INTERNATIONAL STANDARD

ISO 10382

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Soil quality — Determination of organochlorine pesticides and polychlorinated biphenyls — Gas-chromatographic method with electron capture detection

Qualité du sol — Dosage des pesticides organochlorés et des biphényles polychlorés — Méthode par chromatographie en phase gazeuse avec détection par capture d'électrons

Reference number
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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 3.

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 International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 10382 was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

Annexes A, B, C and D of this International Standard are for information only.

Soil quality — Determination of organochlorine pesticides and polychlorinated biphenyls — Gas-chromatographic method with electron capture detection

1 Scope

This International Standard specifies a method for quantitative determination of seven polychlorinated biphenyls and seventeen organochlorine pesticides in soil.

This International Standard is applicable to all types of soil.

Under the conditions specified in this International Standard, limits of detection of 0,1 μg/kg to 4 μg/kg (expressed as dry matter) can be achieved.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 10381-1, *Soil quality — Sampling — Part 1: Guidance on the design of sampling programmes*

ISO 10381-2, *Soil quality — Sampling — Part 2: Guidance on sampling techniques*

ISO 11465:1993, *Soil quality — Determination of dry matter and water content on a mass basis — Gravimetric method*

ISO 14507, *Soil quality — Pretreatment of samples for the determination of organic contaminants*

3 Principle

After pretreatment, the soil test sample is extracted with a hydrocarbon solvent.

The extract is concentrated; polar compounds are removed by passing the concentrated extract through a column filled with aluminium oxide. The eluate is concentrated.

Elemental sulfur is removed from the concentrated extract, if necessary, by treatment with tetrabutylammonium sulfite reagent.

The extract is analysed by gas chromatography. The various compounds are separated using a capillary column with an immobile phase of low polarity. Detection occurs with an electron-capture detector (ECD).

Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) are assigned and quantified by comparison of relative retention times and relative peak heights (or peak areas) with respect to injection standards

added, with the corresponding variables of an external standard solution. The efficiency of the procedure depends on the composition of the soil that is investigated. The described procedure does not take account of incomplete extraction due to the structure and composition of the soil sample.

The limit of detection is dependent on the determinands, the equipment used, the quality of chemicals used for extraction of the soil sample, and the clean-up of the extract.

NOTE 1 For confirmation of the identity of detected compounds and the concentrations found, further investigation is necessary. Confirmation can be carried out by repeating the gas chromatographic analysis using a column of different polarity and/or using gas chromatography/mass spectrometry (GC/MS).

NOTE 2 Other non-volatile organochlorine compounds, e.g. some chlorobenzenes, can also be identified and quantified by this method.

4 Reagents

All reagents shall be of recognized analytical grade. The purity of the reagents used shall be checked by running a blank determination as described in 8.1.

4.1 Petroleum ether, boiling range 40 °C to 60 °C.

4.2 Acetone.

4.3 n-Hexane.

4.4 Diethyl ether.

Diethyl ether can contain peroxides which may oxidize some of the determinands. Check for the absence of peroxides, e.g. by shaking with a freshly prepared 10 % (mass fraction) KI solution.

4.5 Anhydrous sodium sulfate, heated for at least 6 h to 550 °C ± 20 °C, cooled to about 200 °C in a furnace and then to ambient temperature in a desiccator containing magnesium perchlorate or a suitable alternative.

The anhydrous sodium sulfate shall be kept carefully sealed.

4.6 Aluminium oxide, basic or neutral, areic mass 200 m^2/g, activity Super I according to Brockmann.

4.7 Aluminium oxide, deactivated with 10 % water.

To 90 g of aluminium oxide (4.6) add 10 g of water. Shake until all lumps have disappeared. Allow the aluminium oxide to condition before use for approximately 16 h, sealed from the air.

4.8 Silica gel, particle size 60 µm to 200 µm, deactivated with 5 % water.

Heat 95 g of silica gel for at least 24 h in an oven at 150 °C. Then allow to cool in a desiccator and add 5 g of water. Shake until all lumps have disappeared. Allow the silica gel to condition before use for approx. 16 h, sealed from the air.

For each new batch of aluminium oxide or silica gel, the elution pattern should be checked against a standard solution of PCB and OCP. If necessary, the deactivation of the adsorbent should be adjusted (see 8.4).

4.9 Standards.

4.9.1 Polychlorinated biphenyls.

PCB- 28: 2,4,4'-trichlorobiphenyl	CAS number[1)]: 7012-37-5
PCB- 52: 2,2',5,5'-tetrachlorobiphenyl	CAS number: 35693-99-3
PCB-101: 2,2',4,5,5'-pentachlorobiphenyl	CAS number: 37680-73-2
PCB-118: 2,3',4,4',5-pentachlorobiphenyl	CAS number: 31508-00-6
PCB-138: 2,2',3,4,4',5'-hexachlorobiphenyl	CAS number: 35065-28-2
PCB-153: 2,2',4,4',5,5'-hexachlorobiphenyl	CAS number: 35065-27-1
PCB-180: 2,2',3,4,4',5,5'-heptachlorobiphenyl	CAS number: 35065-29-3

NOTE The numbers 28, 52, etc. correspond with the sequential numbers of chlorobiphenyls according to the IUPAC rules for the nomenclature of organic compounds.

4.9.2 Organochlorine pesticides.

Hexachlorobenzene (HCB)	CAS number: 118-74-1
α-Hexachlorocyclohexane (α-HCH)	CAS number: 319-84-6
β-Hexachlorocyclohexane (β-HCH)	CAS number: 319-85-7
γ-Hexachlorocyclohexane (γ-HCH)	CAS number: 58-89-9
Aldrin	CAS number: 309-00-2
Dieldrin	CAS number: 60-57-1
Endrin	CAS number: 72-20-8
Heptachlor	CAS number: 76-44-8
Heptachloro epoxide (exo-, *cis*- or a-isomer)	CAS number: 28044-83-9
Heptachloro epoxide (endo-, *trans*- or b-isomer)	CAS number: 1024-57-3
α-Endosulfan	CAS number: 959-98-7
p,p'-DDE	CAS number: 72-55-9
o,p'-DDD	CAS number: 53-19-0
o,p'-DDT	CAS number: 784-02-6
p,p'-DDD	CAS number: 72-54-8
o,p'-DDE	CAS number: 3424-82-6
p,p'-DDT	CAS number: 50-29-3

1) Registration used by the Chemical Abstracts Service.

4.9.3 Injection standards.

PCB-155: 2,2',4,4',6,6'-hexachlorobiphenyl CAS number: 33979-03-2

Select a second injection standard, not interfering with the analytes, from the following substances:

PCB-143: 2,2',3,4,5,6'-hexachlorobiphenyl CAS number: 68194-15-0

PCB-207: 2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl CAS number: 52663-79-3

Mirex CAS number: 2385-85-5

4.10 Tetrabutylammonium reagent (TBA sulfite reagent).

Saturate a solution of tetrabutylammonium hydrogen sulfate in a mixture of equal volumes of water and 2-propanol, $c[(C_4H_9)_4NHSO_4] = 0{,}1$ mol/l, with sodium sulfite.

NOTE 25 g of sodium sulfite is normally sufficient for 100 ml of solution.

4.11 n-Heptane.

5 Apparatus

5.1 Customary laboratory glassware.

All glassware to be used shall be thoroughly cleaned, preferably in a dishwasher using a customary cleaning procedure, followed by rinsing with acetone and a subsequent rinsing with petroleum ether or hexane.

5.2 Glass sample bottles, of nominal capacity 1 l, with screw top and polytetrafluoroethene seal (PTFE).

5.3 Shaking device, with horizontal movement (200 to 300 strokes per minute).

5.4 Water bath, capable of being heated to 100 °C.

5.5 Shaking funnels, with a capacity of 2 l.

5.6 Conical flasks, with a capacity of 500 ml.

5.7 Evaporator, Kuderna Danish (see Figure 1).

Other evaporators, e.g. a rotary evaporator, may be used if found to be equally suitable.

5.8 Quartz wool or silanized glass wool, rinsed with petroleum ether or hexane.

WARNING Working with quartz wool imposes a risk to health through the release of fine quartz particles. Prevent inhalation of these by using a fume cupboard and wearing a dust mask.

5.9 Boiling chips, of glass or porcelain beads, rinsed with petroleum ether or hexane.

5.10 Calibrated test tubes, with a capacity of 15 ml and ground glass stoppers.

5.11 Chromatography tubes (see Figure 2).

5.12 Gas chromatograph, equipped with a non-discriminating injection system, capillary column and electron-capture detector (ECD) based on ^{63}Ni.

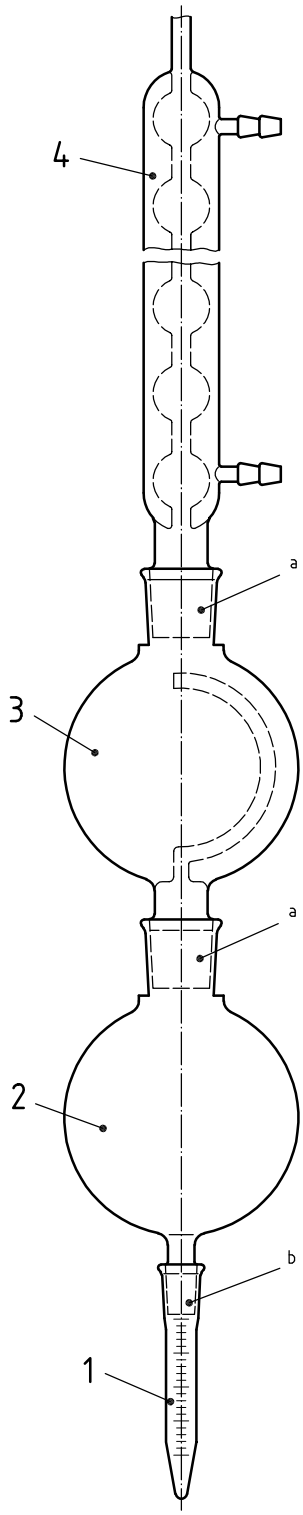
NOTE 1 Working with an encapsulated radioactive source such as that present in an ECD requires a licence in accordance with the appropriate national regulations.

NOTE 2 Gas chromatographs equipped with two detectors and with facilities for connecting two capillary columns to the same injection system are very well suited for this analysis; with such apparatus the confirmatory analysis can be performed simultaneously.

5.13 Capillary column, of fused silica, with a length of 50 m and an internal diameter of about 0,25 mm coated with a film of cross-linked polysiloxane.

Other columns can also be used, although in some cases unsatisfactory separation is obtained. A column coated with a moderate polar phase, e.g. CP-Sil 19, OV 1701 etc., shall be used to confirm the result obtained.

NOTE The retention times for PCB and OCP on capillary columns coated with CP-Sil 8 and CP-Sil 19 are given in annex A.



Key

1 Graduated test tube, capacity 15 ml
2 Distillation flasks
3 Receiver flask
4 Reflux condenser

[a] ISO 383 29/32
[b] ISO 14/23

All joints shall be in accordance with ISO 383.

Figure 1 — Example of evaporator (Kuderna Danish)

Dimensions in millimetres

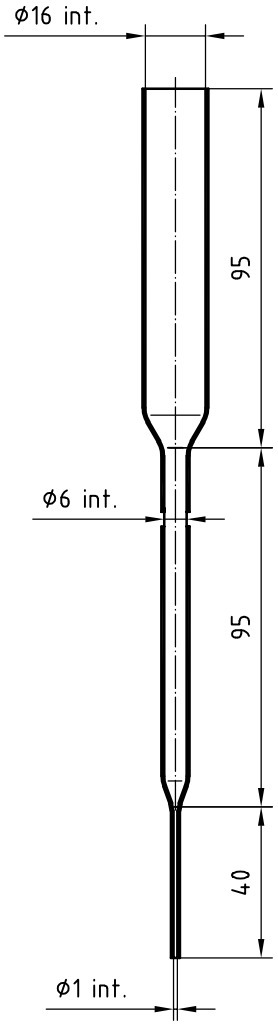


Figure 2 — Example of chromatography tube

6 Preparation of standard solutions of PCB and OCP

Prepare individual concentrated primary standard solutions of mass concentration about 0,4 mg/ml in n-heptane by weighing approx. 10 mg of each of the standards (4.9) to the nearest 0,1 mg and dissolving them in 25 ml of n-heptane.

Check the purity of the primary standard solutions by means of a gas chromatogram of the solutions concerned. Preferably a relatively non-specific detector, such as a flame ionization detector (FID) or a heat conductivity detector (TCD), shall be used.

Combine small quantities (2 ml to 10 ml) of the individual primary standard solutions into a mixed standard solution of PCB and OCP including the injection standards (see annex B). Using this solution, prepare the working standard solutions in accordance with annex B by dilution.

Components present in mixed standard solutions should be completely separated by the gas chromatographic columns used.

Store the primary and diluted standard solutions in a dark place at a temperature of less than 4 °C.

NOTE The solutions are stable for at least one year, provided that evaporation of solvent is negligible.

7 Sampling and preservation of samples

7.1 Sampling

Obtain representative soil samples in accordance with ISO 10381-1 using sampling apparatus in accordance with ISO 10381-2.

7.2 Sample preservation and pretreatment

Samples shall be pretreated as soon as possible. Store the samples in a dark place at a temperature below 10 °C, if possible in a refrigerator. For OCP testing, the storage times for field-moist soil samples shall not be longer than 7 days. Determine the content of dry matter in the field-moist soil in accordance with to ISO 11465. Grind the samples if there is insufficient homogeneity for taking a representative test sample. Grinding should take place cryogenically after chemical drying with anhydrous sodium sulfate (4.5) in accordance with ISO 14507.

It is permissible for dried samples, if kept sealed, to be stored for a longer period at room temperature (approx. one month).

8 Procedure

8.1 Blank

Before treating the samples, perform a blank determination as described in 8.2 to 8.5 using the same amount of reagents that are used for the extraction, clean-up and analysis of a sample. For cryogenically ground samples, perform the blank using 8 g of sodium sulfate (4.5) and 2 g of talcum, to which all the necessary reagents are added.

If the blank value is unreasonably high, i.e. more than 10 % of the lowest value of interest, find the cause through a step-by-step examination of the whole procedure.

For measurements at the limit of determination, even reagents suitable for residue analyses may not fulfil this criterion. In that case, sufficient blank determinations shall be incorporated in each series of samples.

Values obtained from analysis of blanks should be smaller than the detection limit for the analytes concerned.

8.2 Extraction and concentration

8.2.1 Cryogenically ground samples

Take 20 g of cryogenically ground sample and place it in a conical flask (5.6). Add 50 ml of acetone (4.2) to the test sample and extract by shaking thoroughly for 15 min on a shaking device (5.3). Then add 50 ml of petroleum ether (4.1) and shake again thoroughly during 15 min. Repeat the extraction again with 50 ml of petroleum ether (4.1). Collect the extracts in a separating funnel of 2 litre capacity and remove the acetone by shaking twice with 500 ml of water. Dry the extract over anhydrous sodium sulfate and transfer the dried extract to the concentrator (5.7). Rinse the sodium sulfate three times with 10 ml of petroleum ether and add the rinsings to the extract.

8.2.2 Field-moist samples

Take 20 g of field-moist sample and place it in a conical flask (5.6). Add 50 ml of acetone (4.2) to the test sample and extract by shaking thoroughly for 15 min on a shaking device (5.3). Then add 50 ml of petroleum ether (4.1) and shake again thoroughly during 15 min. Repeat the extraction again with 50 ml of petroleum ether (4.1).

If the water content of the sample is greater than 25 %, increase the amount of acetone. The ratio acetone:water should be at least 9:1. The ratio acetone:petroleum ether shall be kept constant at 1:2.

Collect the extracts in a separating funnel of 2 litre capacity and remove the acetone by shaking twice with 500 ml of water. Dry the extract over anhydrous sodium sulfate and transfer the dried extract to the concentrator (5.7). Rinse the sodium sulfate three times with 10 ml of petroleum ether and add the rinsings to the extract.

Other extraction techniques, such as ultrasonic extraction, microwave or pressurized extraction, may be suitable. However, if using other extraction techniques, the comparability of such techniques to the method described in this International Standard shall be proven.

8.2.3 Concentration

Add a boiling chip (5.9) to the extract and concentrate the extract to approx. 10 ml. Transfer the concentrated extract to a calibrated test tube (5.10) and further concentrate to 1 ml using a gentle stream of nitrogen at room temperature.

NOTE Too high temperatures and a too high flow of nitrogen may result in loss of the more volatile PCBs and OCPs.

8.3 Clean-up of the extract

Prepare an adsorption column by placing a small plug of quartz wool (5.8) in the chromatography tube (5.11) and packing it dry with 2,0 g $\pm$ 0,1 g of aluminium oxide (4.7).

Before use, the elution pattern of each series of aluminium oxide columns and the necessary elution volume should be verified using a standard solution of PCB and OCP.

With a pipette, transfer the extract to the dry packed adsorption column; rinse the test tube twice with 1 ml of petroleum ether and transfer the rinsings to the column with the same pipette as soon as the liquid level reaches the upper side of the column packing. Elute with approx. 20 ml of petroleum ether.

Divide the eluate into two equal parts and store one part for an eventual analysis of the diluted extract. Concentrate the other part of the eluate with a gentle stream of nitrogen, without additional heating, to a final volume of about 1 ml.

NOTE 1 Commercially available disposable columns may be used as an alternative if found equally suitable.

The presence of sulfur in the extract of PCBs and non-polar OCPs can cause interferences in the chromatogram. If elemental sulfur is expected to be present (this occurs amongst others in anaerobic soils), remove it as follows.

Add 2 ml of TBA sulfite reagent (4.10) to 1 ml of concentrated extract and shake for 1 min. Add 10 ml of water and shake again for 1 min. Separate the organic phase from the water with a Pasteur pipette and add a few crystals of anhydrous sodium sulfate to remove the remaining traces of water.

NOTE 2 Other methods to remove sulfur, e.g. with pyrogenic copper (see annex D), may be used as an alternative if found equally suitable.

If no further clean-up is required, to the final extract add 10 µl of the injection standard solution containing 100 times as much of the injection standards (4.9.3) per millilitre as is present per millilitre of working standard solution (see annex B).

8.4 Column-chromatographic separation of PCBs and non-polar OCPs from several polar OCPs

In the case of very complex samples, insufficient separation may be obtained with gas chromatographic analysis. In this case an additional chromatographic separation, using the whole concentrated extract, may overcome this problem.

The whole concentrated extract is separated by column chromatography on silica gel (4.8) into two fractions. The first fraction contains the PCBs and non-polar OCPs (HCB, *p,p*'-DDT, heptachlor, aldrin and *p,p*'-DDT). The second fraction contains the rather more polar OCPs (α-HCH, β-HCH, γ-HCH, dieldrin, endrin, *o,p*'-DDD and α-endosulfan). Check the elution pattern with the aid of a standard solution of PCB and OCP. If necessary, adjust the

activity of the silica gel by adding more water if the compounds referred to above from the first fraction appear in the second fraction, or if the first fraction does not contain the compounds mentioned above. Add less water to the silica gel if the compounds mentioned above from the second fraction appear in the first fraction.

Separate the extract as follows. Place a small plug of quartz wool in the chromatography tube. Pack it dry with (1,5 ± 0,1) g of silica gel (4.8) and top it with 1 cm of sodium sulfate (4.5). With a pipette, transfer the concentrated extract to the dry packed column. Rinse the test tube twice with 1 ml of hexane. Transfer the rinsings with the same pipette to the column as soon as the liquid level just reaches the upper edge of the column packing. Elute by adding to the column in succession 25 ml of hexane (fraction 1) and 25 ml of a mixture of hexane and diethyl ether (volume ratio 75:25) (fraction 2).

NOTE Commercially available disposable columns may be used as an alternative if found equally suitable.

Divide each of the two eluates into two equal parts, and for each eluate store one part for a possible repetition of the analysis in a dilution of the extract. Evaporate the other two separate fractions in test tubes to 1 ml volume.

Add 10 µl of the injection standard solution to each of the two fractions, containing 100 times as much of the injection standards (4.9.3) per millilitre as is present per millilitre of working standard solution (see annex B).

8.5 Gas chromatographic analysis

8.5.1 Optimizing the gas chromatograph

Optimize the gas chromatograph (5.12) in such a way that optimum separation is achieved. The plate number and capacity factor for component PCB-138 shall be greater than 6×10^4 and 6 respectively at 220 °C. The chromatographic peaks of PCB-28 and PCB-31 shall be resolved sufficiently (resolution at least 0,5) for integrating the PCB-28 peak.

The following settings may be used to start the optimization of the gas chromatograph:

Injection temperature (applicable only with splitless injection):	210 °C
Oven temperature:	80 °C for 4 min; 4 °C/min up to 300 °C
Detector temperature:	300 °C
Carrier gas:	Helium
Gas flow:	20 cm/s to 30 cm/s

8.5.2 Calibration

8.5.2.1 General

Two types of calibration are distinguished: the initial calibration (8.5.2.2) and the daily calibration (validity check of the initial calibration); the latter is called recalibration (8.5.2.3).

The initial calibration serves to establish the linear working range of the calibration curve. This calibration is performed when the method is used for the first time and after maintenance and/or repair of the equipment.

The recalibration checks the validity of the linear working range of the initial calibration curve and is performed before each series of samples.

NOTE Non-linear calibration methods are allowed, provided that they are validated.

8.5.2.2 Initial calibration

Take a gas chromatogram of a series of at least five standard solutions with equidistant concentrations as given in annex B, including the solvent blank (see annex B). Identify the peaks by consulting annex A and if necessary the gas chromatograms of the individual compounds. Prepare a calibration graph for each compound.

In general, the use of peak heights instead of peak areas is recommended.

Calculate by linear regression a straight line for the whole range of the calibration solutions. If the origin falls within the 95 % confidence limits of the calculated line, recalculate by linear regression the line through the origin. This line is called the initial calibration line.

If the origin does not fall within the 95 % confidence limits, omit the highest concentration and repeat the calculation.

Determine the deviations between the measured values and the initial calibration line. When the deviation for the highest concentration is less than 5 %, assume linearity exists for the whole range. When this deviation is more than 5 %, decrease the range by deleting the value for the highest concentration.

Choose as a working standard the calibration solution with the concentration closest to the middle of the linear range. When the range of the samples is lower than the linear range found, it is permissible for a working standard with a lower concentration to be chosen, corresponding to the middle of the sample range.

8.5.2.3 Recalibration

Before each series of samples, verify the validity of the initial calibration line as follows.

Inject at least two calibration standards with concentrations of 20 ± 10 % and 80 ± 10 % of the established linear range and calculate the straight line from these measurements. If the straight line falls within the 95 % confidence limits of the initial calibration line, the initial calibration line is assumed to be valid. If not, a new calibration line has to be established according to 8.5.2.2.

After establishing the validity of the initial calibration line, proceed as follows.

Record the gas chromatogram of the working standard. Determine on the basis of this chromatogram the relative retention times of all PCBs and OCPs with respect to the injection standards, as follows.

The relative retention time t_{RRX} of compound X with respect to injection standard PCB-155 is defined as:

$$t_{RRX} = \frac{t_{ARX}}{t_{AR\,PCB\text{-}155}} \tag{1}$$

where

t_{ARX} is the absolute retention time of compound X;

$t_{AR\,PCB-155}$ is the absolute retention time of injection standard PCB-155.

Next determine for all PCBs and OCPs the relative response with respect to the injection standard PCB-155, as follows.

The relative response r_{relX} of compound X with respect to injection standard PCB-155 is defined as:

$$r_{relX} = \frac{r_X}{r_{PCB\text{-}155}} \cdot \frac{c_{PCB\text{-}155}}{c_X} \tag{2}$$

where

r_X is the response of compound X;

$r_{PCB\text{-}155}$ is the response of injection standard PCB-155;

c_X is the concentration of compound X;

$c_{PCB\text{-}155}$ is the concentration of injection standard PCB-155.

8.5.3 Measurement

Measure the gas chromatograms of the extracts obtained under 8.4. With the aid of the absolute retention times, identify the peaks of the internal standards. For the other relevant peaks in the gas chromatograms, determine the relative retention times as against both injection standards. Assign the name of a compound if the relative retention time differs from the relative retention time obtained under 8.5.2 by less than 0,2 %.

Confirm the presence of any assigned compound by repeating the gas chromatographic analysis from 8.5.1, using a column with a moderate polar phase (5.13) or using GC/MS.

8.5.4 Calculation

8.5.4.1 Principle

The PCBs and OCPs are quantified using an injection standard added to the extract. Mistakes are probable when a peak of an interfering compound appears at the same position in the chromatogram as that of the injection standard. Therefore two injection standards are added to the extract to determine whether interfering compounds are present or absent. Depending on the separation characteristics of the capillary columns used, suitable injection standards are selected. An injection standard can only be used if its retention time on both columns does not interfere with the retention time of one of the analytes.

The presence or absence of interfering compounds is determined from the measured responses of the injection standards. When no interfering compounds are present in the extract, the ratio between the responses of the injection standards in the extracts is equal to that ratio in the standard solutions. The quotient of these two ratios is called the relative response ratio, R_{rel_r}. When no interfering compounds are present in the extract, the value of R_{rel_r} is in principle 1,00. In this International Standard, it is assumed that no interfering compounds are present in the extract when $R_{rel_r} = 1{,}00 \pm 0{,}05$.

When the value of R_{rel_r} deviates from $1{,}00 \pm 0{,}05$, it is assumed that the response of one of the injection standards is influenced by an interfering compound present in the extract. In this case, the determinands are quantified using the undisturbed injection standard. In practice this can be done by quantifying all extracts with respect to the same injection standard and by calculating the values of R_{rel_r} for all extracts. Only in those cases that $R_{rel_r} > 1{,}05$, the response of the injection standard chosen is influenced by an interfering compound. In such cases, the quantification with respect to the other standard can be carried out by multiplying the calculated contents by the value of R_{rel_r} for the extract considered.

This check on the absence of interfering compounds only considers the possible interference on the position of the injection standards in the chromatogram. The absence of interfering compounds on the positions of the PCB and OCP is determined by confirmation of the presence of the detected compounds (8.4). It is assumed that no interfering compounds are present at the positions of the PCB and OCP in the chromatogram when checks or confirmation tests give results that are within 10 % of the original results.

When the confirmation results in a lower content, it is assumed that the content found earlier is influenced by an interfering compound and in that case the lower content is reported as the *more* probable true value.

8.5.4.2 Calculation procedure

Quantify the PCB and OCP with respect to the injection standard as described below.

Verify the correctness of the response of the injection standards as follows:

Calculate the relative response ratio R_{rel_r} for the PCB and OCP injection standards, by using the following equation:

$$R_{rel_r} = \frac{r_{e,155}}{r_{e,2}} \cdot \frac{r_{s,2}}{r_{s,155}} \quad (3)$$

where

R_{rel_r} is the relative response ratio;

$r_{e,155}$ is the response of PCB-155 in the extract;

$r_{e,2}$ is the response of the selected second injection standard in the extract;

$r_{s,155}$ is the response of PCB-155 in the working standard solution;

$r_{s,2}$ is the response of the selected second injection standard in the working standard solution.

The theoretical value of the relative response ratio R_{rel_r} is 1,00. If $R_{rel_r} = 1{,}00 \pm 0{,}05$, regard the injection standards as correctly quantified and enter the value 1,00 for R_{rel_r} in the formula below. If $R_{rel_r} < 0{,}95$ or $R_{rel_r} > 1{,}05$, the gas chromatogram shall be checked for correct quantification of both injection standards. Take particular note of the peak shapes and peak widths. If the quantification has been correctly carried out, make no correction for $R_{rel_r} < 0{,}95$ ($R_{rel_r} = 1{,}00$), but make a correction for $R_{rel_r} > 1{,}05$ ($R_{rel_r} =$ the calculated value) when calculating the contents.

Quantify the assigned compounds against the injection standard PCB-155 in the following way:

$$\rho_{m,i} = \frac{r_{e,i}}{r_{e,155}} \cdot \frac{m_{e,155}}{r_{rel,i,155}} \cdot \frac{2 f_t}{m_s \cdot \rho_d} \cdot R_{rel_r} \quad (4)$$

where

$\rho_{m,i}$ is the mass fraction found of individual PCB or OCP in the sample, expressed in micrograms per kilogram (µg/kg) on the basis of the dry substance;

$r_{e,i}$ is the response of the PCB or OCP in the extract;

$r_{e,155}$ is the response of injection standard PCB-155 in the extract;

$m_{e,155}$ is the mass of the injection standard PCB-155 in the extract, expressed in nanograms;

$r_{rel,i,155}$ is the relative response of the PCB or OCP as against the PCB-155 in the standard solution;

f_t is the addition factor in accordance with ISO 14507;

m_s is the mass of the analytical sample used for the calculation, in grams;

ρ_d is the mass fraction of dry matter in the field-moist sample, determined by drying at 105 °C in accordance with ISO 11465, in kilograms per kilogram;

R_{rel_r} is the relative response ratio (see 8.5.4).

If the mass fraction of one or more PCB or OCP found exceeds the upper limit of the linear area on the chromatogram for the compound concerned, the extract shall be analysed in dilute form. For this purpose, use the part of the eluate separated under 8.3. Dilute this portion of the extract, until the content falls within the linear area. In accordance with the last sentence of 8.4, add injection standards solution and repeat the analysis as from 8.5.

NOTE For the method of calculation adopted, the dilution factor need not be included in the calculation.

Round off the results in accordance with Table 1.

Table 1 — Rounding off of the results

Mass fraction μg/kg	**Rounded off at** μg/kg
>1 to <100	1
⩾100 to <1000	10

9 Test report

The test report shall contain at least the following data:

a) the information required to identify the sample;

b) a reference to this international standard: ISO 10382;

c) the columns used and the gas chromatographic conditions;

d) the mass fractions of individual PCB and OCP, in micrograms per kilogram, on the basis of dry matter, rounded off in accordance with the table;

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

10 Accuracy

Annex C presents the results of an interlaboratory trial for the evaluation of the Dutch National Standard NEN 5734, which is essentially the same method as this International Standard. Five different soil samples have been investigated by six to ten laboratories. The results presented are the relative standard deviation (rsd) of the reproducibility and the mean value of the contents present in the samples.

Annex A
(informative)

Table of retention times of polychlorinated biphenyls and organochlorine pesticides for two different capillary columns

Table A.1 — Retention times

Component	Retention time min	
	Column A[a]	Column B[b]
1,3,5-trichlorobenzene	12,67	12,16
1,2,4-trichlorobenzene	13,75	13,59
1,2,3-trichlorobenzene	14,81	14,69
1,2,3,5-tetrachlorobenzene	18,25	17,35
1,2,4,5-tetrachlorobenzene	18,25	17,35
1,2,3,4-tetrachlorobenzene	19,82	19,34
Pentachlorobenzene	24,19	23,12
Hexachlorobenzene	29,50	28,38
α-HCH	29,01	30,36
β-HCH	30,22	35,41
γ-HCH	30,63	32,29
Aldrin	35,75	34,82
Dieldrin	40,40	40,76
Isodrin	37,00	36,53
Endrin	41,57	41,86
Telodrin	36,38	35,93
Heptachlorobenzene	34,13	33,55
Heptachloroepoxide (*trans*-)	37,60	37,90
Heptachloroepoxide (*cis*-)		
α-Endosulfan	39,12	39,01
o,p'-DDD	40,55	41,33
p,p'-DDD	42,27	43,92
o,p'-DDE	38,58	38,36
p,p'-DDE	40,05	39,87
o,p'-DDT	42,56	42,28
p,p'-DDT	44,64	45,19
PCB-28	33,32	32,98
PCB-52	34,85	34,54
PCB-101	38,71	38,27
PCB-118	41,89	41,61
PCB-138	45,00	44,54
PCB-153	43,18	42,49
PCB-180	50,41	49,47

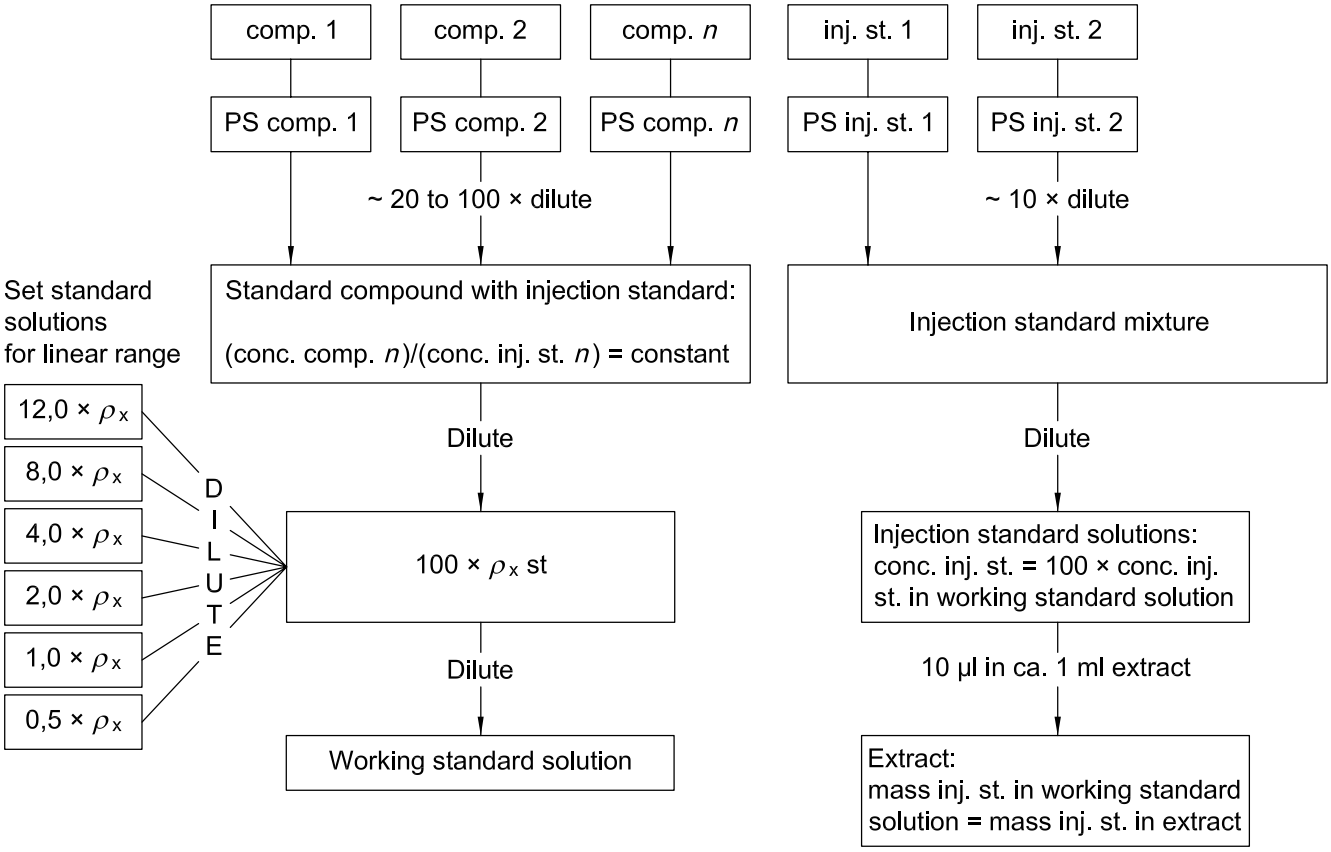
NOTE Depending upon the column used, the co-elution of the stated PCB with other congeners is possible. For co-elution information, consult the column specification or column procedures.

[a] 50 m CP-Sil 8; radius 0,22 mm; film layer 0,12 μm.

[b] 50 m CP-Sil 19; radius 0,22 mm; film layer 0,12 μm.

Annex B
(informative)

Scheme for the preparation of standard solutions including injection standards



Use for ρ_x at first 10 µg/l

comp. *n* is one of the standards 4.9.1 and 4.9.2

inj. st. *n* is one of the injection standards 4.9.3

PS is the individual concentrated primary standard solution (clause 6)

Annex C
(informative)

Results of an interlaboratory trial carried out in the Netherlands

Table C.1 — Results of an intralaboratory trial carried out in the Netherlands

Component	Detection limit, soil (mg/kg)·ρ_d	Detection limit, sediment (mg/kg)·ρ_d	Repeatability, soil *r*, %	Repeatability, sediment *r*, %
PCB				
PCB-28	1,0	1,5	10	10
PCB-52	1,7	1,0	9	9
PCB-101	0,5	0,4	8	7
PCB-118	0,5	0,5	5	10
PCB-138	3,1	0,3	6	4
PCB-153	0,8	0,2	5	10
PCB-180	0,4	0,3	5	5
OCP				
Aldrin	0,2	0,5	13	8
Dieldrin	0,3	0,2	9	9
Endrin	0,4	0,3	8	14
2,4'-DDT/4,4'-DDT	0,4/4,4	0,3/0,2	7/9	34
2,4'-DDD/4,4'-DDT	0,3/0,4	0,14/0,15	7/5	9/6
2,4'-DDE/4,4'-DDE	0,3/0,8	0,13/0,10	10/5	11/12
α-Endosulfan	0,1	0,39	12	7
α-HCH	0,1	0,23	14	12
β-HCH	0,3	0,24	8	12
γ-HCH (lindane)	0,2	0,24	13	11
Heptachlor	0,3	0,51	12	13
trans-heptachloroepoxide	0,2	0,3	9	7
trans/cis-chlordane	0,3/0,3	0,3/0,2	9/9	12/10
Hexachlorobutadiene	0,2	0,7	27	22
Trichlorobenzene	1,6	0,6	7	27
Tetrachlorobenzene	0,7	0,8	13	10
Pentachlorobenzene	0,3	0,5	12	10
Hexachlorobenzene	0,4	0,5	11	7

Table C.2 — Results of an intralaboratory trial carried out in the Netherlands

Component	Matrix									
	Clay SC101		Peat SP111		Sand SS155		Sediment WC 102		Sediment WC 106	
PCB	rsd[a]	$\bar{w}$[b]	rsd[a]	$\bar{w}$[b]	rsd[a]	$\bar{w}$[b]	rsd[a]	$\bar{w}$[b]	rsd[a]	$\bar{w}$[b]
PCB-28	29	3			89	490	59	62	130	64
PCB-52	59	3			61	370	54	37	104	110
PCB-101	27	5			103	700	52	47	52	29
PCB-118	29	4			46	490	47	34		
PCB-138	40	7			23	610	66	41		
PCB-153	27	8			40	480	47	50	142	110
PCB-180	20	5			79	260	57	24	93	30
OCP										
Aldrin			34	110	146	23 000			58	3 100
Dieldrin			49	67	64	12 000			73	6 100
Endrin			49	13	43	1 800			65	550
DDT	49	53	78	690	106	13 0000	47	26	80	23 0000
DDD	49	13	81	110	72	12 000	117	19	51	11 0000
DDE	29	120	42	81	84	12 000	66	16	85	4 400
α-endosulfan			23		56	3 500			61	5 500
α-HCH			74	8	28	390			47	7
β-HCH			49	14	66	2 300			52	530
γ-HCH (lindane)			43	7	29	860			66	32
Heptachlor			76	2	125	580			71	130
Heptachloroepoxide					77	620			67	35
Chlordane										
Hexachlorobutadiene										
Chlorobenzene										
Trichlorobenzene										
Tetrachlorobenzene										
Pentachlorobenzene							65	7		
Hexachlorobenzene							60	14		

[a] Relative standard deviation (%).

[b] Mean mass fraction [$(\mu g/kg)\cdot\rho_d$].

Table C.3 — Results of an interlaboratory trial carried out in the Netherlands

Compound	Number of laboratories	r [a] %	R [b] %
Clay			
PCB	10	4 to 10	20 to 60
OCP	10	4 to 13	30 to 50
Chlorobenzene	10	10 to15	-
Peat			
PCB	9	-	-
OCP	9	-	25 to 80
Chlorobenzene	9	-	-
Sand			
PCB	10	-	25 to 100
OCP	10	-	30 to 150
Chlorobenzene	10	-	-
Sediment			
PCB	10	-	50 to 65
OCP	10	-	50 to 120
Chlorobenzene	10	-	60 to 65
Sediment			
PCB	10	4 to 10	50 to 140
OCP	10	4 to 15	45 to 85
Chlorobenzene	10	5 to 15	-

[a] Repeatability coefficient of variation

[b] Reproducibility coefficient of variation

Annex D
(informative)

Clean-up to remove elemental sulfur and some other organic sulfur compounds

D.1 Reagents

D.1.1 Copper(II) sulfate pentahydrate, $Cu_5SO_4 \cdot 5\ H_2O$.

D.1.2 Hydrochloric acid, HCl, $c = 2$ mol/l.

D.1.3 Zinc granules, particle size 0,3 mm to 1,4 mm.

D.1.4 Anionic detergent aqueous solution, e.g. 35 % mass concentration n-dodecane-1-sulfonic acid, sodium salt, $CH_3(CH_2)_{11}SO_3Na$.

NOTE Other commercially available detergents may also be suitable.

D.1.5 Deoxygenated water.

D.1.6 Acetone.

D.1.7 Hexane.

D.2 Procedure for preparation of pyrogenic copper

WARNING — Pyrogenic copper is spontaneously flammable. Take suitable precautions.

Dissolve 45 g copper(II) sulfate pentahydrate (D.1.1) in 480 ml water containing 20 ml hydrochloric acid (D.1.2) in a 1 000 ml beaker.

Take 15 g of zinc granules (D.1.3), add 25 ml water and one drop of anionic detergent solution (D.1.4) in another 1000 ml beaker.

Stir with a magnetic stirrer at a high speed to form a slurry. Then while stirring at this high speed, carefully add the copper(II) sulfate solution drop by drop using a glass rod.

Hydrogen is liberated and elemental pyrogenic copper is precipitated (red-coloured precipitate).

Continue stirring until hydrogen generation almost ceases. Then allow the precipitated copper to settle. Carefully remove the supernatant water and wash the product with deoxygenated water (D.1.5) three times to eliminate residual salts.

Carefully replace the water with 250 ml acetone (D.1.6) (while continuously stirring the mixture). Repeat this operation twice more to ensure elimination of water.

Repeat the above procedure three times with 250 ml hexane (D.1.7), to ensure elimination of the acetone.

Carefully transfer the copper with hexane into an Erlenmeyer flask and store under hexane. Seal the flask to prevent ingress of air and store in an explosion-proof refrigerator at 2 °C to 8 °C.

The shelf life of the pyrogenic copper is at least two months, after which the clean-up efficiency of the copper will decline. The copper will change colour as the clean-up efficiency decreases.

D.3 Clean-up using pyrogenic copper

Add 1 ml to 2 ml of the extract (in petroleum ether of boiling point range 40 °C to 60 °C) to a centrifuge tube. Add 100 mg pyrogenic copper powder prepared according to the procedure given above. Centrifuge the tube for at least 5 min at approx. 3 500 r/min (ensure that there is no visible turbidity). Remove the extract and if necessary, clean up further using column chromatography.

Bibliography

[1] ISO 383, *Laboratory glassware — Interchangeable conical ground joints*

[2] DIN 38407-3, *Standard methods for the determination of water, waste water and sludge — Jointly determinable substances (Group F) — Part 3: Determination of polychlorinated biphenyls (F3)*

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