VEE KVALITEET. KLOORORGAANILISTE PESTITSIIDIDE (OCP) MÄÄRAMINE VEE KOGUPROOVIDES, KASUTADES TAHKE FAASI EKSTRAKTSIOONI (SPE) JA GAASIKROMATOGRAAFIAT MASSISPEKTROMEETRILISE DETEKTEERIMISEGA (GC-MS)

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)

EESTI STANDARDIKESKUS
ESTONIAN CENTRE FOR STANDARDISATION

EESTI STANDARDI EESSÕNA

NATIONAL FOREWORD

See Eesti standard EVS-EN 16693:2015 sisaldab Euroopa standardi EN 16693:2015 ingliskeelset teksti.	This Estonian standard EVS-EN 16693:2015 consists of the English text of the European standard EN 16693:2015.
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.
Euroopa standardimisorganisatsioonid on teinud Euroopa standardi rahvuslikele liikmetele kättesaadavaks 23.09.2015.	Date of Availability of the European standard is 23.09.2015.
Standard on kättesaadav Eesti Standardikeskusest.	The standard is available from the Estonian Centre for Standardisation.

Tagasisidet standardi sisu kohta on võimalik edastada, kasutades EVS-i veebilehel asuvat tagasiside vormi või saates e-kirja meiliaadressile standardiosakond@evs.ee.

ICS 13.060.50

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 16693

September 2015

ICS 13.060.50

English Version

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.

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

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

Ref. No. EN 16693:2015 E

Contents

Page

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.

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.

According to the CEN/CENELEC Internal Regulations, the national standards organisations of the following countries are bound to implement this European Standard: 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.

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.

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

Substance	Molecular formula	Molar mass g/mol	EC Number [a]	CAS RN [b]
Alachlor	$C_{14}H_{20}ClNO_2$	269,77	240–110–8	15972–60–8
Cyclodiene pesticides:				
Aldrin	$C_{12}H_8Cl_6$	364,91	206–215–8	309–00–2
Dieldrin	$C_{12}H_8Cl_6O$	380,91	200–484–5	60–57–1
Endrin	$C_{12}H_8Cl_6O$	380,91	200–775–7	72–20–8
Isodrin	$C_{12}H_8Cl_6$	364,91	207–366–2	465–73–6
DDT-total:				
op´-DDT	$C_{14}H_9Cl_5$	354,49	212–332–5	789–02–6
pp´-DDT	$C_{14}H_9Cl_5$	354,49	200–024–3	50–29–3
pp´-DDD	$C_{14}H_9Cl_4$	320,04	200–783–0	72–54–8
pp´-DDE	$C_{14}H_9Cl_4$	318,03	200–784–6	72–55–9
Hexachlorobenzene (HCB)	C_6Cl_6	284,80	204–273–9	118–74–1
Hexachlorobutadiene (HCBD)	C_4Cl_6	260,76	201–765–5	87–68–3
Hexachlorocyclohexane [c]:				
alpha-HCH	$C_6H_6Cl_6$	290,83	206–270–8	319–84–6
beta-HCH	$C_6H_6Cl_6$	290,83	206–271–3	319–85–7
delta-HCH	$C_6H_6Cl_6$	290,83	206–272–9	319–86–8
gamma-HCH	$C_6H_6Cl_6$	290,83	200–401–2	58–89–9
Pentachlorobenzene	C_6HCl_5	250,34	210–172–0	608–93–5
Trichlorobenzene [c]:				
1,2,3-TCB	$C_6H_3Cl_3$	181,45	201–757–1	87–61–6
1,2,4-TCB	$C_6H_3Cl_3$	181,45	204–428–0	120–82–1
1,3,5-TCB	$C_6H_3Cl_3$	181,45	203–608–6	108–70–3
Endosulfan [c]:				
Endosulfan-I (alpha)	$C_9H_6Cl_6O_3S$	406,93	–	959–98–8
Endosulfan-II (beta)	$C_9H_6Cl_6O_3S$	406,93	–	33213–65–9

[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] 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

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