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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

Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

This third edition cancels and replaces the second edition (ISO 15009:2012), 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 aromatic 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 quantification 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 quantification apply (expressed on basis of dry matter):

Typical limit of quantification when using GC-FID:

— Volatile aromatic hydrocarbons: 0,1 mg/kg

Typical limit of quantification when using GC-ECD:

— Volatile halogenated hydrocarbons: 0,01 mg/kg

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

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.

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 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, if necessary, 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 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 FID and ECD, 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 This International Standard follows the description of an ‘off-line purge and trap’ method. The use of commercially 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 manual of the manufacturer especially regarding the items 5.2.1 to 5.2.9.

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 standards

4.2.1 For the determination of volatile aromatic hydrocarbons preferably two internal standards shall be selected from Table 1. They shall not interfere with compounds present in the sample extract.

Table 1 — Examples of suitable internal standards for the determination of volatile aromatic hydrocarbons

Compound name	CAS-RN[a]	EC-N[b]
Toluene-D8	2037–26–5	218–009–5
Ethylbenzene-D10	25837–05–2	247–292–8
2-Bromofluorobenzene	1072–85–1	214–018–3

[a] Chemical Abstracts Service Registry Number

[b] EC-Number

4.2.2 For the determination of volatile halogenated hydrocarbons preferably two internal standards shall be selected from Table 2. They shall not interfere with compounds present in the sample extract.

Table 2 — Examples of suitable internal standards for the determination of volatile halogenated hydrocarbons

Compound name	CAS-RN[a]	EC-N[b]
1,4-Dichlorobutane	110–56–5	203–778–1
α,α,α-Trifluorotoluene	98–08–8	202–635–0
2-Bromofluorobenzene	1072–85–1	214–018–3

[a] Chemical Abstracts Service Registry Number

[b] EC-Number

4.3 Standard compounds

4.3.1 Volatile aromatic hydrocarbons

Table 3 contains volatile aromatic hydrocarbons for use as standard compounds.

Table 3 — Examples of volatile aromatic hydrocarbons suitable as standard compounds

Compound name	CAS-RN[a]	EC-N[b]
Benzene	71–43–2	202–753–7
Toluene	108–88–3	203–625–9
Ethylbenzene	100–41–4	202–849–4
o-Xylene	95–47–6	202–422–2
m-Xylene	108–38–3	203–576–3
p-Xylene	106–42–3	203–396–5
Styrene	100–42–5	202–851–5
Naphthalene	91–20–3	202–049–5

[a] Chemical Abstracts Service Registry Number

[b] EC-Number

4.3.2 Volatile halogenated hydrocarbons

Table 4 contains volatile halogenated hydrocarbons for use as standard compounds.

Table 4 — Examples of volatile halogenated hydrocarbons suitable as standard compounds

Compound name	CAS-RN[a]	EC-N[b]
Dichloromethane	75–09–2	200–838–9
Trichloromethane	67–66–3	200–663–8
Tetrachloromethane	56–23–5	200–262–8
1,1-Dichloroethane	75–34–3	200–863–5
1,2-Dichloroethane	107–06–2	203–458–1
1,1,1-Trichloroethane	71–55–6	200–756–3
1,1,2-Trichloroethane	79–00–5	201–166–9
1,2-Dichloropropane	78–87–5	201–152–2
1,2,3-Trichloropropane	98–18–4	202–486–1
cis-1,3-Dichloropropene	10061–01–5	233–195–8
trans-1,3-Dichloropropene	10061–02–6	208–826–5
cis-1,2-Dichloroethene	156–59–2	205–859–7
trans-1,2-Dichloroethene	156–60–5	205–860–2
3-Chloropropene	107–05–1	203–457–6
Trichloroethene	79–01–6	201–61–04
Tetrachloroethene	127–18–4	204–825–9
Monochlorobenzene	108–90–7	203–628–5
1,2-Dichlorobenzene	95–50–1	202–425–9

[a] Chemical Abstracts Service Registry Number

[b] EC-Number

4.4 Methanol

Methanol (see Table 5) is used as solvent for the extraction of soil samples and for the preparation of standard solutions.

Table 5 — Registration data

Compound name	CAS-RN[a]	EC-N[b]
Methanol	67–56–1	200–659–6

[a] Chemical Abstracts Service Registry Number

[b] EC-Number

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-phenylene oxide (CAS-RN 24938–68–9) 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 (5.2). A temperature of about 10 °C is recommended. A cryostat shall be used if the temperature of the cooling water is too high.

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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.

4.7 Inert 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 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

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 at a temperature of (4 ± 2) °C in the dark. Prior to use, they shall be brought to ambient temperature.

Weigh about 100 mg of the individual internal standards (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.

4.9.3 Calibration solutions

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

Dilute the amounts indicated in Table 6 of the solutions obtained according to 4.9.2 and 4.9.1 with methanol (4.4) to 100 ml.

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

Table 6 — 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 7.3).

4.10 Methanol containing internal standards

Prepare methanol containing a suitable concentration of the internal standards (e.g. 0,4 µg/ml). The concentration shall be such that the end concentration in the water extract in the purge vessel is of the same level as in the calibration solutions.

5 Apparatus

5.1 General

Usual laboratory glassware, free of interfering compounds.

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

5.2 Purge and trap apparatus

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

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

5.2.2 Gas inlet tube with a tip of sintered glass.

5.2.3 Ball and cup stopcock with polytetrafluoroethylene (PTFE) ring.

5.2.4 Flow adjustment with a nitrogen flow set to (40 ± 2) ml/min.

5.2.5 Inlet tube for the thermocouple.

5.2.6 Allihn or Graham type condenser (see ISO 4799).

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

5.2.8 Adsorption 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 PTFE ring, 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.

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.

5.2.9 Heating block, with thermocouple, suitable for heating 100 ml flasks.

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

5.4 Centrifuge tubes with a volume of 200 ml.

5.5 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 7.4.1 and Annex A.

5.6 Gas chromatograph, equipped with one or two appropriate detectors. Detectors like flame ionization detector (FID), electron capture detector (ECD), photo ionization detector (PID) or electrolytic conductivity detector (ELCD) and mass spectrometer (MS) can be used, depending on the substances to be analysed and their target level of contamination. The mass spectrometer should be able 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.

5.7 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.

5.8 Electronic integrator or **automatic recorder** or **computer with chromatographic software**.

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

5.10 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 on their receipt in the laboratory. If it is necessary to store samples, they shall be stored cool 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 to use one of the procedures described in 6.2 and 6.3.

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 pre-filled with methanol

Transfer a defined volume of soil using an appropriate device into a preweighed vial which is filled with a defined volume of methanol already containing internal standards (4.10). 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 containing internal standards (4.10). 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 containing internal standards (4.10) and close the cap of the vial. If blank values are unusually high (more than 50 % of the lowest value of interest) the reason for these high blanks shall be investigated.

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

NOTE The procedure described here assumes that methanol containing internal standards is used. It is also acceptable that the internal standards are added in the methanol in the laboratory at the start of the extraction procedure.

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). This method 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.

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 days; 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 6.2).

7 Procedure

7.1 Blank determination

For each series of samples, a blank determination shall be carried out by treating 50 ml water (4.1), to which 5 µl to 50 µl of methanol containing internal standards (4.10) has been added, as a sample. Ensure that no contamination occurs from the laboratory atmosphere. If blank values are unusually high (more than 50 % of the lowest value of interest) the reason for these high blanks shall be investigated.

7.2 Extraction

Using sampling procedure 6.2, the addition of methanol is carried out in the field; if using sampling procedure 6.3, the addition of methanol is carried out in the laboratory. In both cases the extraction, i.e. the shaking, 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) with a screw cap with PTFE-coated septum and filled with a defined amount of methanol containing internal standards (4.10) (25 ml to 50 ml). Weigh and place the vials on the horizontal shaking machine (5.10) and shake for 30 min.

Take the tube out of the shaking machine and allow it to stand for 10 min to 15 min for the settling of solid materials. If there is no settling of solid materials on standing, centrifuge for 10 min at a rotation frequency that results into a radial acceleration of 2 000*g*.

NOTE The procedure described here assumes that methanol containing internal standards is used. It is also acceptable that the internal standards are added in the methanol at the start of the extraction procedure.

7.3 Purge and trap

Transfer 50 ml water (4.1) into a purge vessel. Inject 5 µl to 50 µl of the methanol extract, obtained according to 7.2, to the bottom of the purge vessel. Heat the sample to 95 °C in about 15 min and then purge the sample 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 (5.2.8).

NOTE 1 Automated equipment in which the different steps of the analytical procedure are combined can be used.

For dichloromethane, break-through on the adsorption tube (5.2.8) can occur. In that case, the purge time should be shortened to 15 min. The total purge volume should not exceed 600 ml.

NOTE 2 Other solvent/water ratios can be used if the validity is proven.

The procedures employed for sample desorption depend on the type of GC interface used. Consult the instructions from the manufacturer of the purge-and-trap system and the supplier of the trap packing material. Trap temperatures up to 220 °C may be employed. However, the higher temperatures will shorten the useful life of the trap. Trap temperatures may vary depending on the trap material.

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. Restek2) columns: Rxi-5MS, Rtx-1701 or Rxi-624SIL MS
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

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2) Restek Rxi-5MS, Rtx-1701 or Rxi-624SIL MS 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.

Detector temperature: 300 °C (FID)

Carrier gas: helium

Gas flow: 20 cm/s to 30 cm/s

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 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 case of a non-specific detector, like 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 as FID and ECD, the 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 also ISO 22892 shall be consulted.

7.4.2 Calibration

Prepare the complete series of calibration solutions according to 4.9.3. Analyse the solutions according to 7.3.

As a minimum, perform a five point calibration for each compound by using one or more internal standards. Based on this, calculate the calibration function for each individual compound.

In this International Standard a linear calibration model is specified. Other calibration models (e.g. a quadratic calibration function) may be used if proven to be suitable.

The calibration function is only valid under specific operational conditions and should be re-established if these conditions are changed. The calibration function does not need to be renewed for every batch of samples. For routine analysis, it is sufficient to check the calibration function by a two-point calibration.

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

Calculate, by using linear regression of peak height (or peak area) 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.

Chose 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 RRT_i of compound i with respect to the selected internal standard s is defined in Formula (1):

$$RRT_i = \frac{|t_i|}{|t_s|} \tag{1}$$

where

t_i is the retention time of compound i;

t_s is the retention time of the internal standard s.

Determine the relative response for all volatile aromatic hydrocarbons with respect to the internal standard ethylbenzene-D10 or other (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).

Establish a linear calibration function for analyte i using the pairs of values y_{ie}/y_{se} and ρ_{ie}/ρ_{se} of the measured calibration solutions in Formula (2):

$$y_{ie} / y_{se} = m_{\text{is}} \cdot \rho_{ie} / \rho_{se} + b_{\text{is}} \tag{2}$$

where

y_{ie} is the (dependent variable) measured response of the analyte i in the calibration, depending on ρ_{ie} e.g. peak area;

y_{se} is the measured response of the internal standards s in the calibration, depending on ρ_{se} e.g. peak area;

ρ_{ie} is the (independent variable) mass concentration of the substance i in the calibration solution, in micrograms per litre, µg/l;

ρ_{se} is the mass concentration of the internal standard s in the calibration solution, in micrograms per litre, µg/l;

m_{is} is the slope of the calibration curve from y_{ie}/y_{se} as a function of the mass concentration ratio ρ_{ie}/ρ_{se}, often called the response factor;

b_{is} is the axis intercept of the calibration curve on the ordinate;

i refers to analyte i;

s refers to the internal standard s;

e refers to values connected to the calibration function.

7.4.3 Measurement

Analyse the spiked water samples prepared according to 7.3 in the same manner as described for the calibration (7.4.2). 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 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

8.1 Calculation of the concentration of a volatile compound in the water sample

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 in order to determine if interfering compounds are present.

Calculate the mass concentration of analyte *i* in the spiked water sample using Formula (3) after solving Formula (2):

$$\rho_i = \left(\left(y_i / y_s - b_{\text{is}}\right) \cdot \rho_s\right) / m_{\text{is}} \tag{3}$$

where

ρ_i	is the mass concentration of the analyte *i* in the spiked water sample, in micrograms per litre, µg/l = $c_{i\text{W}}$;
y_i	is the measured response of the analyte *i* in the water sample, e.g. peak area;
y_s	is the measured response of the internal standard *s* in the water sample, e.g. peak area;
ρ_s	is the mass concentration of the internal standard *s* in the water sample, in micrograms per litre, µg/l;
m_{is}	is the slope of the calibration curve from y_{ie}/y_{se} as a function of the mass concentration ratio ρ_{ie}/ρ_{se}, often called the response factor, as determined under calibration (7.4.2).
b_{is}	is the axis intercept of the calibration curve on the ordinate, as determined under calibration (7.4.2).

8.2 Calculation of the concentration of a volatile compound in the soil sample

Calculate the content of a specific volatile compound in the soil sample by using Formula (4):

$$w_{i\text{dm}} = \frac{\rho_{i\text{W}} \cdot V_{\text{E}} \cdot V_{\text{W}}}{V_{\text{a}} \cdot m_{\text{dm}}} \tag{4}$$

where

$w_{i\text{dm}}$	is the content of the individual volatile compound *i* in the sample, in milligrams per kilogram, mg/kg, of dry matter;
$\rho_{i\text{W}}$	is the mass concentration of the analyte *i* in the spiked water sample, in micrograms per litre, µg/l;
m_{dm}	is the mass of the test sample of dry matter used for extraction, in grams, g;
V_{E}	is the total volume of the extract i.e. (volume of methanol added to the soil sample + volume of water present in the field moist sample obtained from the determination of dry matter content according to ISO 11465) in millilitres, ml;
V_{a}	is the volume of the aliquot of methanol extract used for the spiking of water sample for headspace measurement in microlitres, µl;
V_{W}	is the volume of the spiked water sample for headspace measurement in millilitres, ml.

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 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 at least the following information:

a) a reference to this International Standard (ISO 15009);

b) 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 following columns: CP-Sil 5 CB and CP-Sil 13 CB

Table A.1 shows examples of suitable target and qualifier ions and relative retention times with respect to ethylbenzene-D10 of volatile aromatic hydrocarbons and volatile halogenated hydrocarbons on the columns CP-Sil 5 CB and CP-Sil 13 CB[3].

Table A.1 — Example of suitable target and qualifier ions and relative retention times with respect to ethylbenzene-D10 of volatile aromatic hydrocarbons and volatile halogenated hydrocarbons on following columns: CP-Sil 5 CB and CP-Sil 13 CB

Compound	**Relative retention time**		**Target** *m/z*	**Qualifier** *m/z*
	CP-Sil 5 CB column	**CP-Sil 13 CB column**		
Dichloromethane	0,212	0,254	129	127
trans-1,2-Dichloroethene	0,253	0,247	96	61
cis-1,2-Dichloroethene	0,312	0,342	96	61
Trichloromethane	0,331	0,360	83	85
1,2-Dichloroethane	0,385	0,404	62	64
1,1,1-Trichloroethane	0,404	0,434	97	99
Benzene	0,441	0,454	78	77
Tetrachloromethane	0,453	0,454	117	119
1,2-Dichloropropane	0,512	0,539	63	62
Trichloroethene	0,536	0,565	130	132
cis-1,3-Dichloropropene	0,625	0,692	75	110
trans-1,3-Dichloropropene	0,684	0,728	75	110
1,1,2-Trichloroethane	0,699	0,740	97	99
Toluene D-8	0,720	0,780	98	100
Toluene	0,731	0,802	91	92
Tetrachloroethene	0,868	0,849	166	164
1,3-Dichlorobutane	0,882	0,961	55	90
Monochlorobenzene	0,956	1,000	112	77
Ethylbenzene D-10	1,000	1,000	101	116
Ethylbenzene	1,014	1,018	106	91
m-Xylene/*p*-Xylene	1,042	1,034	106	91
Styrene	1,091	1,113	104	103
o-Xylene	1,106	1,121	106	91
1,2,3-Trichloropropane	1,124	1,188	110	75
NOTE Temperature programme used: 5 min at 40 °C, 10 °C/min to 100 °, 2 min at 100 °C, 15 °C/min to 250 °C, 5 min at 250 °C.				

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[3] Restek CP-Sil 5 CB and CP-Sil 13 CB 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 these products.

Table A.1 *(continued)*

Compound	**Relative retention time**		**Target** m/z	**Qualifier** m/z
	CP-Sil 5 CB column	**CP-Sil 13 CB column**		
Cumene	1,129	1,242	105	120
1,3-Dichlorobenzene	1,380	1,396	146	148
1,4-Dichlorobenzene	1,391	1,412	146	148
1,2-Dichlorobenzene	1,437	1,461	146	148
Naphthalene	1,697	1,744	128	127
NOTE Temperature programme used: 5 min at 40 °C, 10 °C/min to 100 °, 2 min at 100 °C, 15 °C/min to 250 °C, 5 min at 250 °C.				

Annex B
(normative)

Check on internal standards

If a non-specific detector is used the presence of interfering compounds have 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 ratio 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 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.