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Soil quality — Gas chromatographic determination of volatile aromatic and halogenated hydrocarbons and selected ethers — Static headspace method

Qualité du sol — Dosage des hydrocarbures aromatiques et halogénés volatils et de certains éthers par chromatographie en phase gazeuse — Méthode par espace de tête statique

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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.

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 22155:2011), which has been technically revised.

Soil quality — Gas chromatographic determination of volatile aromatic and halogenated hydrocarbons and selected ethers — Static headspace method

1 Scope

This International Standard specifies a static headspace method for quantitative gas chromatographic determination of volatile aromatic and halogenated hydrocarbons and selected aliphatic ethers in soil.

This International Standard is applicable to all types of soil.

The limit of quantification is dependent on the detection system 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 quantifications apply (expressed on basis of dry matter).

Typical limit of quantification when using GC-FID:

- volatile aromatic hydrocarbons: 0,2 mg/kg;
- aliphatic ethers as methyl tert.-butyl ether(MTBE) and tert.-amyl methyl ether (TAME): 0,5 mg/kg.

Typical limit of quantification when using GC-ECD:

- volatile halogenated hydrocarbons: 0,01 mg/kg to 0,2 mg/kg.

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

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 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, *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. An aliquot of the methanol extract is transferred into a headspace vial with a defined amount of water and sealed. The temperature of the vials is stabilized in a thermostatic system to a temperature within the range 50 °C to 80 °C to achieve specified equilibrium conditions. Gas chromatographic analysis of the volatile compounds in gaseous phase in equilibrium with the water in the vials is carried out by using headspace injection and an appropriate capillary column. Volatile organic compounds are detected with appropriate detectors 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 is made by comparison of retention times and peak heights (or peak areas) comparing to the internal standard added.

When using non-specific detectors 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.

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 organic compounds

Water, free from volatile organic contaminants shall show negligible interferences in comparison with the smallest concentration to be determined. 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

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

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

[a] Chemical Abstracts Service Registry Number.

[b] EC-Number.

Table 4 *(continued)*

Compound name	**CAS-RN**[a]	**EC-N**[b]
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 Aliphatic ethers

Table 5 contains aliphatic ethers for use as standard compounds.

Table 5 — Examples of aliphatic ethers suitable as standards compounds

Compound name	**CAS-RN**[a]	**EC-N**[b]
methyl tert.-butyl ether (MTBE)	1634–04–4	216–653–1
tert.-amyl methyl ether (TAME)	994–05–8	213–611–4

[a] Chemical Abstracts Service Registry Number.

[b] EC-Number.

NOTE This method can also be used for volatile organic compounds not included in this International Standard, provided it has been validated for each new compound.

4.5 Methanol

Methanol (see Table 6) is used as solvent for the extraction of soil samples and for the preparation of standard solutions.

Table 6 — 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.

NOTE Other solvents which are readily soluble in water and do not interfere with the analytical process can be used as well, for example dimethylformamide (DMF) and dimethylsulfoxide (DMSO).

4.6 Gases for gas chromatography

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

4.7 Standard solutions

4.7.1 Standard stock solutions for the volatile compounds in methanol

Prepare the stock solutions by adding defined amounts (e.g. 100 µl) of each standard compound (4.3, 4.4 and 4.5) with a microlitre syringe (5.8). Immerse the tip of the needle in the solvent methanol and weigh with an accuracy of 0,1 mg.

NOTE 1 A convenient concentration (4 mg/ml) of the standard stock solution is obtained by weighing 100 mg of the standard substance and dissolving it in 25 ml of the solvent. The stock solution is stable for about 6 m when stored at −18 °C.

NOTE 2 For practical reasons, mixed standard stock solutions can also be prepared.

4.7.2 Internal standard stock solutions in methanol

The containers containing the solutions shall be 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.

Prepare the internal standard stock solutions with the individual internal standard compounds (4.2.1 and 4.2.2) in the same procedure as in 4.7.1.

4.7.3 Intermediate mixed standard solutions

Prepare intermediate mixed standard solutions by mixing a defined volume of each individual standard stock solution or a mixed standard stock solution and dilute with methanol.

NOTE A typical concentration is 40 µg/ml.

Store the intermediate mixed standard solutions at (4 ± 2) °C not longer than 3 m.

4.7.4 Working standard solutions

Prepare at least five different concentrations (e.g. from 0,2 µg/ml to 3,2 µg/ml) by suitable dilutions of the intermediate mixed standard solutions adding 50 µl to 500 µl of 4.7.3 to methanol (10 ml) using a microlitre syringe (5.8).

4.7.5 Working internal standard solutions

Prepare the internal standard solutions of defined concentration (e.g. 0,4 µg/ml) as described in 4.7.3.

4.7.6 Aqueous calibration standard solutions

Prepare the calibration solutions (see Table 7) by adding a defined amount (e.g. 50 µl) of working standard solutions and internal standard solutions to a defined volume (e.g. 10 ml) of water in an appropriate headspace vial. Use a syringe and immerse the top of the needle in the water. Seal the vial tightly with a crimp cap fitted with polytetrafluoroethylene (PTFE) coated septum. The total volume of the methanol used for calibration shall be the same which will be taken for the methanol extract of the soil sample (see 7.3). Make sure that the content of the organic solvent in the final aqueous calibration standard solution does not exceed the volume fraction of 2 %.

Table 7 — Example for the preparation of calibration solutions

Calibration solution	Working standard solution (4.7.4) µl	Working internal standard standards (4.7.5) µl	Concentration in working standard solution µg/ml	Quantity in calibration solution of 10 ml (sample) water ng	Concentration in aqueous calibration solution µg/l
1	50	50 (methanol)	0	0	0
2	50	50	0,2	10	1
3	50	50	0,4	20	2
4	50	50	0,8	40	4
5	50	50	1,6	80	8
6	50	50	3,2	160	16

4.8 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 headspace vial is of the same level as in the calibration standards.

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 Glass vials with suitable septum.

Glass vials (50 ml to 100 ml) and screw cap, fitted with a PTFE-coated septum for field moist soil samples taken in the field. Glass vials (10 ml for 5 ml water and 22 ml for 10 ml water) with a PTFE-coated septum and crimped metallic cap, compatible with the headspace system connected to an appropriate gas chromatographic system. The vials shall be capable of being hermetically sealed in the field as well as at elevated temperatures.

5.2 Crimping pliers.

5.3 Headspace system.

This method was developed for using a totally automated equilibrium headspace analyser available from several commercial sources. The system used shall meet the following specifications.

The system shall be capable of keeping the vials at a constant temperature (between 50 °C and 80 °C).

The system shall be capable of transferring accurately a representative portion of the headspace into a gas chromatograph fitted with capillary columns.

5.4 Shaking machine, with horizontal movement (200 to 300 movements per minute).

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 separation of more volatile compounds.

Examples are given in 7.4.1.

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 Electronic integrator or computer with chromatographic software.

5.8 Syringe, volume 5 µl, 10 µl, 50 µl, 100 µl, 250 µl, and 500 µl.

5.9 Centrifuge, with a capacity of a rotation frequency that results into a radial acceleration of at least 2000*g*.

6 Sampling, preservation, and sample pretreatment

6.1 General

Sampling shall be carried out according to ISO 10381-1 using equipment according to ISO 10381-2 after coordination with the analytical laboratory.

Samples shall be stored cool according to ISO 18512 (2 °C to 8 °C). Samples are not pretreated. Exposure of samples to air, even during sampling, shall be avoided as far as possible.

Sampling for volatile compounds can be carried out with several techniques. It is strongly recommended to use one of the following procedures described in 6.2 and 6.3 in order to prevent losses by volatilization.

Determine the dry matter content of the field moist sample according to 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 (4.8). 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 (4.8). 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 the filling with soil sample. Add methanol containing internal standards (4.8) 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, by 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 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 cool at a temperature of 2 °C to 8 °C no longer than 4 d; see ISO 18512.

In the laboratory during sub-sampling, take care that no volatile compounds are lost. 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 solvent blank determination shall be carried out by adding 10 µl to 100 µl of methanol containing internal standards (4.8) to 5 ml to 10 ml of water (4.1), as it is done with 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 in 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 (4.8) (25 ml to 50 ml). Weigh and place the vials on the horizontal shaking machine (5.5) 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 (5.10) for 10 min at a rotation frequency that results into a radial acceleration of 2000 *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 Head-space analysis

Transfer a defined volume of water (5 ml to 10 ml) into a head space vial. Inject 10 µl to 100 µl of the methanol extract, obtained according to 7.2 to the bottom of the vial and seal the cap fitted with PTFE-coated septum tightly. From this on, after preparing the spiked water samples, proceed to the analysis. Prepare the calibration samples in the same way with the same volume 10 µl to 100 µl of the calibration solutions (4.7.6).

NOTE 1 A lower detection limit could be achieved by addition of sodium chloride, NaCl, or other salts (e.g. 3 g per 10 ml).

Place the vials of water samples in the thermostated tray of the headspace system at a fixed temperature in the range from 50 °C to 80 °C, for at least 30 min and for the same time for all vials.

NOTE 2 For specific equipment working at equilibrium, the time required to reach equilibrium can vary, depending on the volatile organic substance and the volume of the vials used. Experience has shown that at least 30 min are necessary.

7.4 Gas chromatographic analysis

7.4.1 General

Example of gas chromatographic conditions for this analysis:

Stationary phase:	low polarity e.g. Restek[a] columns: Rxi-5MS, Rtx-1701 or Rxi-624SIL MS
Film thickness:	1 µm to 3 µm
Column length:	50 m to 60 m
Internal diameter:	0,25 mm to 0,32 mm
Oven temperature:	40 °C during 4 min
	4 °C/min up to 200 °C
	200 °C during 10 min
Detector temperature:	300 °C (FID)
Carrier gas:	Helium
Gas flow:	20 cm/s to 30 cm/s
Inlet:	200 °C
Split ratio:	1:20

[a] 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 these products.

Example for headspace sampler conditions:

Oven:	80 °C
Needle or transfer line:	90 °C
Sampling volume:	1 ml
Vial equilibrium time:	30 min

NOTE The separation of the peaks should be better than 90 % (R = 2). Under the described conditions, the critical pair for separation is ethylbenzene and ethylbenzene-D10.

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 aqueous calibration solutions according to 4.7.6 and 7.3. 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.

Record the gas chromatogram of the calibration standard solutions (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 (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):

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

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 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 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):

$$\rho_\mathrm{i} = \left(\left(y_\mathrm{i} / y_\mathrm{s} - b_\mathrm{is}\right) \cdot \rho_\mathrm{s}\right) / m_\mathrm{is} \tag{3}$$

where

ρ_i is the mass concentration of the analyte *i* in the spiked water sample, in micrograms per litre, µg/l = c_iW;

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 $y_\mathrm{ie}/y_\mathrm{se}$ as a function of the mass concentration ratio $\rho_\mathrm{ie}/\rho_\mathrm{se}$, 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):

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

where

w_{idm}	is the content of the individual volatile compound *i* in the sample, in milligrams per kilogram, mg/kg, of dry matter;
ρ_{iW}	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.

9 Expression of results

Report 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

This test report shall contain at least the following information:

a) the test method used, together with a reference to this International Standard, i.e. ISO 22155:2016;

b) identification of the sample;

c) the storage time of samples;

d) the 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 times with respect to ethylbenzene-D10 of volatile aromatic hydrocarbons and volatile halogenated hydrocarbons — Examples of suitable target and qualifier ions

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 CB1).

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
NOTE 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.				

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1) 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		
1,2,3-Trichloropropane	1,124	1,188	110	75
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 °C, 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 at least two internal standards (1 for the aromatic and 1 for the halogenated compounds) 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 that *RRR* > 1,05 the response of the internal standard chosen is 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 (7.4.2). It is assumed that no interfering compounds are present at the positions of the hydrocarbons in the chromatogram when confirmation results into 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.

Annex C
(informative)

Validation (general)

Annex C gives results of a validation carried out in Germany. Table C.1 shows the results for an inter laboratory comparison of volatile compounds in soil. The results on BTEX and ethers with high level contamination are presented in Table C.2 and with low level contamination in Table C.3. The results on halogenated hydrocarbons with high level contamination are presented in Table C.4 and with low level contamination in Table C.5.

Table C.1 — Results of an inter laboratory comparison carried out in Germany (Volatile organic compounds in soil, November 1999)

Parameter	Soil sample[a]					Soil sample under methanol layer[b]				Spiking[c]	Reference value[d]	
	x	s_R	s_r	l	n	x	s_R	l	l	f	x	s_r
Dichloromethane	0,87	52,5	26,3	7	27	3,20	50,8	10	10	9,6	1,04	20,3
Trichloromethane	16,2	40,0	16,4	7	27	40,5	55,4	11	11	109,0	30,2	15,4
1,2-Dichloroethane	20,6	35,2	12,7	7	26	29,3	38,5	11	11	66,8	18,0	12,2
Trichlororethene	1,45	47,3	17,4	7	26	2,70	39,7	11	11	5,2	1,69	12,6
Tetrachloroethene	13,4	19,5	12,6	7	27	21,8	45,0	11	11	37,6	24,5	8,0
Sum volatile halogenated hydrocarbons	52,8	26,3	12,7	7	27	97,2	43,2	11	11	228,2	75,4	11,9
Benzene	2,71	77,1	16,5	8	31	4,48	37,4	12	12	8,6	1,85	16,7
Toluene	11,4	37,7	17,0	8	29	17,0	42,1	12	12	27,6	16,1	8,9
Ethylbenzene	77,5	41,9	12,2	8	31	102,7	50,6	12	12	115,2	100	4,9
m-Xylene/*p*-Xylene	13,3	31,1	10,9	8	31	15,3	36,5	12	12	18,1	22,4	4,4
o-Xylene	68,1	29,5	7,2	8	30	77,1	33,3	12	12	102,2	108	4,0
Sum BTX	173,2	32,6	12,0	8	31	216,6	32,8	12	12	271,8	248	4,7
Sum volatile halogenated hydrocarbons/ BTX	224,8	30	9,1	7	28	314,7	33,9	11	11	500,0	324	6,3

Explanation of symbols:

x is the average value in milligrams per kilogram dry matter;

s_R is the reproducibility variation coefficient in percent;

s_r is the repeatability variation coefficient in percent;

l is the number of laboratories;

n is the number of values taken for evaluation;

[a] Evaluation of independent results from 4 soil samples according to ISO 5725-5;

[b] Average value x and reproducibility variation coefficient s_R, each laboratory received one soil sample under methanol layer.

[c] Spiked value, calculated theoretically from gravimetric values, in milligrams per kilogram, mg/kg.

[d] "*Reference value*" is the average value of the homogeneity measurements of the samples immediately after bottling, with n = 9.