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Soil quality — Risk-based petroleum hydrocarbons —

Part 1: Determination of aliphatic and aromatic fractions of volatile petroleum hydrocarbons using gas chromatography (static headspace method)

Qualité du sol — Hydrocarbures de pétrole à risque —

Partie 1: Détermination des fractions aliphatiques et aromatiques des hydrocarbures de pétrole volatiles par chromatographie en phase gazeuse (méthode par espace de tête statique)

Reference number
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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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Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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*.

ISO 16558 consists of the following parts, under the general title *Soil quality — Risk-based petroleum hydrocarbons*:

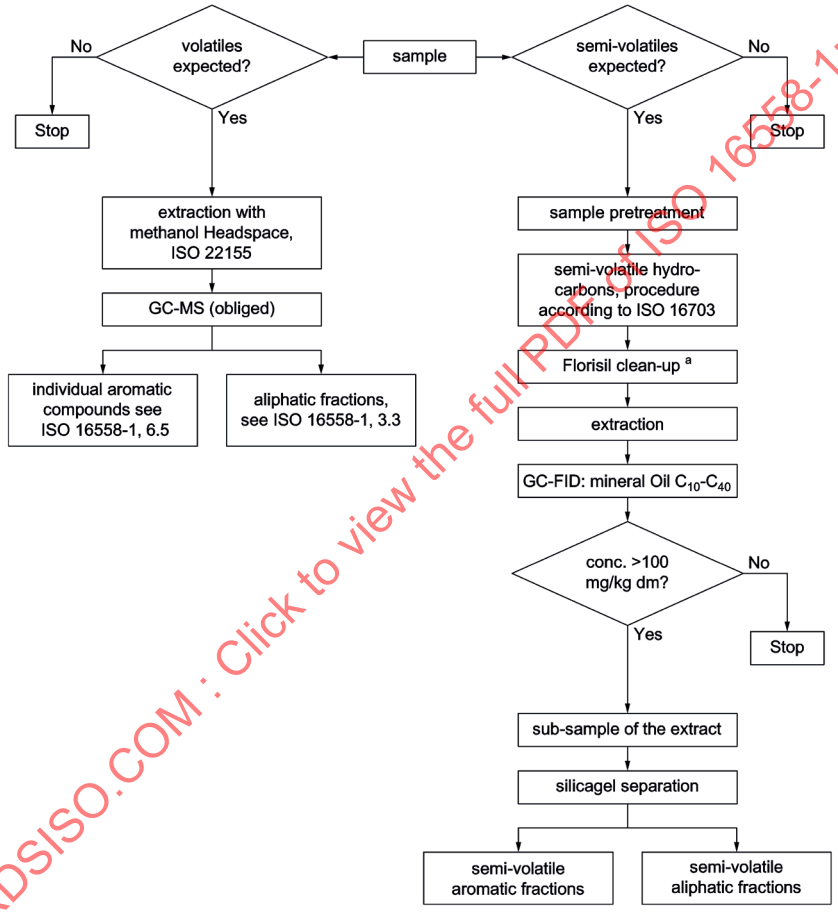
— *Part 1: Determination of aliphatic and aromatic fractions of volatile petroleum hydrocarbons using gas chromatography (static headspace method)*

— *Part 2: Determination of aliphatic and aromatic fractions of semi-volatile petroleum hydrocarbons using gas chromatography with flame ionization detection (GC/FID)* [Technical Specification]

Introduction

ISO 11504 establishes a basis for the choice of fractions and individual compounds when carrying out analysis for petroleum hydrocarbons in soils and soil-like materials including sediments. It provides guidance for the appropriate use of the analytical results in risks assessment. This part of ISO 16558 specifies methods for the quantitative determination of the appropriate fractions of aliphatic and aromatic compounds. The methods described are based on existing standards [mineral oil (ISO 16703) and volatile hydrocarbons (ISO 22155)].

The general use and relation between the two different parts of this International Standard is given in Figure 1.



Key

a Florisil®[b] clean-up: Only to be applied in case the test according to ISO 16703 is carried out. If the aliphatic and aromatic fractions have to be analysed, florisil clean-up should not be carried out. Florisil® is a trade name for a prepared diatomaceous substance mainly consisting of anhydrous magnesium silicate.

b Florisil® 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.

Figure 1 — Use of different analytical International Standards during risk assessment of petroleum hydrocarbons

Soil quality — Risk-based petroleum hydrocarbons —

Part 1: Determination of aliphatic and aromatic fractions of volatile petroleum hydrocarbons using gas chromatography (static headspace method)

1 Scope

This part of ISO 16558 specifies a method for the quantitative determination of the total extractable volatile, the volatile aliphatic, and aromatic fractions of petroleum hydrocarbon content in field moist soil samples by gas chromatography with mass spectrometric detection. The aromatic fractions are determined by the sum of individual aromatic compounds.

The sum of the volatile aliphatic (C_5 to C_{10}) and aromatic (C_6 to C_{10}) fractions can be referred to as "volatile oil".

The results of the test carried out can be used for risk assessment studies related to contaminations with petroleum hydrocarbons.

This part of ISO 16558 provides a method applicable to petroleum hydrocarbon contents from about 5 mg/kg soil expressed as dry matter for the whole aliphatic fraction C_5 to C_{10} and about 5 mg/kg soil expressed as dry matter for the aromatic fraction in the boiling range of C_6 to C_{10}.

With this method, all hydrocarbons with a boiling range of 36 °C to 184 °C, *n*-alkanes between C_5H_{12} to $C_{10}H_{22}$, isoalkanes, cycloalkanes, BTEX, and di- and tri-alkyl benzenes compounds are determined as total volatile petroleum hydrocarbons C_5 to C_{10}. In addition, volatile aliphatic and aromatic fractions are specified.

For the determination of semi-volatile aliphatic and aromatic fractions of petroleum hydrocarbons in soil samples, see ISO/TS 16558-2.

NOTE The sub-fractions proposed in this part of ISO 16558 have shown to be suitable for risk assessment studies. However, other sub-fractions between C_5H_{12} to $C_{10}H_{22}$ can be determined in conformity with this part of ISO 16558.

On the basis of the peak pattern of the gas chromatogram and of the boiling points of the individual *n*-alkanes listed in Annex A, the approximate boiling range of the mineral oil and some qualitative information on the composition of the contamination can be achieved.

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 8466-1, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

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

ISO 22155, *Soil quality — Gas chromatographic determination of volatile aromatic and halogenated hydrocarbons and selected ethers — Static headspace method*

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

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
total content of volatile petroleum hydrocarbon fractions by gas chromatography
sum of compounds extractable with methanol that can be measured by headspace gas chromatography with a mass spectrometric detector and eluted on a non-polar capillary column with retention times between those of *n*-pentane (C_5H_{12}) EC 5 and hexane (C_6H_{14}) EC 6, between EC 6 and *n*-octane (C_8H_{18}) EC 8, and between EC 8 and 1,2-diethylbenzene ($C_{10}H_{14}$) EC 10

Note 1 to entry: Substances that comply with that definition are mainly short chain or branched, olefenic, alicyclic, aliphatic hydrocarbons, and BTEX or alkyl substituted aromatic hydrocarbons.

3.2
volatile aromatic compounds and fraction between EC numbers 9 to 10 of petroleum hydrocarbons
single mono-aromatic BTEX compounds and the fraction between EC numbers 9 to 10 containing di- and tri-alkylated aromatic compounds which can be measured by headspace gas chromatography with a mass spectrometric detector

Note 1 to entry: For example compounds, see Table 1.

3.3
volatile aliphatic fractions of petroleum hydrocarbons
quantitative values for the aliphatic fractions of the volatile petroleum hydrocarbons (olefenic, alicyclic branched, and paraffinic short hydrocarbons) between EC numbers 5 to 6, 6 to 8, and 8 to 10 which can be measured with headspace gas chromatography with a mass spectrometric detector

Note 1 to entry: For example compounds, see Table 1.

Table 1 — EC number ranges and respective example aliphatic and aromatic compounds

Structure type	EC number range Carbon number of *n*-alkanes	Boiling range °C	Example compounds
Aliphatic compounds	5 to 6	≥ 36 to 69	Pentane, 2- and 3-methylpentane, 2,2- and 2,3-dimethylbutane, cyclopentane, 2,3-dimethyl-butadiene, hexane
	> 6 to 8	> 69 to 128	Cyclohexane, methylcyclopentane, dimethyl-cyclopentane, methyl- and dimethyl-cyclohexane, branched C_7- and C_8-alkane
	> 8 to 10	> 128 to 175	*n*-nonane, 2-methylnonane, 1,1,3-trimethyl-cyclohexane, 2,3-dimethylheptane, *n*-decane

Table 1 *(continued)*

Structure type	EC number range Carbon number of *n*-alkanes	Boiling range °C	Example compounds
Aromatic compounds	> 6 to 9	> 69 to 151	BTEX single compounds, styrene
	> 9 to 10	> 151 to 184	Allylbenzene, *i*- and *n*-propylbenzene, 2- and 3- and 4-ethyltoluene, 1,2- and 1,3-diethylbenzene, 1,2,3- and 1,2,4- and 1,3,5-trimethylbenzene, isopropenylbenzene

4 Interferences

Compounds not related to petroleum hydrocarbon contaminations with boiling point between C_5 and C_{10} (e.g. halogenated hydrocarbons and ethers as MTBE and TAME) can interfere with the aliphatic fractions.

5 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 (see ISO 22155 for further information).

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. The compounds are detected with a mass spectrometric detector (MS).

The procedure as described in ISO 22155 is followed for determination of the individual aromatic compounds. Several aromatic fractions are then determined by summation of individual aromatic compounds.

On the basis of the peak pattern of the gas chromatogram and of the boiling points of the individual *n*-alkanes between C_5H_{12} to $C_{10}H_{22}$ (retention time standard), the sub-fractions of the volatile aliphatic hydrocarbons can be fixed and the peak areas of the sub-fractions can be integrated and hence used for quantification.

The total peak areas between the EC range defining standards between *n*-pentane and *n*-decane is measured and the content of the volatile aliphatic hydrocarbons in the sample is quantified against an external standard mix consisting of different types of volatile aliphatic compounds which are typical for petroleum hydrocarbons.

6 Reagents

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

6.1 Water, free of volatile organic compounds.

Water, free from organic contaminants. It shall show negligible interferences in comparison with the smallest concentration to be determined. Sufficient water from the same batch should be available to complete each batch of analyses including all preparations.

Water can be heated in a round bottom flask for about 30 min to remove remains of volatile compounds.

6.2 Methanol (CAS-RN[1)] 67-56-1).

Solvent for the extraction of soil samples and for the preparation of standard solutions.

6.3 Internal standard compounds.

For the determination of volatile aromatic hydrocarbons by GC-MS, two or more internal standards shall be selected. They shall not interfere with compounds present in the methanol extract.

Examples of suitable internal standards are the following:

a) toluene-D8 (CAS-RN 2037-26-5);

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

c) 1,3,5-trimethylbenzene D3 (CAS-RN 38574-14-0).

Example of suitable non-deuterated internal standard:

— *ααα*-trifluorotoluene (CAS-RN 98-08-8).

6.4 Retention time standard solution.

It is the fraction range defining standard solution containing *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane.

Prepare a mixture of equal amounts, on a mass basis, of the *n*-alkanes with carbon numbers from C_5 to C_{10}, dissolved in methanol (6.2), to give concentrations of about 50 mg/l of each *n*-alkane. Store at room temperature.

NOTE This solution is used to give information of the retention times of the *n*-alkanes to define the volatile hydrocarbon fractions in the samples.

6.5 Volatile aromatic hydrocarbon standards between EC numbers range 6 to 10 for calibration of headspace GC-MS system.

Compound	CAS-RN
EC number range 6 to 9	
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
EC number range 9 to 10	
allylbenzene	300–57–2
isoproprenylbenzene	98–83–9

1) CAS-RN: Chemical Abstracts Service Registry Number.

2-ethyltoluene	611–14–3
3-ethyltoluene	620–14–4
4-ethyltoluene	622–96–8
1,2,3-trimethylbenzene	526–73–8
1,2,4-trimethylbenzene	95–63–6
1,3,5-trimethylbenzene	108–67–8
isopropylbenzene	98–82–8
sec-butylbenzene	135–98–8
1,2-diethylbenzene	135–01–3
1,3-diethylbenzene	141–93–5

The detector responses of these selected compounds are measured by headspace gas chromatography with a mass spectrometric detector (electron ionization with selected ion monitoring of mass fragments *m/z* 78 for benzene and *m/z* 91 for toluene, ethylbenzene, and xylenes, *m/z* 104 for styrene, and *m/z* 91+105+117+118+119+120+134 for di- and tri-alkylated benzene), which are used for quantification.

6.6 Volatile aliphatic hydrocarbon standards between EC numbers range 5 to 10 for calibration of headspace GC-MS system.

Aliphatic compound	**CAS-RN**
n-pentane	109–66–0
n-hexane	110–54–3
n-heptane	142–82–5
n-octane	111–65–9
n-nonane	111–84–2
n-decane	124–18–5
Cyclopentane	287–92–3
2-methylpentane	107–83–5
3-methylpentane	96–14–0
methylcyclopentane	96–37–7
2,2-dimethylpentane	590–35–2
2,3-dimethylbutane	79–29–8
Trans-Pentadiene	2004–70–8
Cyclohexane	110–82–7
Methylcyclohexane	108–87–2
1,1-Dimethylcyclohexane	590–66–9

The detector responses of these selected compounds are measured by headspace gas chromatography with a mass spectrometric detector (electron ionization with selected ion monitoring of mass fragments *m/z* 41+43+55+56+57+69+70+71 for olefenic, alicyclic branched, and paraffinic short hydrocarbons), which are used for quantification.

6.7 Carrier gases for gas chromatography.

Helium or nitrogen gases for headspace gas chromatography shall be used in accordance with the instrument manufacturer's instructions.

6.8 Standard solutions.

6.8.1 Standard stock solutions for the volatile compounds in methanol.

Prepare the stock solutions by adding to methanol defined amounts (e.g. 100 µl) of each standard compound 6.5 or 6.6 with a microlitre syringe. Immerse the tip of the needle in the solvent methanol and weigh with an accuracy of 0,1 mg.

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.

For practical reasons, mixed standard stock solutions can also be used.

6.8.2 Internal standard for GC-MS and retention time standard stock solutions in methanol.

Prepare the internal standard stock solutions with the individual internal standard compounds (6.3) and the individual aliphatic retention standard compounds (6.4) in the same procedure as in 6.8.1.

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

6.8.3 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 ± 2) °C no longer than 3 months.

6.8.4 Working standard solutions.

Prepare at least five different concentrations (e.g. from 0,2 µg/ml to 3,2 µg/ml) by suitable dilutions, adding 50 µl to 500 µl of the intermediate mixed standard solutions (6.8.3) to methanol (10 ml) using a microlitre syringe.

6.8.5 Working internal standard for GC-MS and retention time standard solutions.

Prepare the internal standard and retention standard solutions of defined concentration (e.g. 0,4 µg/ml) as described in 6.8.2.

6.8.6 Aqueous calibration standard solutions.

Prepare the calibration solutions (see Table 2) 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 9.3). Make sure that the content of the organic solvent in the final aqueous calibration standard solution does not exceed 1 % (*V/V*).

Table 2 — Examples for preparation of aqueous calibration standard solutions

Calibration solution	Working standard solution (6.8.4) µl	Working internal standard solutions (6.8.5) 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

6.8.7 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.

7 Apparatus

Use usual laboratory glassware free of interfering compounds.

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

7.1 Glass vials with suitable septum.

Use 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.

7.2 Crimping pliers.

7.3 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:

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

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

7.4 Shaking machine.

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

7.5 Capillary columns.

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

NOTE Examples are given in 9.4.

7.6 Gas chromatograph equipped with a mass spectrometer (MS).

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.

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

7.8 Bottle-top dispenser.

8 Sampling, preservation, and sample pretreatment

8.1 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 analysed as soon as possible. Samples shall be stored cool according to 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 8.2 and 8.3 in order to prevent losses by volatilization.

Determine the dry matter content of the field moist sample according to ISO 11465. In case sampling method 8.2 is used, a separate sample should be delivered to the laboratory for determination of the dry matter.

8.2 Sampling using vials pre-filled with methanol

Transfer a defined volume of soil using an appropriate device into a pre-weighed vial which is filled with a defined volume of methanol already containing internal standards (6.8.7). 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 already containing internal standards (6.8.7). 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 (6.2) 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). Weigh the vial with methanol and sample on the laboratory.

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

8.3 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 at least 200 ml which is filled *in situ*, retrieved and capped with a non-permeable material, e.g. stainless steel or aluminium foil. The tube should be filled completely.

This method is not suitable for very stony soils.

Store cool at a temperature of 2 °C to 8 °C 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 9.2).

9 Procedure

9.1 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 (6.8.7) to 5 ml to 10 ml of water (6.1) as it is done with a sample. Ensure that no contamination occurs from the laboratory atmosphere.

9.2 Extraction

Using sampling procedure 8.2, the addition of methanol is carried out in the field. In case of using sampling procedure 8.3, 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 Clause 8 with a sampling device into a pre-weighed vial (50 ml to 100 ml) (7.1) with a screw cap with PTFE-coated septum and filled with a defined amount of methanol containing internal standards (6.8.7) (25 ml to 50 ml). Weigh and place the vials on the horizontal shaking machine (7.4) and shake for 30 min.

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

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.

9.3 Headspace-analysis

Transfer a defined volume of water (5 ml to 10 ml) into a headspace vial with bottle-top dispenser. Inject 10 µl to 100 µl of the methanol extract obtained according to 9.2 to the bottom of the vial and seal the cap fitted with PTFE-coated septum tightly. From this point 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 (6.8.6).

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

Stabilization of sample temperature in headspace system

Place the headspace vials 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.

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.

9.4 Gas chromatographic analysis

9.4.1 General

Example of gas chromatographic conditions for this analysis.

Stationary phase:	non-polar e.g. VF-624ms 20 m × 0,15 mm × 0,84 µm (Agilent) method (SIMDest)

NOTE VF-624ms is an example of a suitable product available commercially. This information is given for the convenience of users of this part of ISO 16558 and does not constitute an endorsement by ISO of this product.

Film thickness:	0,5 µm to 3 µm
Column length:	30 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
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

Examples of chromatograms are given in Figure A.1 (aliphatic compounds), Figure A.2 (aromatic compounds), and Figure A.3 (gasoline).

9.4.2 Calibration

Use the guidelines given in ISO 8466-1 for the calibration procedure.

Use the guidelines given in ISO 22892 for the identification of individual aromatic compounds.

Analyse the complete series of aqueous calibration solutions (6.8.6) according to 9.3.

9.4.2.1 Sum of aromatic standard compounds

As a minimum, perform a five-point internal calibration for each compound by using one or more internal standard compounds. The GC-MS measurement shall be made in electron ionization mode with selected ion monitoring of mass fragments *m/z* 78 for benzene and *m/z* 91 for toluene, ethylbenzene, and xylenes, *m/z* 104 for styrene, and *m/z* 91+105+117+118+119+120+134 for di- and tri-alkylated benzene, which can be used for quantification. Between the fraction range defining standards C_6 to C_9, single BTEX compounds are determined. For the aromatic fraction between C_9 to C_{10}, sum of the peak areas of the compounds according to 6.5 are measured. Based on this, calculate the calibration function for each BTEX individual compound and for the fraction between C_9 to C_{10}.

The calibration function is only valid under specific operational conditions and should be reestablished 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.

Determine the relative response for all volatile aromatic hydrocarbons with respect to the internal standard ethylbenzene-D10 or others (6.3).

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 (1):

$$y_{ie} / y_{se} = m_{is} \cdot \rho_{ie} / \rho_{se} + b_{is} \quad (1)$$

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 analyte "*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.

9.4.2.2 Sum of single aliphatic standard compounds

As a minimum, perform a five point external calibration for each compound. The GC-MS measurement shall be made in electron ionization mode with selected ion monitoring of mass fragments *m/z* 41+43+55+56+57+69+70+71 for olefenic, alicyclic branched, and paraffinic short hydrocarbons which can be used for quantification. Sum of the peak areas of the compounds between the fraction range defining standards, e.g. after C_5 to C_6, after C_6 to C_8, and after C_8 to C_{10} are measured. Based on this; calculate the calibration function for each fraction.

The calibration function is only valid under specific operational conditions and should be reestablished 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 (6.8.6). On the basis of this chromatogram, determine the retention times of each aliphatic hydrocarbon standard *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane to fix the retention time range of the fractions.

Calculate the concentration for each aliphatic fraction using Formula (1) where y_{ie} and ρ_{se} refer to the aliphatic fraction instead of to analyte "*i*".

9.4.3 Measurement

Analyse the prepared extracts (see 9.3) in the same manner as described for the calibration samples in 9.4.2.

The volatile aromatic single compounds or EC-fraction C_9 to C_{10} and the aliphatic fractions shall be quantified with respect to the same selected internal standards used for calibration, e.g. with respect to ethylbenzene-D10 or others using the respective calibration function (see Formula 1).

All chromatograms should be checked visually for correct integration. The start and stop times of the integration should be visible on the chromatogram.

The range of the carbon numbers of *n*-alkanes, i.e. EC fractions present in the sample, is determined by comparing the gas chromatogram of the sample extract with that of the *n*-alkane standard solution (6.4).

10 Calculation

10.1 Calculation of the concentration in the spiked water sample

10.1.1 Volatile aromatic hydrocarbon compounds with internal standard method

Calculate the mass concentration of analyte "*i*" in the spiked water sample using Formula (2) after solving Formula (1):

$$\rho_i = \left(y_i / y_s - b_{is}\right) \cdot \rho_s / m_{is} \qquad (2)$$

where

ρ_i is the mass concentration of the analyte "*i*" in the spiked water sample in micrograms per litre, µg/l = ρ_{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 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_{ie}/y_{se} as a function of the mass concentration ratio ρ_{ie}/ρ_{se}, often called the response factor as determined under calibration (9.4.2);

b_{is} is the axis intercept of the calibration curve on the ordinate as determined under calibration (9.4.2).

10.1.2 Volatile aliphatic fractions

Calculate the mass concentration of the aliphatic fractions "*i*" in the spiked water sample using Formula (2) reading fraction "*i*" instead of analyte "*i*".

10.2 Calculation of the concentration of a volatile compound or fraction in the soil sample

Calculate the content of a specific volatile aromatic compound or aliphatic fraction in the soil sample by using Formula (3):

$$w_{i\mathrm{dm}} = \frac{\rho_{i\mathrm{W}} \cdot V_{\mathrm{E}} \cdot V_{\mathrm{W}}}{V_{\mathrm{a}} \cdot m_{\mathrm{dm}}} \tag{3}$$

where

$w_{i\mathrm{dm}}$ is the content of the individual aromatic volatile compound or of the volatile hydrocarbon fractions "*i*" in the sample in milligrams per kilogram (mg/kg) of dry matter;

$\rho_{i\mathrm{W}}$ is the mass concentration of the individual aromatic compound or of the volatile hydrocarbon fraction "*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).

10.3 Calculation of the concentration of volatile oil in the soil sample

The concentration of volatile oil (C_5-C_{10}) in the soil sample is equal to the total sum of all aliphatic (C_5-C_{10}) and aromatic (C_6-C_{10}) fractions.

11 Expression of results

Report results in milligrams of individual volatile aromatic compound or of individual volatile aromatic and aliphatic fraction per kilogram of dry soil and up to two significant figures.

12 Precision

For precision data, refer to ISO 22155.

13 Test report

The test report shall include at least the following information:

a) a reference to this part of ISO 16558, i.e. ISO 16558-1;

b) complete identification of the sample;

c) storage time of samples;

d) the results of the determination according to Clause 11;

e) any details not specified in this part of ISO 16558 or which are optional as well as any other factor which could have affected the results.