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Soil quality — Gas chromatographic determination of the content of volatile aromatic hydrocarbons, naphthalene and volatile halogenated hydrocarbons — Purge-and-trap method with thermal desorption

Qualité du sol — Détermination par chromatographie en phase gazeuse des teneurs en hydrocarbures aromatiques volatils, en naphtalène et en hydrocarbures halogénés volatils — Méthode par purge et piégeage avec désorption thermique

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Contents

Page

Foreword

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

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

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

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

ISO 15009 was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

This second edition cancels and replaces the first edition (ISO 15009:2002), which has been technically revised.

Soil quality — Gas chromatographic determination of the content of volatile aromatic hydrocarbons, naphthalene and volatile halogenated hydrocarbons — Purge-and-trap method with thermal desorption

1 Scope

This International Standard specifies a method for quantitative gas chromatographic determination of volatile hydrocarbons, naphthalene and volatile halogenated hydrocarbons in soil.

This International Standard is applicable to all types of soil.

NOTE In the case of unsaturated peaty soils, absorption of the extraction solution may occur.

The lower limit of determination is dependent on the equipment used and the quality of the methanol grade used for the extraction of the soil sample.

Under the conditions specified in this International Standard, the following limits of determinations apply (expressed on a basis of dry matter):

a) Typical limit of determination when using gas chromatography/flame ionization detection (GC/FID):

— volatile aromatic hydrocarbons: 0,1 mg/kg.

b) Typical limit of determination when using gas chromatography/electron capture detector (GC/ECD):

— volatile halogenated hydrocarbons: 0,01 mg/kg

Lower limits of determination for some compounds can be achieved by using mass spectrometry (MS) with selected ion detection.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 4799, *Laboratory glassware — Condensers*

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 10381-5, *Soil quality — Sampling — Part 5: Guidance on the procedure for the investigation of urban and industrial sites with regard to soil contamination*

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

ISO 11465:1993/Cor 1:1994, *Soil quality — Determination of dry matter and water content on a mass basis — Gravimetric method — Technical Corrigendum 1*

ISO 15680, *Water quality — Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption*

ISO 18512, *Soil quality — Guidance on long and short term storage of soil samples*

ISO 22892, *Soil quality — Guidelines for the identification of target compounds by gas chromatography and mass spectrometry*

3 Principle

Test samples are taken from an untreated field-moist soil sample. To prevent losses of the volatiles, samples are taken as undisturbed as possible in the field with a tube corer or by adding methanol immediately in the field.

The test sample is extracted with methanol. After centrifugation, part of the methanol extract is brought into a purge vessel filled with water. The volatile compounds are purged with nitrogen or helium and adsorbed on a suitable adsorbing agent. The adsorbed compounds are desorbed thermally and by means of a carrier gas flow, whether or not via a cold trap, brought into a gas chromatograph. The various compounds are separated by using a capillary column with an immobile phase of low polarity. Volatile organic compounds are detected with appropriate detectors such as: mass spectrometric detector (MS), flame ionization detector (FID), electron capture detector (ECD), photo ionization detector (PID) or electrolytic conductivity detector (ELCD). Identification and quantification takes place by comparison of retention times and peak heights (or peak areas) towards an internal standard 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 into account incomplete extraction caused by structure and composition of the soil sample.

When using non-specific detectors such as FIDs and ECDs, the confirmation of the identity of the detected compounds and their concentrations should be done by repeating the gas chromatographic analysis using a column of different polarity. When using gas chromatography/mass spectrometry (GC/MS), the identity confirmation and the quantification can be done in a single run.

NOTE 1 This International Standard follows the description of an off-line purge-and-trap method. The use of commercial available online instruments is allowed, provided that equivalent results are obtained during validation of this equipment. With such an instrument, purge and trap occurs on line with gas chromatography and detection. Follow the manufacturer's manual, especially regarding the items composing the apparatus which are listed in 5.1.1 to 5.1.9.

NOTE 2 Other injection techniques, such as static headspace followed by thermal desorption (ISO 22155) or solid-phase micro-extraction (SPME), can be used, provided that their applicability is proven.

4 Reagents

All reagents shall be of recognized analytical grade. Verify whether the reagents are applicable for this specific purpose and free of interfering compounds.

4.1 Water, free of volatile aromatic and volatile halogenated hydrocarbons

Usually boiler water with a temperature of at least 80 °C and 1 day old can be applied. Purging with an inert gas, e.g. a flow of 10 ml/min of nitrogen for 30 min, is another means of removing interfering compounds from water. A sufficient amount of water from the same batch should be available to complete each batch of analyses, including all preparations.

4.2 Internal standard compounds

4.2.1 For the determination of volatile aromatic hydrocarbons, preferably two internal standard compounds shall be selected that do not interfere with compounds present in the sample extract.

Examples of suitable internal standards are

— toluene-D8 (CAS RN 2037-26-5),

— ethylbenzene-D10 (CAS RN 25837-05-2), and

— 2-bromofluorobenzene (CAS RN 1072-85-1).

4.2.2 For the determination of volatile halogenated hydrocarbons, preferably two internal standard compounds shall be selected that do not interfere with compounds present in the sample extract.

Examples of suitable internal standards are:

— 1,4-dichlorobutane (CAS RN 110-56-5);

— *α*,*α*,*α*-trifluorotoluene (CAS RN 98-08-8);

— 2-bromofluorobenzene (CAS RN 1072-85-1).

4.3 Standard compounds

4.3.1 Volatile aromatic hydrocarbons

— benzene (CAS RN 71-43-2);

— toluene (CAS RN 108-88-3);

— ethylbenzene (CAS RN 100-41-4);

— *o*-xylene (CAS RN 95-47-6);

— *m*-xylene (CAS RN 108-38-3);

— *p*-xylene (CAS RN 106-42-3);

— styrene (CAS RN 100-42-5);

— naphthalene (CAS RN 91-20-3).

4.3.2 Volatile halogenated hydrocarbons

— dichloromethane (CAS RN 75-09-2);

— trichloromethane (CAS RN 67-66-3);

— tetrachloromethane (CAS RN 56-23-5);

— 1,1-dichloroethane (CAS RN 75-34-3);

— 1,2-dichloroethane (CAS RN 107-06-2);

— 1,1,1-trichloroethane (CAS RN 79-01-6);

— 1,1,2-trichloroethane (CAS RN 79-00-5);

— 1,2-dichloropropane (CAS RN 78-87-5);

— 1,2,3-trichloropropane (CAS RN 98-18-4);

— *cis*-1,3-dichloropropene (CAS RN 10061-01-5);

— *trans*-1,3-dichloropropene (CAS RN 10061-02-6);

— *cis*-1,2-dichloroethene (CAS RN 156-59-2);

— *trans*-1,2-dichloroethene (CAS RN 156-60-5);

— 3-chloropropene (CAS RN 107-05-1);

— trichloroethene (CAS RN 79-01-6);

— tetrachloroethene (CAS RN 127-18-4);

— monochlorobenzene (CAS RN 108-90-7);

— 1,2-dichlorobenzene (CAS RN 95-50-1).

4.4 Methanol (CAS RN 67-56-1)

The methanol used shall not contain more than 100 µg/l of the individual volatile aromatic compounds and not more than 10 µg/l of the volatile halogenated hydrocarbons that are to be analysed.

4.5 Adsorbing agent

Polymer of 2,6-diphenyl-*p*-phenoxide (40 mesh to 60 mesh) of a grade suitable for thermal desorption.

NOTE 1 2,6-diphenyl-*p*-phenoxide is commercially available as Tenax TA[1)].

NOTE 2 Other adsorbing agents may be used provided that their suitability has been tested.

4.6 Cooling water for purge and trap

The temperature of the cooling water depends on the dimensions of the purge-and-trap equipment (5.1). A temperature of about 10 °C is recommended. A cryostat shall be used if the temperature of the cooling water is too high.

4.7 Inert carrier gas for the gas chromatograph

Helium, nitrogen or argon-methane mixture ultra-pure. Other gases for gas chromatography shall be used in accordance with the instrument manufacturer's instructions.

4.8 Nitrogen or helium as inert gas for the purge equipment

4.9 Standard solutions

4.9.1 Standard stock solutions for volatile aromatic and halogenated compounds in methanol, 4 g/l.

Weigh about 100 mg of the individual standard compounds (4.3) with an accuracy of 0,1 mg into a closed septum flask containing 25 ml of methanol. Transfer the standard compounds into the flask by using a syringe.

NOTE The stock solution is stable for about 6 months when stored at –18 °C.

4.9.2 Internal standard solutions in methanol, 4 g/l.

Weigh about 100 mg of the individual internal standard compounds (4.2.1 and 4.2.2), accurate to 0,1 mg, into a closed septum flask containing 25 ml of methanol. Using a syringe, transfer the standard compounds into the flask.

The containers containing the solutions shall be marked or weighed so that any evaporation losses of the solvent may be recognized. The solutions shall be stored in the dark at a temperature of 4 °C ± 2 °C. Prior to use, they shall be brought to ambient temperature.

4.9.3 Calibration solutions

Calibration solutions containing 0 mg/l to 200 mg/l of each standard (4.3) and the selected internal standard compounds (4.2), 200 mg/l. The calibration solutions are prepared in methanol.

Dilute the amounts indicated in Table 1 of the solutions obtained according to 6.2 and 6.3 with methanol (4.4) to 100 ml.

Other volumes of methanol may be used as long as suitability is proven.

1) Tenax TA is an example of a suitable product available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

Table 1 — Example for preparation of calibration solutions

Calibration solution	Internal standard solution (4.9.2) ml	Standard stock solution (4.9.1) ml	Concentration in the calibration solution mg/l	Quantity in µg/5 µl calibration solution in 100 ml (sample) water
1	5	0	0	0
2	5	1	40	0,2
3	5	2	80	0,4
4	5	3	120	0,6
5	5	4	160	0,8
6	5	5	200	1,0

The total volume of the methanol used for calibration shall be the same as that which will be taken for the methanol extract of the soil sample (see 7.2).

5 Apparatus

Usual laboratory glassware, free of interfering compounds.

All glassware shall be cleaned according to the usual procedures for this type of analysis.

5.1 Purge-and-trap apparatus

The instrument described here is for an off-line purge-and-trap method. As mentioned in Note 1 to Clause 3, commercially available automated systems are allowed provided the requirements of this International Standard are met. Annex D gives some considerations for the use of such systems.

5.1.1 Round-bottom flask with three angled side necks; volume 100 ml.

5.1.2 Gas inlet tube with a tip of sintered glass.

5.1.3 Ball-and-cup stopcock with a polytetrafluoroethylene (PTFE) ring.

5.1.4 Flow adjustment; the nitrogen flow shall be 40 ml/min ± 2 ml/min.

5.1.5 Inlet tube for the thermocouple.

5.1.6 Allin- or Graham-type condenser (see ISO 4799).

5.1.7 Screw cap with cut-off ring made of silicone rubber with PTFE inlay.

5.1.8 Adsorption tubes

Tubes made of glass or stainless steel, filled with at least 240 mg of adsorbing agent (4.5).

The adsorbent is kept in place by using inert material, e.g. silanized glass fibre. The tubes shall be suitable for direct use in connection with the apparatus for thermal desorption. The tubes shall be marked on one side. The tubes shall be provided with caps of inert material, e.g. polyethylene or metal, with screw caps and a PTFE ring, that allow tight closing after purging.

Before use, the adsorbent shall be activated and purified by slowly heating the tubes to 250 °C and keeping them at that temperature for 3 h while a nitrogen flow of 10 ml/min is maintained. The adsorbent shall be cooled under

nitrogen and the tubes analysed. The result of a blank determination shall not exceed the equivalent of 1 ng of a compound to be analysed. When the result is higher than this, the adsorbent shall be desorbed once more.

NOTE The use of commercially available tubes is recommended.

Tubes that are used should not be used again, unless the blank determination meets the above-mentioned requirements.

Care should be taken to avoid cross-contamination. A heavily loaded tube can contaminate a lightly loaded tube in the sample change platform.

5.1.9 Heating block with thermocouple, suitable for heating 100 ml flasks

5.2 Centrifuge, suitable for centrifuging tubes of 200 ml with such a rotation frequency that the radial acceleration is 2 000g to 3 000g.

5.3 Centrifuge tubes, with a volume of 200 ml.

5.4 Capillary columns

Fused silica capillary columns with a non-polar or semipolar stationary phase allowing sufficient separation of the compounds of interest. A thick film of stationary phase increases the efficiency of the more volatile compounds.

Examples are given in 7.4 and Annex A.

5.5 Gas chromatograph, equipped with one or two appropriate detectors. Detectors, such as flame ionization detectors (FIDs), electron capture detectors (ECDs), photo-ionization detectors (PIDs) or electrolytic conductivity detectors (ELCDs), and a mass spectrometer (MS) can be used, depending on the substances to be analysed and their target level of contamination. The mass spectrometer should be capable of operating over the total mass range of interest and being equipped with a data system capable of quantifying ions using selected m/z values.

5.6 Apparatus for thermal desorption

The apparatus used shall meet the following requirements:

— a primary desorption oven with adjustable desorption temperature up to 250 °C and adjustable desorption time;

— a cold trap/secondary desorption oven;

— a connecting tube to the gas chromatograph, with adjustable heating up to 150 °C;

— adjustable carrier-gas flow rate up to 40 ml/min.

NOTE Instruments for thermal desorption are commercially available.

5.7 Electronic integrator or automatic recorder

5.8 Syringe, of volume 5 µl, readable to 0,1 µl, and of volume 50 µl, readable to 1 µl.

5.9 Horizontal shaking machine

A shaking machine with horizontal movement (200 to 300 movements per minute).

6 Sampling, preservation and sample pretreatment

6.1 General

Sampling shall be carried out in accordance with ISO 10381-1 and ISO 10381-5, as appropriate, using equipment according to ISO 10381-2, after coordination with the analytical laboratory.

Samples shall be analysed as soon as possible upon their receipt in the laboratory. If it is necessary to store samples, they shall be stored in cool conditions in accordance with ISO 18512. Samples are not pretreated. Exposure of samples to air, even during sampling, shall be avoided.

Samples for the determination of volatile compounds can be obtained using several techniques. It is strongly recommended that one of the procedures described in 6.2 and 6.3 be used.

Determine the dry matter content of the field-moist sample in accordance with ISO 11465. In case the sampling method in 6.2 is used, a separate sample should be delivered to the laboratory for determination of the dry matter.

6.2 Sampling using vials prefilled with methanol

Transfer a defined volume of soil using an appropriate device into a pre-weighed vial which is filled with a defined volume of methanol (4.4). Prevent leakages by cleaning the top of the vessel before sealing.

The soil samples should be taken from undisturbed material using an appropriate sample cutter of known volume, e.g. a modified 20 ml disposable plastic syringe with the tip cut off. The soil sample should be collected immediately after exposing a fresh soil surface of the drilling core, e.g. of an open-window sampler or the trial pit wall. The incorporation of material-like roots or stones should be avoided as far as possible.

Make sure that the sample is completely covered with methanol (4.4). Then close the cap of the PTFE-coated septum. At least one blank sample on every site shall be prepared in the field by opening the prepared vial for the same time period as necessary for filling with the soil sample. Add methanol (4.4) and close the cap of the vial.

The sampling vials should be kept dark in a cooler (before and after sampling) throughout the whole transportation. For details, see ISO 18512.

6.3 Sampling using coring tube method

This method, which consists of taking an undisturbed sample, greatly reduces or eliminates common losses (e.g. due to evaporation, diffusion, sorption onto plastics). It involves a stainless-steel coring tube of minimal volume 200 ml which is filled *in situ*, retrieved and capped with a non-permeable material, e.g. stainless steel, aluminium foil. The tube should be filled totally.

NOTE This method is not suitable for very stony soils.

Store in cool conditions at a temperature of 2 °C to 8 °C for no longer than 4 d; see ISO 18512.

In the laboratory during sub-sampling, take care that no volatile compounds are lost. Start as soon as possible with the cooled sample. Use the whole content of the coring tube or take a sub-sample with a suitable instrument, e.g. an apple corer, and put it directly into the vial (see 7.2).

7 Procedure

7.1 Blank determination

For each series of samples, a blank determination shall be carried out by treating 50 ml of water (4.1), to which 5 µl to 50 µl of methanol (4.4) has been added, as a sample. Ensure that no contamination occurs from the laboratory atmosphere.

7.2 Extraction

Using sampling procedure 6.2, the extraction is carried out in the field; if using sampling procedure 6.3, the extraction is carried out in the laboratory.

Add a defined amount of test sample (25 g to 50 g), collected as described during sampling (Clause 6) with a sampling device, into a pre-weighed vial (50 ml to 100 ml) (see 6.2) filled with a defined amount of methanol (25 ml to 50 ml) and screw-cap the vial with a PTFE-coated septum. Weigh and place the vials on the horizontal shaking machine (5.9) and shake for 30 min.

Take the tube out of the shaking machine and allow it to stand for 10 min to 15 min to allow solid materials to settle. If the solid materials do not settle on standing, centrifuge for 10 min at a rotation frequency that results in a radial acceleration of 2 000g.

7.3 Purge and trap

Transfer 50 ml of water (4.1) into a purge vessel. Inject 5 µl to 50 µl of the methanol extract, obtained according to 7.2, and 5 µl of the calibration solution (4.9.3) to the bottom of the purge vessel. Heat the sample to 95 °C in about 15 min, then purge it for 30 min with nitrogen at a flow rate of 40 ml/min.

Remove the adsorption tube from the cooler and close with the cap (see 5.1.8).

NOTE 1 Use of automated equipment in which the different steps of the analytical procedure are combined is permitted.

NOTE 2 For dichloromethane, breakthrough on the adsorption tube (5.1.8) can occur. In that case, the purge time should be shortened to 15 min. The total purge volume should not exceed 600 ml.

NOTE 3 Use of other solvent/water ratios is permitted provided their validity is proven.

7.4 Gas chromatographic analysis

7.4.1 Gas chromatographic conditions

Example of gas chromatographic conditions for this analysis:

Stationary phase:	low polarity, e.g. DB 5, DB 624, DB 1701 Restek volatiles [2)]
Film thickness:	2 µm to 5 µm
Column length:	50 m to 60 m
Internal diameter:	0,25 mm to 0,32 mm
Oven temperature:	80 °C during 2,5 min
	10 °C/min up to 280 °C
	280 °C during 10 min
Detector temperature:	300 °C (FID)
Carrier gas:	helium
Gas flow:	20 cm/s to 30 cm/s

2) DB 5, DB 624, DB 1701 Restek volatiles are examples of suitable products available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

When a column with an internal diameter of 0,53 mm or more is used, the cold trap mentioned in 7.3 can be deleted. Using a thinner film thickness has an influence on the starting temperature of the oven. A lower temperature will be necessary.

The separation of the peaks shall be better than 90 % ($R = 2$). Under the described conditions, the critical pair for separation is ethylbenzene and ethylbenzene-D10 in the case of a non-specific detector such as an FID.

Use an electron capture detector (ECD) or an electrolytic conductivity detector (ELCD, hall detector) to detect halogenated hydrocarbons. The sensitivity of an ECD varies with the species to be analysed and can be more sensitive than MS for tri- or tetra-halogenated compounds. A flame ionization detector (FID) can be used as a universal detector for hydrocarbons (aliphatic, aromatic and some halogenated), a photo-ionization detector (PID) can be used for the detection of aromatic compounds.

When using non-specific detectors such as FIDs and ECDs, confirmation of the identity of the detected compounds and their concentrations should be achieved by repeating the gas chromatographic analysis using a column of different polarity.

GC/MS analysis: mass spectrometers can be used to confirm and detect all the volatile organic compounds. Compounds are identified on the basis of their retention times and mass spectra. For the criteria of GC/MS identification and mass-selective detection, ISO 15680 and ISO 22892 shall be consulted.

7.4.2 Calibration

Analyse the complete series of calibration solutions (4.9.3) as follows:

Transfer 50 ml of water (4.1) into a purge vessel. Inject, for example, 5 µl of each calibration solution to the bottom of the purge vessel. Purge for 30 min with a nitrogen gas flow of 40 ml/min, after the sample is heated up to 95 °C in about 15 min. Prepare a calibration graph for each compound by measuring the adsorbed compounds according 7.4.3.

The linear range of each calibration graph is determined as follows:

Calculate, by using linear regression of peak height over concentration, a straight line for the range of the complete series of calibration solutions. Determine the deviations between the measured values and the straight line. When the deviations are less than 5 %, linearity shall be assumed to exist for the complete range. When these deviations are more than 5 %, the range shall be reduced by deletion of the measured value of the highest concentration and again a straight line is calculated by linear regression and checked.

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

Record the gas chromatogram of the working standard after desorption of the adsorbed compounds (7.4.3). Determine, on the basis of this chromatogram, the relative retention times of all volatile aromatic and halogenated hydrocarbons with respect to the internal standard(s).

The relative retention time $t_{\mathrm{rel},x}$ of compound x with respect to the selected internal standard y is defined as:

$$t_{\mathrm{rel},x} = \frac{\left| t_x \right|}{\left| t_{\mathrm{IS}y} \right|} \tag{1}$$

where:

t_x is the absolute retention time of compound x;

$t_{\mathrm{IS}y}$ is the absolute retention time of the internal standard y.

Determine the relative response for all volatile aromatic hydrocarbons with respect to the internal standard ethylbenzene-D10 or another (see 4.2.1) and for all volatile halogenated hydrocarbons with respect to the internal standard 1,4-dichlorobutane or other compounds (see 4.2.2).

The relative response $R_{\text{rel},x,y}$ of compound x with respect to internal standard y is defined as:

$$R_{\text{rel},x,y} = \frac{R_x}{R_{\text{IS}\,y}} \cdot \frac{C_{\text{IS}\,y}}{C_x} \tag{2}$$

where:

R_x is the relative response of compound x;

$R_{\text{IS}y}$ is the relative response of the internal standard y;

$C_{\text{IS}y}$ is the concentration of the internal standard y;

C_x is the concentration of compound x.

7.4.3 Measurement

Desorb the adsorbed compounds (see 7.2) from the adsorption column at a temperature of 240 °C for 10 min, trap these compounds in a cold trap and inject the compounds into the column of the gas chromatograph according to the instructions given by the manufacturer.

Identify the peaks of the internal standards by using the absolute retention times. Determine, for all the other relevant peaks in the gas chromatograms, the relative retention times with respect to the internal standards. Assume that a compound is demonstrated to be present when the relative retention time does not deviate by more than 0,5 % from the relative retention time observed in 7.4.2. In case of the use of a non-specific detector, confirm the presence of a compound by repeating the gas chromatographic analysis using a column with a different polarity.

The volatile compounds shall be quantified with respect to the same selected internal standards used for calibration, e.g. volatile aromatic hydrocarbons with respect to ethylbenzene-D10 and the volatile halogenated hydrocarbons with respect to 1,4-dichlorobutane.

8 Calculation

The volatile aromatic hydrocarbons and volatile halogenated hydrocarbons are quantified by using an internal standard added to the extract. Mistakes can be made when, on the position of the internal standard in the chromatogram of the extract, an interfering compound is present especially when a non-specific detector like a FID or ECD is used. In this case, use the procedure in Annex B to determine if any interfering compounds are present.

Calculate the content of volatile aromatic hydrocarbons and volatile halogenated hydrocarbons in the soil sample by using Equation (3):

$$w_{\text{i}} = \frac{R_{\text{e,i}}}{R_{\text{e,IS}}} \times \frac{m_{\text{e,IS}}}{R_{\text{rel,i,IS}}} \times \frac{100}{m \times w_{\text{d}}} \times \frac{V_{\text{te}} + \dfrac{m \times (100 - w_{\text{d}})}{100}}{V_{\text{pe}}} \tag{3}$$

where:

w_{i} is the content of the individual volatile compound i in the sample, in milligrams per kilogram (mg/kg) of dry mass;

$R_{\text{e,i}}$ is the response of compound i in the sample extract;

$R_{\text{e,IS}}$ is the response of the internal standard used for calculations in the sample extract;

$m_{\text{e,IS}}$ is the mass of the selected internal standard in the extract, in nanograms, ng;

$R_{\text{rel,i,IS}}$ is the relative response of the compound i with respect to the internal standard used for calculations in the working standard;

m is the mass of the test sample used, in grams, g;

w_d is the dry mass content of the sample, as a percentage, %;

V_{te} is the volume of the methanol added to the soil sample, in millilitres, ml;

V_{pe} is the volume of the methanol extract purged, in microlitres, µl.

In the case where, for one or more volatile aromatic or halogenated hydrocarbon compounds, the content found is higher than the upper limit of the linear range for that compound, the sample extract shall be diluted with methanol (4.4) and analysed again.

9 Expression of results

Report the results in milligrams of compound per kilogram of dry soil and up to two significant figures.

10 Precision

Characteristics of the method are established in a validation study. The results are presented in Annex C.

11 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) complete identification of the sample;

c) storage time of samples;

d) expression of results according to Clause 9;

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

Annex A
(informative)

Relative retention time with respect to ethylbenzene-D10 of volatile aromatic hydrocarbons and volatile halogenated hydrocarbons on the following columns: CP-Sil 5 CB and CP-Sil 13 CB

Temperature programme used: 5 min at 40 °C, 10 °C/min to 100 °C, 2 min at 100 °C, 15 °C/min to 250 °C, 5 min at 250 °C.

Compound	Relative retention time	
	CP-Sil 5 CB column	CP-Sil 13 CB column
Dichloromethane	0,212	0,254
trans-1,2-Dichloroethene	0,253	0,247
cis-1,2-Dichloroethene	0,312	0,342
Trichloromethane	0,331	0,360
1,2-Dichloroethane	0,385	0,404
1,1,1-Trichloroethane	0,404	0,434
Benzene	0,441	0,454
Tetrachloromethane	0,453	0,454
1,2-Dichloropropane	0,512	0,539
Trichloroethene	0,536	0,565
cis-1,3-Dichloropropene	0,625	0,692
trans-1,3-Dichloropropene	0,684	0,728
1,1,2-Trichloroethane	0,699	0,740
Toluene D-8	0,720	0,780
Toluene	0,731	0,802
Tetrachloroethene	0,868	0,849
1,3-Dichlorobutane	0,882	0,961
Monochlorobenzene	0,956	1,000
Ethylbenzene D-10	1,000	1,000
Ethylbenzene	1,014	1,018
m/p-Xylene	1,042	1,034
Styrene	1,091	1,113
o-Xylene	1,106	1,121
1,2,3-Trichloropropane	1,124	1,188
Cumene	1,129	1,242
1,3-Dichlorobenzene	1,380	1,396
1,4-Dichlorobenzene	1,391	1,412
1,2-Dichlorobenzene	1,437	1,461
Naphthalene	1,697	1,744

Annex B
(normative)

Check on internal standards

If a non-specific detector is used, the presence of interfering compounds has to be checked.

Therefore, two internal standards are added to the extract to determine whether interfering compounds are present or absent. The presence or absence of interfering compounds can be determined from the measured responses of the internal standards. When no interfering compounds are present in the extract, the ratio between the responses of the internal standards is equal to that in the standard solutions. The quotient of these ratios is called the relative response ratio, RRR. When no interfering compounds are present in the extract, the value of RRR is in principle 1,00. In this International Standard, it is assumed that no interfering compounds are present in the extract when RRR = 1,00 ± 0,05.

When the value of RRR deviates from 1,00 ± 0,05, an interfering compound present in the extract influences the response of one of the internal standards. In that case, the hydrocarbons are quantified by using the undisturbed internal standard. In practice, this can be done by quantifying all extracts with respect to the same internal standard and by calculating the values of RRR for all extracts. Only in those cases when RRR > 1,05 is the response of the internal standard chosen influenced by an interfering compound. In those cases, the quantification with respect to the other standard can be carried out by multiplying the calculated contents with the value of RRR for the extract considered.

This check on the absence of interfering compounds only considers the possible interference on the position of the internal standards in the chromatogram. The absence of interfering compounds on the positions of the volatile aromatic hydrocarbons and the halogenated hydrocarbons is determined by confirmation of the presence of the detected compounds (7.4.3). It is assumed that no interfering compounds are present at the positions of the hydrocarbons in the chromatogram when confirmation results in the same contents being found.

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 most probable true value.

Annex C
(informative)

Validation

This annex gives results of a validation carried out in the Netherlands.

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

Compound	Detection limit		Repeatability		
	FID	ECD	Level	C_V[a] FID	C_V[a] ECD
	mg/kg dm	mg/kg dm	mg/kg dm	%	%
Benzene	0,02	–	1	5,0	–
Toluene	0,06	–	130	2,3	–
Ethylbenzene	0,03	–	50	3,5	–
o-Xylene	0,04	–	25	2,5	–
m-Xylene/*p*-xylene	0,07	–	25	3,1	–
Styrene	0,05	–	100	3,0	–
Naphthalene	0,09	–	50	9,4	–
Dichloromethane	0,2	0,2	20	5,0	2,7
Trichloromethane	0,1	0,02	10	5,3	–
1,1-Dichloroethane	0,1	–	50	3,5	1,6
1,2-Dichloroethane	0,3	1,1	4	4,2	4,7
1,1,1-Trichloroethane	0,5	0,02	50	2,2	–
1,1,2-Trichloroethane	0,4	0,02	50	4,5	–
1,2-Dichloropropane	0,5	0,1	50	1,4	3,7
1,2,3-Trichloropropane	0,4	0,03	50	9,3	9,7
cis-1,3-Dichloropropene	0,3	0,01	50	4,8	–
trans-1,3-Dichloropropene	0,5	0,04	50	2,6	–
cis-1,2-Dichloroethene	0,4	0,5	50	4,2	2,4
trans-1,2-Dichloroethene	0,4	1,1	50	2,8	2,5
3-Chloropropene	0,2	–	1	18,5	–
Trichloroethene	0,2	0,01	60	3,5	–
Monochlorobenzene	0,5	–	10	3,7	–
1,2-Dichlorobenzene	0,3	0,7	10	3,6	8,0

[a] C_V is the variation coefficient.

Table C.2 — Results of an interlaboratory test carried out in the Netherlands

Compound	Sample 1				Sample 2			
	Number of laboratories	Average mg/kg dm	$C_{V,r}$[a] %	$C_{V,R}$[b] %	Number of laboratories	Average mg/kg dm	$C_{V,r}$[a] %	$C_{V,R}$[b] %
Benzene	18	1,10	15	50	14	0,33	20	28
Toluene	15	9,77	17	33	16	0,20	20	39
Ethylbenzene	15	9,15	24	46	16	0,18	18	34
o-Xylene	15	16,0	7,7	75	15	0,38	20	26
m-Xylene and *p*-xylene	16	26,9	9,0	89	15	0,63	22	40
Styrene	7	0,06	12	54	–	–	–	–
Naphthalene	13	3,87	19	73	11	0,09	64	79

[a] $C_{V,r}$ is the repeatability variation coefficient.

[b] $C_{V,R}$ is the reproducibility variation coefficient.

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

Compound	Sample 3				Sample 4			
	Number of laboratories	Average mg/kg dm	$C_{V,r}$[a] %	$C_{V,R}$[b] %	Number of laboratories	Average mg/kg dm	$C_{V,r}$[a] %	$C_{V,R}$[b] %
Dichloromethane	17	5,92	22	88	14	0,16	30	87
Trichloromethane	15	5,56	16	40	–	–	–	–
1,1-Dichloroethane	15	3,18	9,5	45	11	0,06	34	55
1,2-Dichloroethane	17	1,81	20	46	10	0,03	44	63
1,1,1-Trichloroethane	16	0,17	17	39	–	–	–	–
1,1,2-Trichloroethane	14	1,03	15	37	–	–	–	–
cis-1,2-Dichloroethene	13	3,66	8,2	29	9	0,07	16	55
trans-1,2-Dichloroethane	13	3,10	10	31	8	0,05	6,3	63
Trichloroethene	17	0,21	15	73	–	–	–	–
Monochlorobenzene	12	0,13	8,0	35	–	–	–	–

[a] $C_{V,r}$ is the repeatability variation coefficient.

[b] $C_{V,R}$ is the reproducibility variation coefficie.nt