-6	72-55-9
Hexachlorobenzene (HCB)	C <sub>6</sub> Cl <sub>6</sub>	284,80	204-273-9	118-74-1
Hexachlorobutadiene (HCBd)	C <sub>4</sub> Cl <sub>6</sub>	260,76	201-765-5	87-68-3
<u>Hexachlorocyclohexane <sup>c</sup>:</u>				
alpha-HCH	C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub>	290,83	206-270-8	319-84-6
beta-HCH	C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub>	290,83	206-271-3	319-85-7
delta-HCH	C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub>	290,83	206-272-9	319-86-8
gamma-HCH	C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub>	290,83	200-401-2	58-89-9
Pentachlorobenzene	C <sub>6</sub> HCl <sub>5</sub>	250,34	210-172-0	608-93-5
<u>Trichlorobenzene <sup>c</sup>:</u>				
1,2,3-TCB	C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub>	181,45	201-757-1	87-61-6
1,2,4-TCB	C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub>	181,45	204-428-0	120-82-1
1,3,5-TCB	C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub>	181,45	203-608-6	108-70-3
<u>Endosulfan <sup>c</sup>:</u>				
Endosulfan-I (alpha)	C <sub>9</sub> H <sub>6</sub> Cl <sub>6</sub> O <sub>3</sub> S	406,93	-	959-98-8
Endosulfan-II (beta)	C <sub>9</sub> H <sub>6</sub> Cl <sub>6</sub> O <sub>3</sub> S	406,93	-	33213-65-9
<sup>a</sup> EC Number: European inventory of existing commercial substances (EINECS) or European list of notified chemical substances (ELINCS). <sup>b</sup> CAS RN: Chemical Abstracts Service Registry Number. <sup>c</sup> Mixture of isomers.				



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

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

## 3 Principle

Organochlorine pesticides present in the whole water sample are extracted by means of solid-phase extraction using solid-phase extraction disks (SPE-disks). Samples shall not be filtered. An internal standard mixture is added to the sample prior to extraction. Extraction by SPE-disks is a fully automatable procedure. It includes a combined extraction of both the analytes dissolved in the liquid phase of the sample and those adsorbed to the suspended particulate matter. The latter is extracted within the elution step of the procedure.

The extract is concentrated by evaporation and the analytes are separated, identified and quantified by capillary gas chromatography with mass spectrometric detection (GC-MS) using electron impact (EI) ionization mode. The compounds endosulfan-I (alpha) and endosulfan-II (beta) may require additional efforts on either enlargement of sample enrichment and/or large volume injection (LVI) of sample extract. Enlargement of sample enrichment can be achieved by using 2 000 ml sample volume and/or an evaporation of solvent extracts down to a final volume of 0,2 ml or 0,1 ml.

## 4 Interferences

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### 4.1 Interferences with sampling and extraction

To avoid interferences, collect samples according to Clause 7. Sample containers shall consist of materials that do not alter the sample during the contact time. Plastics and other organic materials shall be avoided during sampling or sample storage.

Commercially available SPE-disks can differ frequently in quality. Variations in the selectivity of the materials can occur from batch to batch, and therefore might cause significant deviations in the extraction yield. This does not basically impair their suitability, apart from a resulting higher detection limit of individual substances. To ensure that the measuring results have a high accuracy 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 analyzing the samples.

Make sure that the disk is effectively dried. This can be achieved by using e.g. a vacuum device equipped with a device to dry a stream of nitrogen or air before it is applied to the disk. If the vacuum based automated or manually driven equipment uses ambient air from the laboratory environment, which often contains a certain degree of humidity, drying of the disk is, depending from the moisture content of the air, not effective and often results in a high amount of residual water in the disk (e.g. > 200 µl). Therefore additional drying of air before it is applied to the disk is required, e.g. by integration of a drying flask containing calcium chloride (5.9) or another drying agent (desiccant). This procedure results in very effectively dried disks with low remaining water (<10 µl per disk).

If the applied automated system is not able to process disk drying by using dry nitrogen or dry air, take out the disk for drying and continue, if appropriate, manually as described above.

Extending the drying time does not lead to efficiently dried SPE-disks. Avoid any prolongation of the recommended disk drying process (see 8.2), because this results in low recoveries for some of the

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medium volatile compounds (e.g. 1,2,3-TCB, 1,2,4-TCB and 1,3,5-TCB). The use of a labelled standard for TCBs is recommended.

Acetone is the recommended solvent for extraction and elution (see 8.2). Do not apply any solvent drying step on acetone. As long as the residual water in the disk after disk drying is, as described above, within the range of just a few  $\mu\text{l}$  per disk, there will no interferences occur in GC-MS analysis.

#### 4.2 Interferences with GC-MS

Interferences may be caused, e.g. by the injection system used or by inadequate separation of the analytes. Substances with similar retention times and producing similar masses compared with the analytes to be determined may interfere with the determination. These interferences may lead to incompletely resolved signals. Experienced operators, using the information given in the instrument manuals, may be able to minimize this type of interference. Regular checking of the chromatographic and spectrometric system is required to maintain adequate performance. Required system stability should be checked regularly using a GC standard.

### 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,  $\text{C}_3\text{H}_6\text{O}$  (boiling point: 56 °C),
- ethyl acetate,  $\text{C}_4\text{H}_8\text{O}_2$  (boiling point: 77 °C),
- *iso*-octane (2,2,4-trimethylpentane),  $\text{C}_8\text{H}_{18}$  (boiling point: 99 °C),
- cyclohexane,  $\text{C}_6\text{H}_{12}$  (boiling point: 81 °C),
- toluene,  $\text{C}_7\text{H}_8$  (boiling point: 111 °C).

**5.5 Sodium hydroxide solution**,  $w(\text{NaOH}) = 25$  % mass fraction.

**5.6 Hydrochloric acid**,  $w(\text{HCl}) = 25$  % mass fraction or **sulfuric acid**,  $w(\text{H}_2\text{SO}_4) = 12,5$  % mass fraction.

## 5.7 Internal standard

It is highly recommended to use a deuterium-labelled or  $^{13}\text{C}$ -enriched substance of those listed in Table 1 as internal standard. Examples for suitable internal standards are given in Annex D. For further information see 9.3.

Prepare stock solutions of individual internal standard substances in the same way as specified for individual reference substances (5.8.2) or use commercially available certified solutions of individual substances (e.g. in acetone). Prepare spiking solutions for spiking the samples (see 8.1) by further diluting the stock solutions with a water soluble solvent e.g. acetone (5.4).

## 5.8 Reference substances

### 5.8.1 General requirements

Reference substances (OCP, listed in Table 1) of defined concentration, suitable for the preparation of reference solutions used for gas chromatography and spiking of water samples for calibration of the total procedure (see 9.3) and calculation of the overall recovery (see 9.4).

### 5.8.2 Stock solutions of individual reference substances

For example, place 50 mg of a reference substance and/or the internal standard substances (5.7) into a 100 ml volumetric flask (6.2), dissolve in an appropriate solvent (5.4) and make up to the mark with the same solvent.

Store stock solutions at temperatures between 1 °C and 5 °C, protected from light. Stock solutions are stable for at least 12 months.

NOTE Deep freezing of stock solutions is also possible and commonly applied.

### 5.8.3 Multi-component stock solutions of individual reference substances

For example, transfer 1 ml of each of the solutions of the individual substances (5.8.2) into a 100 ml volumetric flask (6.2) and make up to the mark with solvent (5.4).

NOTE Alternatively, commercially available certified stock solutions of individual (or mixtures of several) reference substances in solvent (5.4) can be used for preparing multi-component stock solutions.

Store multi-component stock solutions at temperatures between 1 °C and 5 °C, protected from light. Multi-component stock solutions are stable for at least 6 months.

### 5.8.4 Multi-component reference solutions of reference substances

Prepare multi-component reference solutions of defined concentration suitable for multipoint calibration (working solution for GC-MS) or spiking of blank samples. Prepare solutions by dilution of the multi-component stock solutions (5.8.3) using an appropriate solvent (5.4).

Store multi-component reference solutions at temperatures between 1 °C and 5 °C, protected from light. Multi-component reference solutions are stable for at least 6 months.

**5.9 Calcium chloride,  $\text{CaCl}_2$ , for drying of air.**

## 6 Apparatus

Equipment or parts of it which have contact with the water sample or its extract shall be free from residues causing interferences. The use of vessels made of glass, stainless steel or polytetrafluoroethylene (PTFE) is recommended.

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- 6.1 Sample flasks**, e.g. brown glass, flat bottomed, with glass or PTFE coated stoppers, e.g. 1 000 ml or 2 000 ml.
- 6.2 Volumetric flasks**, capacity, e.g. 10 ml, 25 ml, 50 ml and 100 ml.
- 6.3 Single volume pipettes**, capacities between 1 ml and 50 ml.
- 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 Non-discriminating GC injector**, e.g. splitless mode of a split or splitless injection system or programmable temperature vaporizer (PTV) programmable for large volume injection (LVI).
- 6.6 Automatic sampler with option for large volume injection (LVI)**, including syringes for normal injection (e.g. 1  $\mu$ l and 2  $\mu$ l) and LVI (e.g. 10  $\mu$ l, 50  $\mu$ l and 100  $\mu$ l).
- 6.7 Capillary columns**, for gas chromatography (examples of chromatograms appear in Annex A). It is advantageous to use non-polar columns (e.g. low-bleed 5 %-phenylsiloxane column).
- 6.8 Solid-phase extraction disks (SPE-disks)**, wide inner diameter between 40 mm and 60 mm, packed with an appropriate reversed phase adsorbent material, e.g. C<sub>18</sub>-based or SDB-based adsorbent (for examples see Annex C).
- 6.9 Vacuum device for solid-phase extraction**, e.g. vacubox, extraction box or automated workstation for solid-phase extraction procedure capable for processing SPE-disks.
- 6.10 Equipment for concentrating the eluates by evaporation**, e.g. a rotary evaporator, adjustable for constant vacuum and with a temperature-controlled water bath, or stripping equipment using nitrogen gas.
- 6.11 Pasteur pipettes**.
- 6.12 pH-meter**, with electrodes.
- 6.13 Drying flask**.

## 7 Sampling

For sampling, use thoroughly cleaned sample flasks (6.1) (see EN ISO 5667-3). Fill the bottles completely with the water to be examined.

If storage is necessary, store the samples according to EN ISO 5667-3 at  $(3 \pm 2)$  °C, protected from light.

It is generally recommended to carry out the extraction as soon as practicable to minimize potential adsorption to the glass wall.

## 8 Procedure

### 8.1 Sample preparation and extraction

The pH value of the water sample only requires adjustment if it is below  $(5 \pm 0,2)$  or above  $(9 \pm 0,2)$ . In this case, adjust to pH  $(7 \pm 0,2)$  with hydrochloric acid (5.6), sulfuric acid (5.6) or sodium hydroxide solution (5.5).

In general, samples are examined without pre-treatment, e.g. suspended particulate matter is not removed prior to analysis. Do not filter the sample.