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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)

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



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## 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of an identical text or by endorsement, at the latest by March 2016, and conflicting national standards shall be withdrawn at the latest by March 2016.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.

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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.

**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

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 µl 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, $C_3H_6O$ (boiling point: 56 °C),

— ethyl acetate, $C_4H_8O_2$ (boiling point: 77 °C),

— *iso*-octane (2,2,4-trimethylpentane), $C_8H_{18}$ (boiling point: 99 °C),

— cyclohexane, $C_6H_{12}$ (boiling point: 81 °C),

— toluene, $C_7H_8$ (boiling point: 111 °C).

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

**5.6 Hydrochloric acid**, $w(HCl)$ = 25 % mass fraction or **sulfuric acid,** $w(H_2SO_4)$ = 12,5 % mass fraction.

### 5.7 Internal standard

It is highly recommended to use a deuterium-labelled or $^{13}C$-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, $CaCl_2$, 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.

**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 µl and 2 µl) and LVI (e.g. 10 µl, 50 µl and 100 µl).

**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. $C_{18}$-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 ± 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 ± 0,2) or above (9 ± 0,2). In this case, adjust to pH (7 ± 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.

Large particles (e.g. leaves, little branches) should be removed using a sieve (screening gap 1 mm).

For the extraction process, add a precisely defined amount (between e.g. 50 µl to 100 µl) of the internal standard (5.7) dissolved in an appropriate solvent (water miscible solvent, e.g. ethyl acetate or acetone, see 5.4), to e.g. 1 000 ml of the whole water sample. Calculate the exact volume of the water sample by weighing the sample flask before extraction and after emptying.

## 8.2 Extraction by SPE-disks

For conditioning of SPE-disk add an amount of acetone (6 ml to 10 ml) and let it pass through the disk in about 20 s, e.g. using a vacuum device. Ensure that the adsorbent does not run dry.

Repeat this step once.

Add an amount of water (6 ml to 10 ml) and let it pass through the disk in about 20 s, e.g. using a vacuum device. Ensure that the adsorbent does not run dry.

Repeat this step once.

For sample loading and extraction of analytes dissolved in the water phase take, e.g. 1 000 ml of the sample to be examined (8.1) and pass it through the disk conditioned as described above at a flow rate of about 50 ml/min.

To transfer particulate matter to the disk that might have remained in the bottle, rinse the sample reservoir (e.g. the sample bottle) twice with e.g. 9 ml of water and pass it through the disk as described above.

Effectively dry the disk using e.g. a vacuum device supported by a stream of dry nitrogen or dry air in front of the disk for about 15 min. When using ambient laboratory air to dry the disks, additional drying of air before applying it to the disk is necessary (see 4.1). This can be achieved e.g. by integration of a drying flask (6.13) containing calcium chloride (5.9) or another drying agent.

NOTE Drying of ambient laboratory air prevents reabsorption of moisture by the disk from the air sucked in.

Add an amount of acetone (6 ml to 10 ml), allowing 5 min for the solvent to soak. Collect the eluate by passing it through the disk in about 20 s.

Add an amount of acetone (4 ml to 8 ml), allowing 5 min for the solvent to soak. Collect the eluate by passing it through the disk in about 20 s.

Repeat the last step twice.

Collect the combined eluates in a glass vessel. No extract-drying step is required. Carefully evaporate the solvent and concentrate the eluate as specified in 8.3.

Other solvents may be used for extraction and elution. However, their suitability should be established in preliminary tests with blank water samples spiked with certified sediment up to 500 mg/l and processed according to Clause 8. Recoveries for each substance under investigation should be ≥ 70 %.

## 8.3 Solvent concentrating

Concentrate the SPE eluate (8.2) carefully to a final volume of about 0,5 ml to 1,0 ml (e.g. in a gentle stream of nitrogen or on a rotary evaporator under reduced pressure). To achieve higher sensitivity, solvent evaporation can be continued to smaller final volumes (e.g. 0,1 ml). The temperature of the eluate during concentration should be kept below 20 °C.

If a solvent change is planned, add e.g. 1 ml of an appropriate solvent (e.g. toluene) prior to solvent concentration.

If an injection standard for volume control is intended to be used, for example, add a defined amount of injection standard (e g. fluoranthene-D10) dissolved in acetone. In case of a planned solvent change, injection standard may be dissolved in the appropriate solvent, e.g. toluene.

## 8.4 Gas chromatography

Check the required system stability regularly. Adjust and optimize instrument parameter settings in accordance with the respective manufacturer's instructions.

For separation, use appropriate capillary columns (6.7) and adjust chromatographic conditions for maximum selectivity (see Annex A for examples).

## 8.5 Identification of individual compounds by means of GC-MS

Identify a compound in the sample by comparing the measured retention times and the corresponding relative intensities of selected identification masses (Table 2) with those of the references substances in the multi-component reference solution (5.8.4).

The target compound in the sample shall be regarded as identified if:

— the relative or absolute retention time (*RT*) of the substance in the SIM chromatogram matches the relative or absolute retention time of the corresponding reference substance in the chromatogram of the most recently measured multi-component reference solution (5.8.4), with a limit deviation of no more than ± 0,2 %;

— at least 3 selected identification masses (see Table 2) are present at the substance-specific retention time;

— the relative intensities of all selected identification masses of individual substances measured in the sample do not deviate by more than ± (0,1 × *I* + 10) % from those of the corresponding substances in the reference solution (where *I* is the relative intensity of the identification mass of the individual reference substance).

EXAMPLE Three selected diagnostic ions have the following relative intensities: 100 %, 50 % and 15 %. The maximum allowed deviation for $I_2$ and $I_3$ in the sample is ($I_1$ is by definition 100 % in both the sample and reference standard):

— $I_2$: ± (0,1 × 50 + 10) % = ± 15 %; the relative intensity in the sample shall be between 35 % and 65 %;

— $I_3$: ± (0,1 × 15 + 10) % = ± 11,5 %; the relative intensity in the sample shall be between 3,5 % and 26,5 %.

In general, the following condition applies: After background subtraction, no ion of significant intensity should be present in the mass spectrum which has a mass larger than the maximum possible mass of a compound to be identified.

NOTE Further guidance on identification is given in EN ISO 22892 [2] and the SANCO/12571/2013 guideline [12].

## 8.6 Blank value measurements

Use periodic blank value measurements (at least one measurement per sequence) to ensure that instruments and chemicals are free from contamination. Blank measurements shall comprise all steps of the analytical procedure. If blank values are unusually high (over 50 % of the lowest reporting level), review every step in the procedure and determine the cause by systematic checks to be able to eliminate the contamination source. Try to reduce the blank values as much as possible by applying various measures, such as avoiding contamination by ambient air and using suitable solvents (5.4) as well as checking the analytical instrumentation (e.g. GC-MS, autosampler, LVI unit). If the concentrations of individual substances in the sample are close to the detection limit, blank values in the chromatogram can be tolerated which have an intensity of more than 50 % of those of the lowest reported value.

**Table 2 — Selected diagnostic ions for identification and quantification in mass spectrometric detection**

| Substance name | Example ions for identification and quantification *m/z* | | |
|---|---|---|---|
| Alachlor | 160 | 188 | 237 |
| Aldrin | 263 | 265 | 261 |
| Dieldrin | 263 | 345 | 381 |
| Endrin | 263 | 261 | 265 |
| Isodrin | 193 | 195 | 263 |
| op´-DDT | 235 | 237 | 165 |
| pp´-DDT | 235 | 237 | 165 |
| pp´-DDD | 235 | 237 | 165 |
| pp´-DDE | 235 | 237 | 165 |
| Hexachlorobenzene (HCB) | 284 | 286 | 282 |
| Hexachlorobutadiene (HCBD) | 225 | 227 | 223 |
| alpha-HCH | 181 | 183 | 219 |
| beta-HCH | 181 | 219 | 183 |
| delta-HCH | 181 | 219 | 183 |
| gamma-HCH | 181 | 183 | 219 |
| Pentachlorobenzene | 250 | 252 | 248 |
| 1,2,3-TCB | 180 | 182 | 145 |
| 1,2,4-TCB | 180 | 182 | 145 |
| 1,3,5-TCB | 180 | 182 | 145 |
| Endosulfan-I (alpha) | 195 | 242 | 265 |
| Endosulfan-II (beta) | 195 | 237 | 239 |
| **Examples of internal standard substances** | | | |
| Alachlor (d13) | 200 | 173 | 172 |
| pp´-DDT ($^{13}$C12) | 247 | 249 | 177 |
| HCB ($^{13}$C6) | 290 | 292 | 294 |
| HCBD ($^{13}$C4) | 231 | 266 | 233 |
| 1,2,4-TCB (d3) | 185 | 183 | 150 |
| Endosulfan-I (alpha) (d4) | 237 | 199 | 235 |
| Fluoranthene (d10) | 212 | 213 | 210 |

# 9 Calibration

## 9.1 General requirements

Correct calibration requires knowing the retention times of the analytes to be determined (see also Table 1). These shall be determined with reference solutions of individual reference substances (5.8.4) at the specified chromatographic conditions.

When setting up the method for the first time, check retention time (*RT*) and ensure identification of each single compound carefully. It is recommended that each compound of Table 1 be single-injected for checking retention time and/or mass spectrum (for examples of chromatograms see Annex A).

The calibration function determined for a substance applies only to the concentration range covered by it; moreover, it depends on the operating condition of the gas chromatograph and shall be checked at regular intervals.

Design the calibration procedure to achieve linear dependence of measurement signal to concentration is achieved for each compound to be determined. Determine the linear working range using at least five concentration levels (which are distributed as evenly as possible over the working range).

For routine operation, it is sufficient to recalibrate by measuring two concentration levels. Recalibrate at regular intervals within one sample sequence (e.g. after 15 to 20 samples).

For each target compound, calibrate the determination procedure using individual or, more conveniently, multi-component reference solutions (5.8.4). Adjust the calibration range to the existing requirements.

Table 3 gives an explanation of the subscripts used in the equations and in the following text.

**Table 3 — Definition of subscripts**

| Subscript | Meaning |
|---|---|
| *i* | Substance |
| e | Calibration step |
| g | Total procedure |
| *j* | Consecutive figure for pairs of values |
| I | Internal Standard |

## 9.2 Calibration of the GC-step

For each analyte, establish a calibration function from at least five points; it is practicable to include in one step all compounds using multi-component reference solutions (5.8.4) of different concentration levels.

For a graphic presentation of the calibration curve, plot the reference function and determine the line of best fit by linear regression according to Formula (1):

$$y_{i\mathrm{e}} = m_i \cdot \rho_{i\mathrm{e}} + b_i \qquad (1)$$

where

$y_{i\mathrm{e}}$ is the measured response (dependent variable) of substance *i* during calibration as a function of $\rho_{i\mathrm{e}}$, the unit depending on the evaluation, e.g. area unit;

$\rho_{i\mathrm{e}}$ is the (independent variable) mass concentration of substance *i* in the reference solution, in micrograms per litre, µg/l;

$m_i$ is the slope of the calibration function of substance *i* (response factor);

$b_i$ is the ordinate intercept of the calibration curve; the unit depends on the evaluation.

## 9.3 Calibration of the total procedure using the internal standard

As internal standard, choose a substance with similar physico-chemical properties (extraction behaviour, retention time) as the substance to be determined (see 5.7 and Annex D). The internal standard should not be present in the sample to be analyzed. The choice of a substance may be difficult and it depends on the problem to be resolved; in any case, the suitability should be checked. The

recovery of the internal standard should be at least 70 % (9.4). It is mandatory to use more than one internal standard.

The use of an internal standard helps to minimize unavoidable minor errors which may occur throughout the procedure, e.g.:

— the determination of the concentrations will become, to a certain degree, independent of matrix effects in the water sample;

— precision by GC-measurement is independent from minor deviations during probe injection;

— minor sample losses throughout sample preparation as well as insufficient adjusting of small sample extract volumes to a precise level do not cause problems in reproducibility.

Add a known mass of the internal standard I to the water sample prior to analysis (see 8.1).

The mass concentration, $\rho_{\mathrm{I}}$, shall be the same for both calibration and the sample series. All multi-component reference solutions suitable for multipoint calibration (5.8.4) should contain the same mass concentration of the internal standard I.

For calibration covering the total procedure, add e.g. 100 µl of multi-component reference solution (5.8.4) to e.g. 1 000 ml water (5.1) and treat and analyze the sample as described in Clause 8.

Based on the values obtained from the ratios of $y_{\mathrm{i}egj}/y_{\mathrm{leg}j}$ and $\rho_{\mathrm{i}egj}/\rho_{\mathrm{leg}j}$, plot the reference function and determine the line of best fit by linear regression according to Formula (2).

$$\frac{y_{i\mathrm{eg}}}{y_{\mathrm{leg}}} = m_{i\mathrm{Ig}}\frac{\rho_{i\mathrm{eg}}}{\rho_{\mathrm{leg}}} + b_{i\mathrm{Ig}} \tag{2}$$

where

$y_{\mathrm{i}eg}$ is the measured value (dependent variable) of substance $i$ during calibration as a function of $\rho_{i\mathrm{e}}$, the unit depending on the evaluation, e.g. area unit;

$y_{\mathrm{leg}}$ is the measured value of internal standard I during calibration, the unit depending on the evaluation, e.g. area unit. All reference solutions contain equal concentrations of the internal standard I;

$\rho_{\mathrm{i}eg}$ is the (independent variable) mass concentration of substance $i$ in the reference solution, in micrograms per litre (µg/l);

$\rho_{\mathrm{leg}}$ is the (independent variable) mass concentration of internal standard I, in micrograms per litre (µg/l);

$m_{i\mathrm{Ig}}$ is the slope of the reference line of $y_{ieg}/y_{\mathrm{leg}}$ as a function of the ratio $\rho_{ieg}/\rho_{\mathrm{leg}}$ (response factor);

$b_{i\mathrm{Ig}}$ is the ordinate intercept of the reference line, the unit depending on the evaluation.

## 9.4 Determination of procedural recovery values

Reliable recovery data are obtained from analysis of spiked water samples at different concentration levels, equidistantly spread over the working range. From these individual results a mean specific recovery $\overline{A_i}$ is calculated.

Using the calibration function in 9.2, calculate the single mass concentration $\rho_{\mathrm{i.N.fnd}}$ for each concentration level N and for each substance *i*.

Calculate the single recovery $A_{i,\mathrm{N}}$ according to Formula (3).

$$A_{i,\mathrm{N}} = \frac{\rho_{i.\mathrm{N.fnd}}}{\rho_{i.\mathrm{N.nom}}} \cdot f \tag{3}$$

where

$A_{i,\mathrm{N}}$ is the recovery of substance *i* on the concentration level N in percent (%);

$\rho_{i.\mathrm{N.fnd}}$ is the recovered mass concentration of substance *i* on the concentration level N, calculated according Formula (1), in micrograms per litre (µg/l);

$\rho_{i.\mathrm{N.nom}}$ is the original mass concentration of substance *i* on the concentration level N, in micrograms per litre (µg/l);

$f$ is the conversion factor, here: $f = 100$.

Calculate with these single results the mean recovery $\overline{A_i}$ according to Formula (4).

$$\overline{A_i} = \frac{\sum_{N=l}^{n} A_{i,\mathrm{N}}}{n} \tag{4}$$

where

$\overline{A_i}$ is the mean recovery of substance *i*, in percent (%);

$A_{i,\mathrm{N}}$ is the recovery of substance *i* on the concentration level N in percent (%);

$n$ is the number of individual measurement values $A_{i,\mathrm{N}}$.

With the described procedure stated in Clause 8, recoveries of > 70 % and up to 120 % are usually achieved. Low or unstable recoveries indicate matrix effects or difficulties during extraction.

## 10 Calculation of the results

Calculate the mass concentration $\rho_{ig}$ of substance *i* in the water sample according to Formula (5), taking into account Formula (2) using the internal standard I.

$$\rho_{i\mathrm{g}} = \frac{\frac{y_{i\mathrm{g}}}{y_{\mathrm{Ig}}} - b_{i\mathrm{Ig}}}{m_{i\mathrm{Ig}}} \cdot \rho_{\mathrm{Ig}} \tag{5}$$

where

$\rho_{ig}$ is the mass concentration of the target substance *i* in the water sample, in micrograms per litre (µg/l);

$y_{ig}$ is the measured value of the target substance *i* in the water sample, e.g. in area units;

$y_{Ig}$ is the measured value of internal standard I in the water sample, the unit depending on the evaluation, e.g. area unit;

$\rho_{Ig}$ is the mass concentration of internal standard I in the water sample, in micrograms per litre (µg/l);

$b_{iIg}$, $m_{iIg}$ see Formula (2).

## 11 Expression of results

The mass concentration, in micrograms per litre (µg/l) or nanograms per litre (ng/l), of the individual compounds listed in Table 1 shall be reported to two significant figures.

| | | |
|---|---|---|
| EXAMPLES | Alachlor | 11 µg/l |
| | 1,2,3-TCB | 1,2 µg/l |
| | Hexachlorobutadiene | 0,14 µg/l |
| | Endrin | 0,021 µg/l |
| | Endosulfan-II (beta) | 0,000 34 µg/l |
| | Endosulfan-II (beta) | 0,34 ng/l |

## 12 Test report

The test report shall contain at least the following information:

a) the applied test method, with a reference to this European Standard (EN 16693);

b) all information necessary for the complete identification of the water sample;

c) sample preparation and extraction;

d) expression of the results, according to Clause 11;

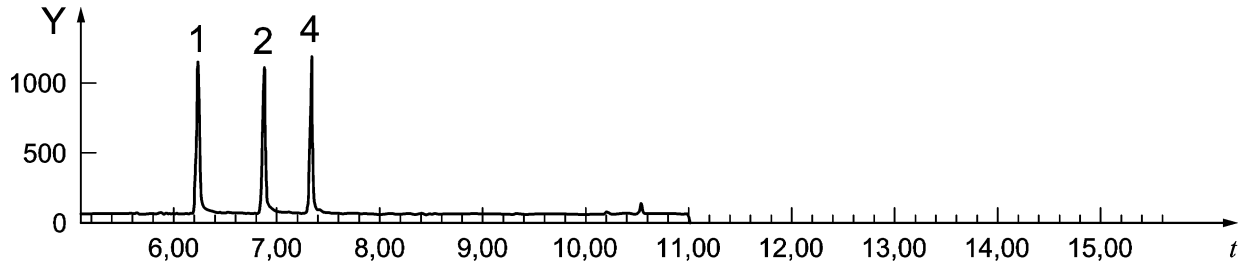
e) any details not specified in this European Standard or which are optional, as well as any factor which may have affected the results.

# Annex A
(informative)

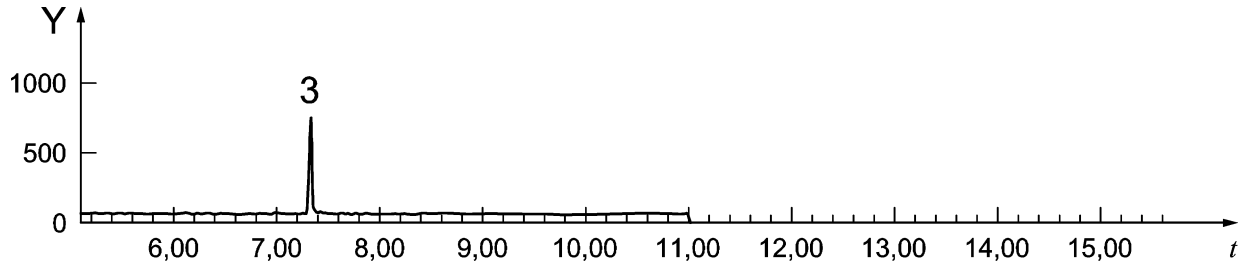
# Suitable gas chromatographic conditions and example chromatograms — GC-conditions of example chromatograms in Figure A.1

| | |
|---|---|
| GC equipment: | Agilent 6890 A[1)], Gerstel MPS 2[1)] |
| Injection: | 1 µl, glass-liner (straight, desactivated, with 1 notch); I.D: 1,0 mm, Gerstel CIS 4[1)], 60 °C; 10 °C/s to 300 °C; 10 min; splitless |
| Capillary column: | Phenomenex Zebron ZB 5ms[1)], 30 m × 0,25 mm × 0,25 µm |
| Concentration: | 10 ng/ml |
| Carrier gas: | helium (5.0); 0,9 ml/min |
| Temperature programme: | 65 °C; 10 °C/min to 300 °C; 10 min |
| MS detector: | Agilent 5973 C MSD[1)], quadrupole-MS, EI, 70 eV, SIM |

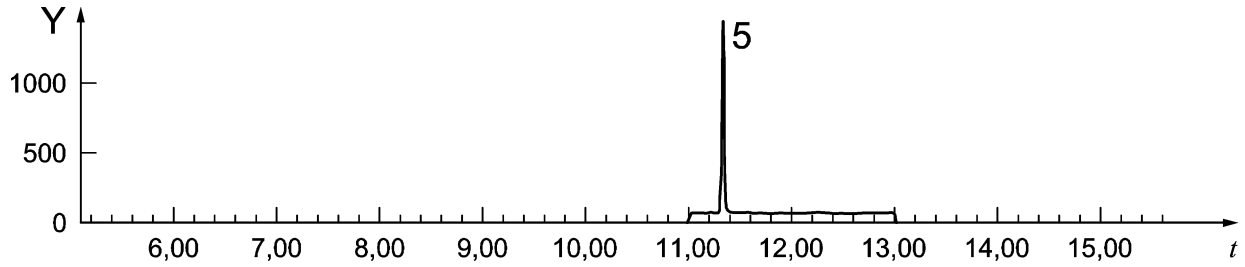
1) Agilent 6890 A, Gerstel MPS 2, Gerstel CIS 4 Phenomenex Zebron ZB 5ms and Agilent 5973 C MSD are examples of suitable products which are commercially available. These examples are given only as information for the users of this European Standard and do not constitute an endorsement by CEN of these products.



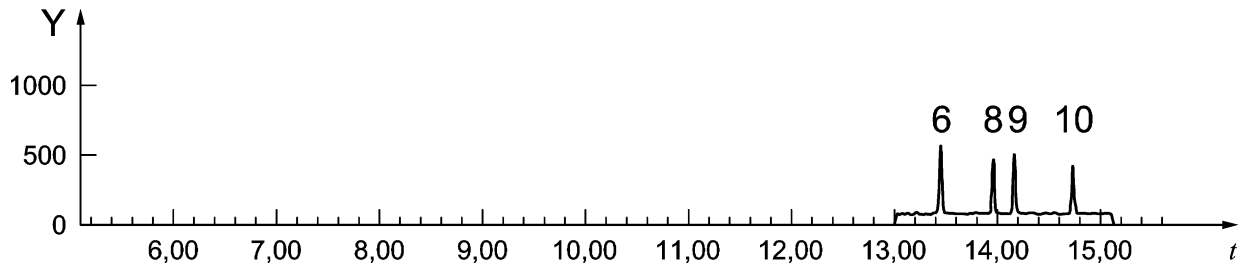

**a) ion 180**



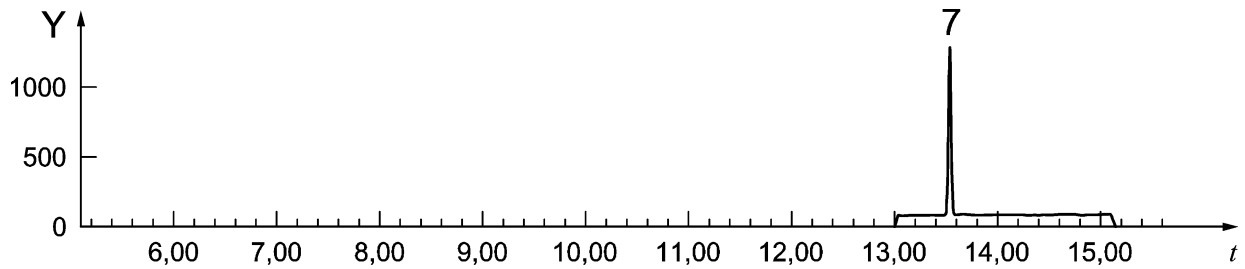

**b) ion 225**



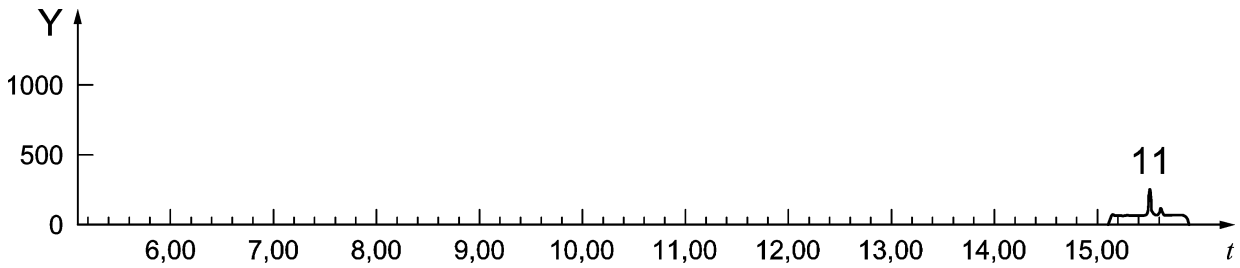

**c) ion 250**



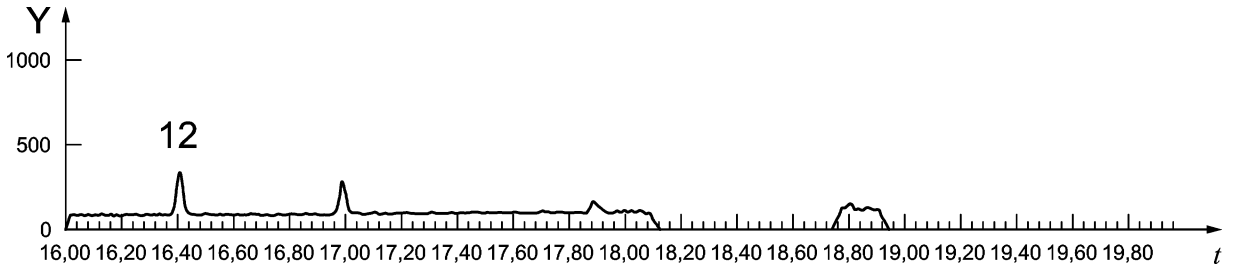

**d) ion 183**



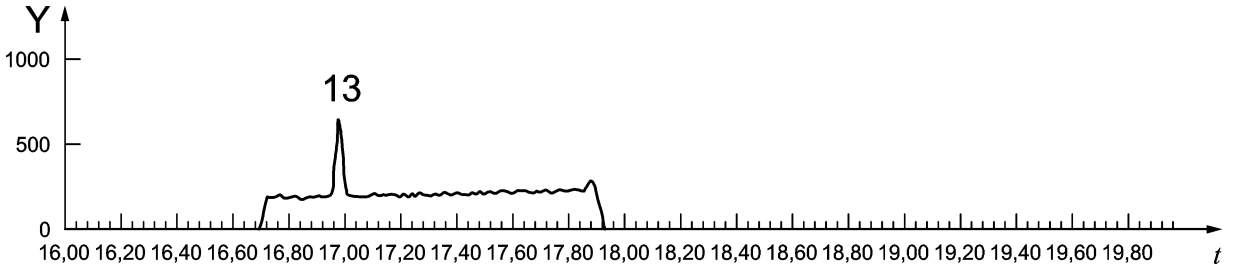

**e) ion 284**



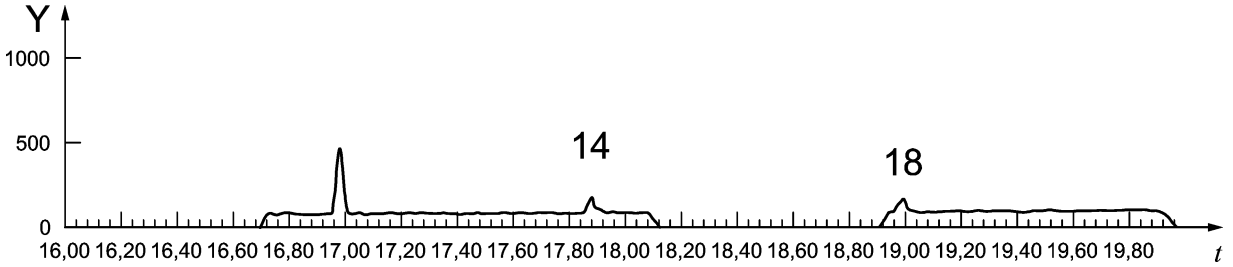

**f) ion 160**



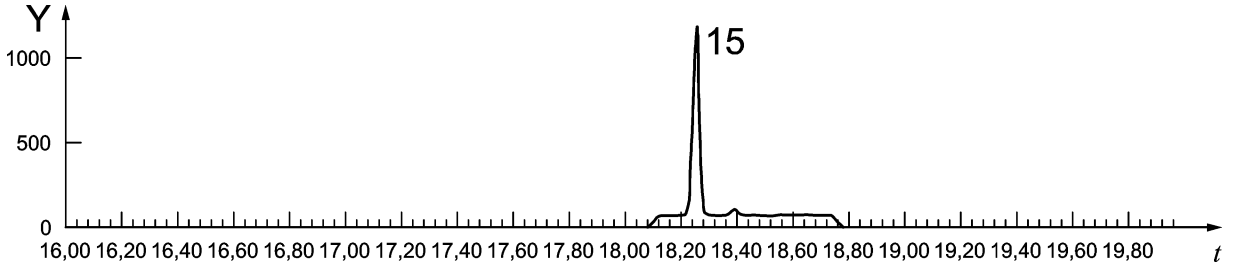

**g) ion 265**



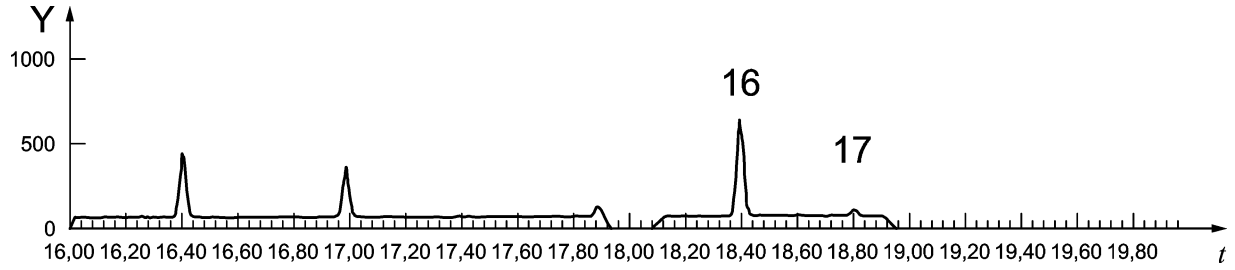

**h) ion 193**



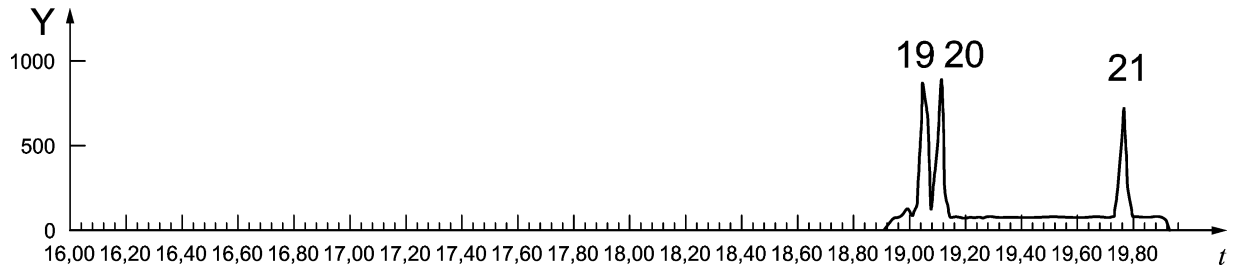

**i) ion 195**



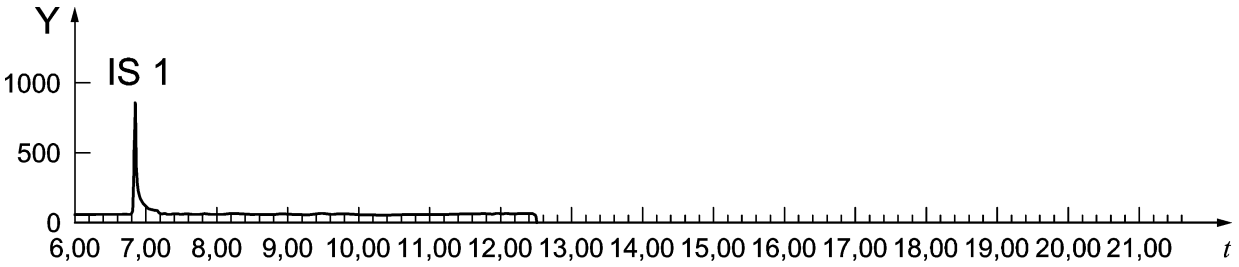

**j) ion 246**



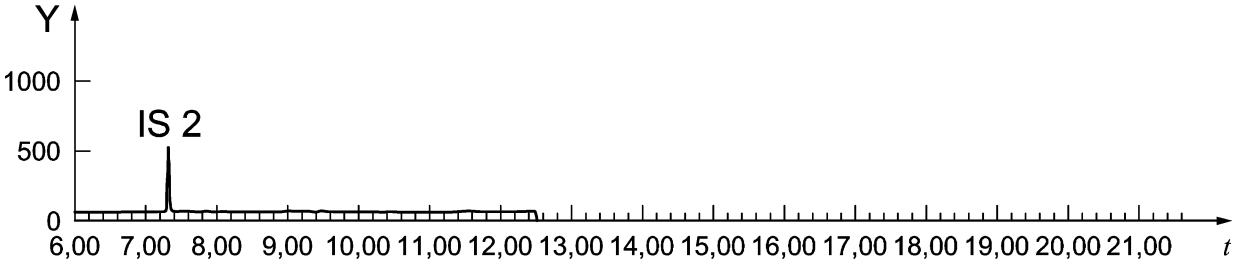

**k) ion 263**



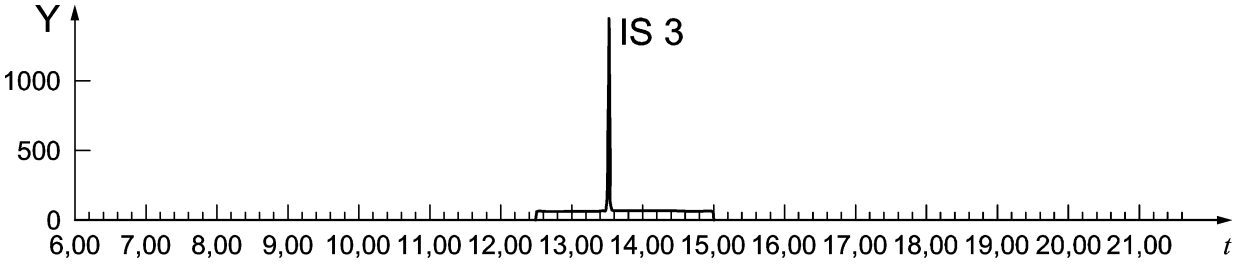

**l) ion 235**



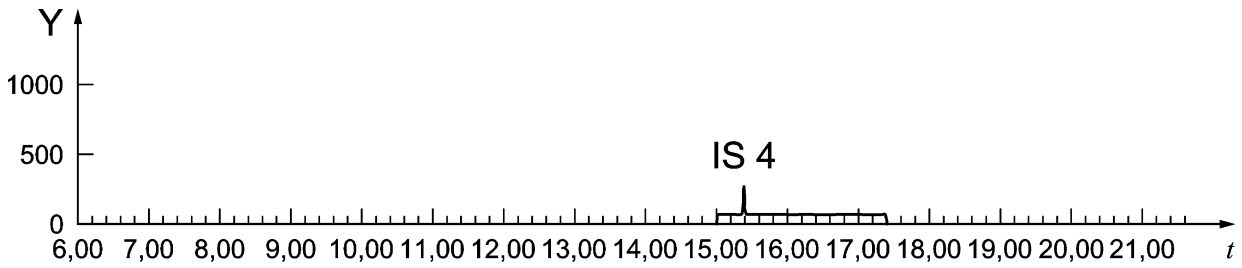

**m) ion 185**



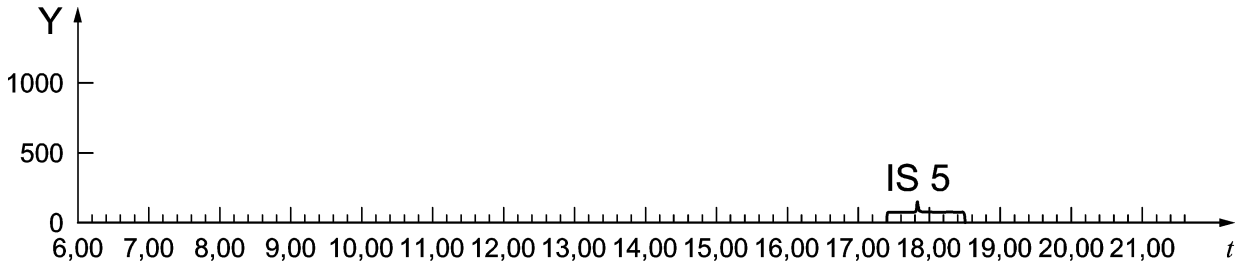

**n) ion 231**



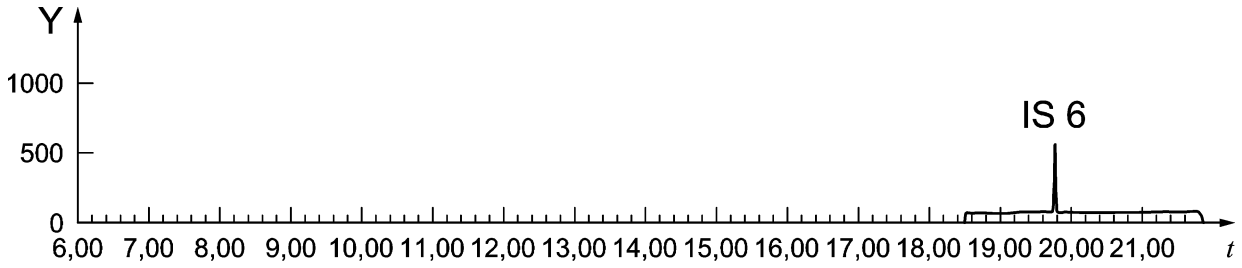

**o) ion 290**




**p) ion 200**




**q) ion 237**




**r) ion 247**

**Key**

| | | | |
|---|---|---|---|
| t | Time in minutes (min) | | |
| Y | Abundance, signal intensity | | |
| 1 | 1,3,5-TCB | 15 | pp´-DDE |
| 2 | 1,2,4-TCB | 16 | Dieldrin |
| 3 | 1,2,3-TCB | 17 | Endrin |
| 4 | Hexachlorobutadiene (HCBD) | 18 | Endosulfan-II (beta) |
| 5 | Pentachlorobenzene | 19 | pp´-DDD |
| 6 | alpha-HCH | 20 | op´-DDT |
| 7 | Hexachlorobenzene (HCB) | 21 | pp´-DDT |
| 8 | beta-HCH | IS 1 | 1,2,4-TCB (d3) |
| 9 | gamma-HCH | IS 2 | HCBD ($^{13}C3$) |
| 10 | delta-HCH | IS 3 | HCB ($^{13}C6$) |
| 11 | Alachlor | IS 4 | Alachlor (d13) |
| 12 | Aldrin | IS 5 | Endosulfan-I (alpha) (d4) |
| 13 | Isodrin | IS 6 | pp´-DDT ($^{13}C12$) |
| 14 | Endosulfan-I (alpha) | | |

**Figure A.1 — Example gas chromatograms of OCP**

# Annex B
(informative)

# Repeatability and reproducibility data

The performance data on repeatability and reproducibility given in Tables B.1, B.2 and B.3 were determined in a European interlaboratory trial for validation carried out in June 2014 on surface water. The water used was taken from an urban and industrialized area (river Ruhr in Muelheim, Germany).

Three samples (sample 1, 2 and 3, see Tables B.1, B.2 and B.3) were spiked with OCP listed in Table 1. Sample 2 and 3 were additionally spiked with different amounts of suspended particulate matter (SPM). The SPM used was an OCP-containing certified reference material (CRM). Evaluation according to ISO 5725-2.

**Table B.1 — Performance data for OCP spiked surface water, sample 1**

| Compound | $l$ | $n$ | $o$ | $X$ | $\overline{\overline{x}}$ | $\eta$ | $s_R$ | $C_{V,R}$ | $s_r$ | $C_{V,r}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | % | µg/l | µg/l | % | µg/l | % | µg/l | % |
| Alachlor | 8 | 16 | 11,1 | 0,162 5 | 0,138 1 | 85,0 | 0,027 6 | 20,0 | 0,014 0 | 10,1 |
| Aldrin | 10 | 20 | 0,0 | 0,015 0 | 0,012 6 | 83,7 | 0,002 6 | 21,1 | 0,001 0 | 7,9 |
| Dieldrin | 12 | 23 | 0,0 | 0,020 0 | 0,021 3 | 106,3 | 0,006 4 | 30,1 | 0,001 8 | 8,5 |
| Endrin | 10 | 20 | 9,1 | 0,020 0 | 0,019 9 | 99,3 | 0,006 5 | 33,0 | 0,001 0 | 5,2 |
| Isodrin | 8 | 16 | 11,1 | 0,020 0 | 0,016 6 | 83,1 | 0,003 8 | 23,0 | 0,000 8 | 4,8 |
| op´-DDT | 12 | 24 | 0,0 | 0,036 0 | 0,038 9 | 108,0 | 0,016 6 | 42,7 | 0,003 4 | 8,7 |
| pp´-DDT | 12 | 24 | 0,0 | 0,022 7 | 0,026 5 | 116,6 | 0,009 8 | 37,2 | 0,002 1 | 7,8 |
| pp´-DDD | 10 | 20 | 16,7 | 0,036 1 | 0,036 5 | 101,1 | 0,011 8 | 32,4 | 0,003 0 | 8,4 |
| pp´-DDE | 11 | 22 | 8,3 | 0,045 0 | 0,039 1 | 86,9 | 0,012 3 | 31,5 | 0,002 4 | 6,2 |
| Hexachlorobenzene (HCB) | 10 | 20 | 0,0 | 0,024 0 | 0,020 7 | 86,0 | 0,007 7 | 37,3 | 0,001 5 | 7,4 |
| Hexachlorobutadiene (HCBD) | 9 | 18 | 0,0 | 0,113 4 | 0,070 6 | 62,3 | 0,019 5 | 27,6 | 0,005 6 | 7,9 |
| alpha-HCH | 11 | 22 | 8,3 | 0,029 9 | 0,024 6 | 82,2 | 0,010 4 | 42,3 | 0,001 6 | 6,4 |
| beta-HCH | 12 | 24 | 0,0 | 0,030 3 | 0,028 8 | 94,9 | 0,012 1 | 42,2 | 0,002 0 | 7,1 |
| delta-HCH | 11 | 22 | 0,0 | 0,037 4 | 0,039 1 | 104,6 | 0,010 9 | 27,9 | 0,001 8 | 4,7 |
| gamma-HCH | 12 | 23 | 0,0 | 0,029 9 | 0,026 6 | 89,0 | 0,013 9 | 52,2 | 0,002 2 | 8,4 |
| Pentachlorobenzene | 9 | 18 | 0,0 | 0,015 1 | 0,015 6 | 103,0 | 0,009 5 | 60,8 | 0,002 8 | 18,1 |
| 1,2,3-TCB | 7 | 14 | 12,5 | 0,324 7 | 0,249 1 | 76,7 | 0,069 5 | 27,9 | 0,007 2 | 2,9 |
| 1,2,4-TCB | 7 | 14 | 12,5 | 0,257 3 | 0,223 9 | 87,0 | 0,058 7 | 26,2 | 0,010 9 | 4,9 |
| 1,3,5-TCB | 8 | 16 | 11,1 | 0,270 0 | 0,210 9 | 78,1 | 0,053 2 | 25,2 | 0,008 8 | 4,2 |
| Endosulfan-I (alpha) | 10 | 20 | 0,0 | 0,013 1 | 0,011 8 | 89,7 | 0,003 9 | 33,5 | 0,001 9 | 15,8 |
| Endosulfan-II (beta) | 10 | 20 | 0,0 | 0,013 2 | 0,010 2 | 77,3 | 0,003 6 | 35,1 | 0,000 9 | 9,3 |

$l$ number of laboratories after outlier rejection
$n$ number of individual test results after outlier rejection
$o$ percentage of outliers
$X$ assigned value
$\overline{\overline{x}}$ overall mean of results (without outliers)
$\eta$ recovery rate
$s_R$ reproducibility standard deviation
$C_{V,R}$ coefficient of variation of reproducibility
$s_r$ repeatability standard deviation
$C_{V,r}$ coefficient of variation of repeatability

**Table B.2 — Performance data for OCP spiked surface water, additionally spiked with 20 mg/l of suspended particulate matter (SPM), sample 2**

| Compound | $l$ | $n$ | $o$ | $X$ | $\overline{\overline{x}}$ | $\eta$ | $s_R$ | $C_{V,R}$ | $s_r$ | $C_{V,r}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | % | µg/l | µg/l | % | µg/l | % | µg/l | % |
| Alachlor | 8 | 16 | 11,1 | 0,325 1 | 0,266 3 | 81,9 | 0,047 0 | 17,6 | 0,022 0 | 8,3 |
| Aldrin | 9 | 18 | 10,0 | 0,020 3 | 0,017 3 | 85,1 | 0,004 6 | 26,4 | 0,002 3 | 13,6 |
| Dieldrin | 10 | 20 | 16,7 | 0,026 5 | 0,027 9 | 105,3 | 0,003 8 | 13,6 | 0,002 1 | 7,6 |
| Endrin | 11 | 22 | 0,0 | 0,027 5 | 0,032 0 | 116,2 | 0,008 4 | 26,4 | 0,003 9 | 12,1 |
| Isodrin | 10 | 20 | 0,0 | 0,030 0 | 0,024 8 | 82,5 | 0,012 0 | 48,3 | 0,002 8 | 11,3 |
| op´-DDT | 11 | 22 | 8,3 | 0,054 0 | 0,045 5 | 84,2 | 0,010 8 | 23,8 | 0,005 2 | 11,4 |
| pp´-DDT | 11 | 22 | 8,3 | 0,030 6 | 0,030 6 | 100,0 | 0,009 3 | 30,3 | 0,004 5 | 14,8 |
| pp´-DDD | 10 | 20 | 16,7 | 0,049 7 | 0,045 8 | 92,2 | 0,014 0 | 30,5 | 0,003 4 | 7,4 |
| pp´-DDE | 12 | 24 | 0,0 | 0,058 4 | 0,053 0 | 90,8 | 0,016 6 | 31,2 | 0,003 7 | 7,0 |
| Hexachlorobenzene (HCB) | 10 | 20 | 0,0 | 0,030 0 | 0,024 9 | 82,8 | 0,007 4 | 29,7 | 0,001 6 | 6,4 |
| Hexachlorobutadiene (HCBD) | 9 | 18 | 0,0 | 0,170 1 | 0,093 8 | 55,1 | 0,030 9 | 33,0 | 0,010 3 | 11,0 |
| alpha-HCH | 11 | 22 | 8,3 | 0,049 3 | 0,042 4 | 85,9 | 0,016 5 | 38,9 | 0,002 4 | 5,7 |
| beta-HCH | 12 | 24 | 0,0 | 0,052 3 | 0,054 3 | 103,9 | 0,025 4 | 46,7 | 0,007 1 | 13,2 |
| delta-HCH | 11 | 22 | 0,0 | 0,061 2 | 0,063 3 | 103,4 | 0,021 7 | 34,4 | 0,009 8 | 15,6 |
| gamma-HCH | 12 | 24 | 0,0 | 0,051 6 | 0,046 3 | 89,6 | 0,018 7 | 40,4 | 0,003 7 | 7,9 |
| Pentachlorobenzene | 8 | 16 | 11,1 | 0,018 9 | 0,014 9 | 79,0 | 0,005 2 | 35,1 | 0,001 3 | 8,4 |
| 1,2,3-TCB | 8 | 16 | 0,0 | 0,405 9 | 0,292 1 | 72,0 | 0,130 4 | 44,6 | 0,074 0 | 25,3 |
| 1,2,4-TCB | 8 | 16 | 0,0 | 0,385 9 | 0,332 4 | 86,1 | 0,088 0 | 26,5 | 0,061 0 | 18,4 |
| 1,3,5-TCB | 9 | 18 | 0,0 | 0,324 0 | 0,276 8 | 85,4 | 0,109 5 | 39,6 | 0,072 2 | 26,1 |
| Endosulfan-I (alpha) | 10 | 20 | 0,0 | 0,013 9 | 0,013 7 | 98,6 | 0,004 7 | 34,6 | 0,002 0 | 14,8 |
| Endosulfan-II (beta) | 10 | 20 | 0,0 | 0,015 0 | 0,013 4 | 89,3 | 0,004 5 | 33,8 | 0,001 2 | 9,1 |
| For explanation of symbols see Table B.1. | | | | | | | | | | |

**Table B.3 — Performance data for OCP spiked surface water, additionally spiked with 200 mg/l of suspended particulate matter (SPM), sample 3**

| Compound | $l$ | $n$ | $o$ | $X$ | $\overline{\overline{x}}$ | $\eta$ | $s_R$ | $C_{V,R}$ | $s_r$ | $C_{V,r}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | % | µg/l | µg/l | % | µg/l | % | µg/l | % |
| Alachlor | 7 | 14 | 22,2 | 0,433 4 | 0,365 2 | 84,3 | 0,072 9 | 19,9 | 0,024 0 | 6,6 |
| Aldrin | 11 | 22 | 0,0 | 0,185 0 | 0,151 1 | 81,7 | 0,032 6 | 21,6 | 0,011 4 | 7,5 |
| Dieldrin | 12 | 24 | 0,0 | 0,125 0 | 0,132 3 | 105,8 | 0,044 2 | 33,4 | 0,009 0 | 6,8 |
| Endrin | 11 | 22 | 8,3 | 0,183 4 | 0,183 0 | 99,8 | 0,076 2 | 41,7 | 0,012 1 | 6,6 |
| Isodrin | 10 | 20 | 0,0 | 0,180 0 | 0,147 8 | 82,1 | 0,041 7 | 28,2 | 0,012 7 | 8,6 |
| op´-DDT | 9 | 18 | 25,0 | 0,240 0 | 0,196 8 | 82,0 | 0,070 5 | 35,8 | 0,008 3 | 4,2 |
| pp´-DDT | 11 | 22 | 8,3 | 0,161 2 | 0,171 5 | 106,4 | 0,066 3 | 38,7 | 0,013 9 | 8,1 |
| pp´-DDD | 10 | 20 | 16,7 | 0,340 6 | 0,302 8 | 88,9 | 0,103 5 | 34,2 | 0,021 2 | 7,0 |
| pp´-DDE | 11 | 22 | 8,3 | 0,205 6 | 0,206 9 | 100,6 | 0,058 5 | 28,3 | 0,013 8 | 6,7 |
| Hexachlorobenzene (HCB) | 10 | 20 | 0,0 | 0,108 0 | 0,090 6 | 83,9 | 0,021 9 | 24,2 | 0,007 0 | 7,7 |
| Hexachlorobutadiene (HCBD) | 9 | 18 | 0,0 | 0,396 9 | 0,218 1 | 55,0 | 0,092 9 | 42,6 | 0,008 6 | 4,0 |
| alpha-HCH | 10 | 20 | 16,7 | 0,224 3 | 0,175 1 | 78,0 | 0,068 6 | 39,2 | 0,010 2 | 5,8 |
| beta-HCH | 10 | 20 | 16,7 | 0,216 4 | 0,194 6 | 89,9 | 0,073 0 | 37,5 | 0,011 6 | 5,9 |
| delta-HCH | 10 | 20 | 9,1 | 0,252 7 | 0,218 5 | 86,5 | 0,061 4 | 28,1 | 0,018 1 | 8,3 |
| gamma-HCH | 11 | 22 | 8,3 | 0,227 4 | 0,195 7 | 86,1 | 0,064 7 | 33,1 | 0,006 3 | 3,2 |
| Pentachlorobenzene | 8 | 16 | 11,1 | 0,090 6 | 0,074 9 | 82,7 | 0,016 7 | 22,3 | 0,005 6 | 7,4 |
| 1,2,3-TCB | 7 | 14 | 12,5 | 0,487 1 | 0,361 4 | 74,2 | 0,129 5 | 35,8 | 0,024 5 | 6,8 |
| 1,2,4-TCB | 7 | 14 | 12,5 | 0,506 5 | 0,375 4 | 74,1 | 0,135 7 | 36,1 | 0,019 0 | 5,1 |
| 1,3,5-TCB | 8 | 16 | 11,1 | 0,486 0 | 0,351 8 | 72,4 | 0,159 8 | 45,4 | 0,012 7 | 3,6 |
| Endosulfan-I (alpha) | 11 | 22 | 0,0 | 0,087 1 | 0,081 4 | 93,4 | 0,030 4 | 37,4 | 0,007 4 | 9,1 |
| Endosulfan-II (beta) | 10 | 20 | 9,1 | 0,062 1 | 0,062 3 | 100,3 | 0,038 1 | 61,2 | 0,005 4 | 8,7 |
| For explanation of symbols see Table B.1. | | | | | | | | | | |

# Annex C
(informative)

# Examples of suitable SPE-disks

Table C.1 lists some examples of SPE-disks, that have been tested within standardization work and which have proved to be suitable for the purpose. Other SPE-disks can be used as well if their suitability has been established in preliminary tests.

**Table C.1 — Examples of suitable SPE-disks**

| **Sorbent (SPE-disk type)** | **Product name (supplier)** [2)] |
|---|---|
| Silica based monolithic sorbent, $C_{18}$ (disk, 50 mm) | SPEC Disk SPE C18 AR (Agilent) |
| Silica based sorbent, $C_{18}$ (cartridge type, 47 mm) | BAKERBOND Speedisk C18 (J.T.Baker) |
| Silica based sorbent, $C_{18}$ (cartridge type, 47 mm) | BAKERBOND Speedisk C18 high capacity (J.T.Baker) |
| Styrene-divinyl benzene (SDB) copolymer (cartridge type, 47 mm) | BAKERBOND Speedisk $H_2O$-phobic DVB (J.T.Baker) |
| Styrene-divinyl benzene (SDB) copolymer (cartridge type, 47 mm) | BAKERBOND Speedisk $H_2O$-phobic DVB high capacity (J.T.Baker) |

2) The listed names are examples of suitable products which are commercially available. 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.

# Annex D
(informative)

# Examples of internal standards

Table D.1 lists examples of internal standards which have been tested as part of the prenormative work and which have proved to be suitable for the purpose. Other substances can be used as well if their suitability has been established in preliminary tests. The recovery of each internal standard should be at least 70 %.

**Table D.1 — Examples of suitable internal standards**

| Substance | Molecular formula | CAS RN | Molar mass<br>g/mol |
|---|---|---|---|
| Alachlor (d13) | $C_{14}H_7D_{13}ClNO_2$ | 1015856–63–9 | 282,85 |
| pp´-DDT ($^{13}C12$) | $C_{14}H_9Cl_5$ | 104215–84–1 | 366,59 |
| HCB ($^{13}C6$) | $C_6Cl_6$ | 93952–14–8 | 290,84 |
| HCBD ($^{13}C4$) | $C_4Cl_6$ | 93951–70–3 | 264,8 |
| 1,2,4-TCB (d3) | $C_6Cl_3D_3$ | 3907–98–0 | 184,47 |
| Endosulfan-I (alpha) (d4) | $C_9H_2Cl_6D_4O_3S$ | 203645–57–2 | 410,95 |
| Fluoranthene (d10) | $C_{16}D_{10}$ | 93951–69–0 | 212,31 |

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