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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

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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 22155 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 22155:2005), 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 determination 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 determination apply (expressed on the basis of dry matter):

Typical limit of determination when using gas chromatography/flame ionization detection (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 determination when using gas chromatography/electron capture detection (GC/ECD):

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

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

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 10381-1:2002, *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 theral 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 in as undisturbed a way 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, such as a mass spectrometry detector (MS), flame ionization detector (FID), electron capture detector (ECD), photo ionization detector (PID) or electrolytic conductivity detector (ELCD).

Identification and quantification are made by comparison of retention times and peak heights (or peak areas), comparing to the internal standard added.

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.

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 contaminants, showing 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 standard compounds

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

Examples of suitable internal standards are:

— toluene-D8 (CAS-RN[1)] 2037-26-5);

— ethylbenzene-D10 (CAS-RN 25837-05-2);

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

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

1) CAS-RN: Chemical Abstracts System Registry Number

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 Volatile aromatic hydrocarbons

Compound	CAS-RN
Benzene	71-43-2
Toluene	108-88-3
Ethylbenzene	100-41-4
o-Xylene	95-47-6
m-Xylene	108-38-3
p-Xylene	106-42-3
Styrene	100-42-5
Naphthalene	91-20-3

4.4 Volatile halogenated hydrocarbons

Compound	CAS-RN
Dichloromethane	75-09-2
Trichloromethane	67-66-3
Tetrachloromethane	56-23-5
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1,1-Trichloroethane	79-01-6
1,1,2-Trichloroethane	79-00-5
1,2-Dichloropropane	78-87-5
1,2,3-Trichloropropane	98-18-4
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
cis-1,2-Dichloroethene	156-59-2
trans-1,2-Dichloroethene	156-60-5
3-Chloropropene	107-05-1
Trichloroethene	79-01-6
Tetrachloroethene	127-18-4
Monochlorobenzene	108-90-7
1,2-Dichlorobenzene	95-50-1

4.5 Aliphatic ethers

Compound	CAS-RN
Methyl *tert*-butyl ether (MTBE)	1634-04-4
tert-Amyl methyl ether (TAME)	994-05-8

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.

4.6 Methanol (CAS-RN 67-56-1), as a solvent for the extraction of soil samples and for the preparation of standard solutions.

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).

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

4.8 Standard solutions

4.8.1 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. Immerse the tip of the needle in the methanol solvent 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 months when stored at −18 °C.

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

4.8.2 Internal standard stock solutions in methanol

Prepare the internal standard stock solutions with the individual internal standard compounds (4.2.1 and 4.2.2) with the same procedure as in 4.8.1.

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 °C ± 2 °C in the dark. Prior to use, they shall be brought to ambient temperature.

4.8.3 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 °C ± 2 °C for not longer than 3 months.

4.8.4 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 these concentrations to methanol (10 ml) using a microlitre syringe.

4.8.5 Working internal standard solutions

Prepare the internal standard solutions of defined concentration (e.g. 0,4 µg/ml) as described in 4.8.3 and 4.8.4.

4.8.6 Aqueous calibration standard solutions

Prepare the calibration solutions (see Table 1) 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 a polytetrafluoroethylene (PTFE) coated septum. The total volume of the methanol used for calibration shall be the same as 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 1 — Example for the preparation of calibration solutions

Calibration solution	**Working standard solution** (4.8.4) µl	**Working standard internal solution** (4.8.5) 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

5 Apparatus

Use ordinary 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 accurately transferring a representative portion of the headspace into a gas chromatograph fitted with capillary columns.

5.4 Shaking machine

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

5.5 Capillary columns

Fused silica capillary columns with a non-polar or semi-polar 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.

5.6 Gas chromatograph

A 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 to operate 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, of volume 5 µl, 10 µl, 50 µl, 100 µl, 250 µl and 500 µl.

6 Sampling, preservation and sample pretreatment

6.1 General

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

Samples shall be analysed as soon as possible. Samples shall be stored cool in accordance with ISO 18512. 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 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 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 preweighed vial which is filled with a defined volume of methanol (4.6). 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 (4.6). 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 (4.6) 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, 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 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 solvent blank determination shall be carried out by adding 10 µl to 100 µl of methanol (4.6) to 5 ml to 10 ml of water (4.1), as is done with a sample. Ensure that no contamination occurs from the laboratory atmosphere.

7.2 Extraction

Using the sampling procedure in 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 preweighed 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 PTFE-coated septum. Weigh and place the vials on the horizontal shaking machine (5.4) 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 in a radial acceleration of 2 000 g.

7.3 Headspace analysis

Transfer a defined volume of water (5 ml to 10 ml) into a headspace vial. Inject 10 µl to 100 µl of the methanol extract, obtained according to 7.2, to the bottom of the vial and seal tightly with a crimp cap fitted with a PTFE-coated septum. Then, after preparing the spiked water samples, proceed to the analysis in a very similar way to water analysis. Prepare the calibration samples in the same way with the same volume 10 µl to 100 µl of the calibration solutions (4.8.6).

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

NOTE 1 A lower detection limit could be achieved by addition of sodium chloride, NaCl (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 is necessary.

7.4 Gas chromatographic analysis

7.4.1 General

Example of gas chromatographic conditions for this analysis:

Stationary phase:	low polarity, e.g. DB 5, DB 624, DB 1701 Restek[2)] volatiles,
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 for 4 min
	4 °C/min up to 200 °C
	200 °C for 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

Example for headspace sampler conditions:

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

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 such 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.

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

For 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 aqueous calibration solutions (4.8.6) which are prepared as follows:

Transfer 10 ml of water (4.1) into a headspace vial. Inject 50 µl of each working standard solution and each internal standard solution to the bottom of the headspace vial and seal tightly with a crimp cap fitted with PTFE-coated septum.

Place the vials on the tray of the headspace sampler. After the sample is heated up to 80 °C for 30 min, a gas chromatographic analysis is done with headspace injection. As a minimum, perform a five-point calibration for each compound by using one or more internal standard compounds. Based on this, calculate the calibration function for each individual compound.

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 (see 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_x of compound X with respect to the selected internal standard Y is defined in Equation (1):

$$RRT_x = \frac{t_x}{t_y} \tag{1}$$

Determine the relative response for all volatile aromatic hydrocarbons with respect to the internal standard ethylbenzene-D10 or other compound (see 4.2.1) and for all volatile halogenated hydrocarbons with respect to the internal standard 1,4-dichlorobutane or other compound (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 Equation (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 standard compound "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 compound "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 compound “s”;

e refers to values connected to the calibration function.

7.4.3 Measurement

Prepare the spiked water samples for measurement by adding 50 µl of the soil extract and 50 µl of the working internal standard solutions to 10 ml of water in headspace vials and analyse in the same manner as described in the calibration (7.4.2).

Identify the peaks of the internal standards by using the absolute retention times. Determine the relative retention times for all the other relevant peaks in the gas chromatograms 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. If a non-specific detector is used, 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 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 Equation (3) after solving Equation (2):

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

where

ρ_{i} is the mass concentration of the analyte “i” in the spiked water sample, in micrograms per litre, µg/l;

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 compound “s” in the water sample, e.g. peak area;

ρ_{s} is the mass concentration of the internal standard compound “s” in the water sample, in micrograms per litre, µg/l;

m_{is} is the slope of the calibration curve from $y_{\mathrm{ie}}/y_{\mathrm{le}}$, 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 Equation (4):

$$w_{idm} = \frac{\rho_{iW} \cdot V_E \cdot V_W}{V_a \cdot m_{dm}} \quad (4)$$

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 in accordance with ISO 11465), in millilitres, ml;

V_a is the volume of the aliquot of methanol extract used for the spiking of the 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 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

This test report shall contain at least the following information:

a) the test method used, together with a reference to this International Standard (ISO 22155:2011);

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 times with respect to ethylbenzene-D10 of volatile aromatic hydrocarbons and volatile halogenated hydrocarbons

Table A.1 — Relative retention times 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[3)]

Temperature programme used: 5 min at 40 °C, 10 °C/min up to 100 °C, 2 min at 100 °C, 15 °C/min up 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-D8	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-D10	1,000	1,000
Ethylbenzene	1,014	1,018
m/*p*-Xylene	1,042	1,034
Styrene	1,091	1,113

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 document and does not constitute an endorsement by ISO of these products.

Table A.1 (*continued*)

Compound	Relative retention time	
	CP-Sil 5 CB column	CP-Sil 13 CB column
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 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 $\pm$ 0,05.

When the value of RRR deviates from 1,00 $\pm$ 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 (see 7.4.2). 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.

Annex C
(informative)

Validation (general)

Table C.1 — Results of an interlaboratory 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
Trichloroethene	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 of 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/*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 of BTEX	173,2	32,6	12,0	8	31	216,6	32,8	12	12	271,8	248	4,7
Sum of volatile halogenated hydrocarbons/BTEX	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 of 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 in accordance with ISO 5725-5.

[b] Average value x and reproducibility variation coefficient s_R; each laboratory received one soil sample under a 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.

Table C.2 — Results of an interlaboratory comparison carried out in Germany (BAM Validation intercomparison 2002) on BTEX and ethers (soil overlaid with methanol) – high-level contamination

Parameter	l	n	n_a	x_{ref}	x	R	σ_r	$C_{V,r}$	σ_R	$C_{V,R}$	Limit of determination mg/kg (GC/FID)
Benzene	12	24	16,67	15,86	15,04	94,84	0,71	4,71	3,08	20,45	0,15
Toluene	12	24	0,00	25,45	23,78	93,45	1,06	4,45	3,23	13,59	0,12
Ethylbenzene	12	24	0,00	18,73	16,29	86,99	0,77	4,71	2,15	13,20	0,10
o-Xylene	12	24	0,00	25,69	23,74	92,41	1,18	4,99	2,80	11,80	0,10
MTBE	11	22	9,10	29,72	25,99	87,47	1,28	4,95	2,50	9,64	0,55
TAME	9	18	11,11	39,12	33,86	86,56	1,82	5,39	5,30	15,67	0,55

l is the number of laboratories;

n is the number of results;

n_a is the number of outliers;

x_{ref} is the reference value = gravimetric spike concentration, in milligrams per kilogram;

x is the mean value, in milligrams per kilogram;

R is the recovery, in percent;

σ_r is the repeatability standard deviation, in milligrams per kilogram;

$C_{V,r}$ is the relative repeatability standard deviation, in percent;

σ_R is the reproducibility standard deviation, in milligrams per kilogram;

$C_{V,R}$ is the relative reproducibility standard deviation, in percent

Table C.3 — Results of an interlaboratory comparison carried out in Germany (BAM Validation intercomparison 2002) on BTEX and ethers (soil overlaid with methanol) – low-level contamination

Parameter	l	n	n_a	x_{ref}	x	R	σ_r	$C_{V,r}$	σ_R	$C_{V,R}$	Limit of determination mg/kg (GC/FID)
Benzene	12	22	36,36	1,55	1,15	74,13	0,080	6,96	0,215	18,75	0,15
Toluene	12	24	8,33	2,50	2,39	95,37	0,107	4,47	0,573	23,99	0,12
Ethylbenzene	12	24	8,33	1,85	1,57	85,11	0,084	5,36	0,363	23,12	0,10
o-Xylene	12	24	0,00	1,28	1,31	102,75	0,106	8,11	0,552	42,15	0,10
MTBE	11	22	0,00	3,55	3,31	93,37	0,187	5,64	0,599	18,08	0,55
TAME	9	18	0,00	3,15	2,66	84,65	0,081	3,05	0,521	19,55	0,55

For an explanation of the symbols, see Table C.2.