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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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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*:

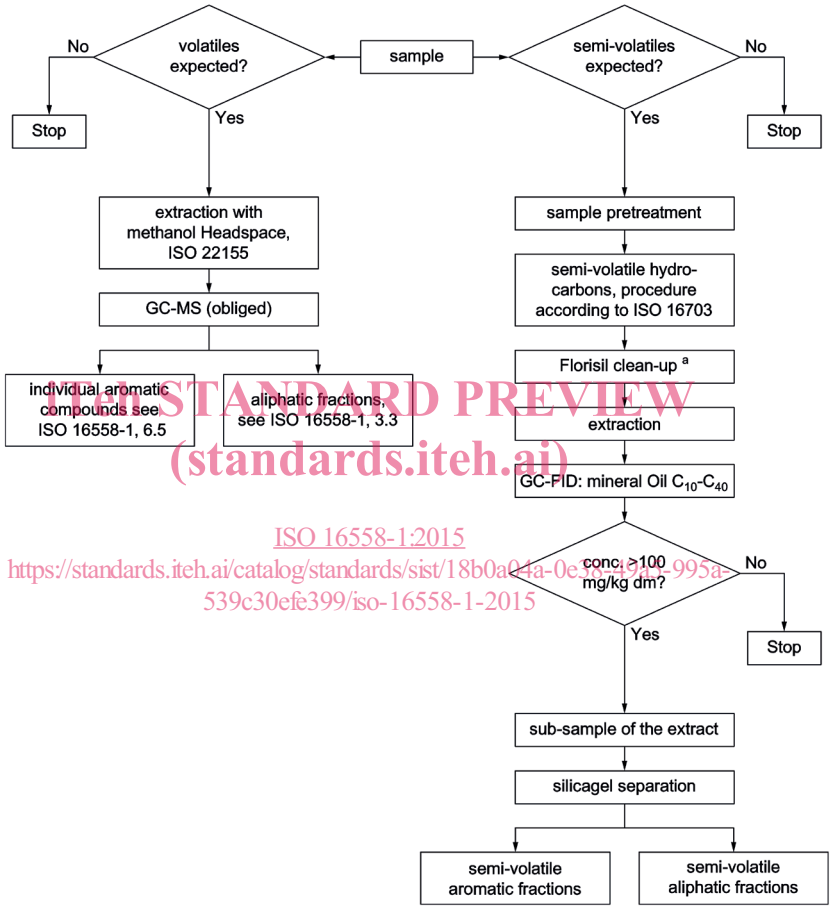
— *Part 1: Determination of aliphatic and aromatic fractions of volatile petroleum hydrocarbons using gas chromatography (static headspace method)*

— *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