

ISO/TC 190/SC 3

Secretariat: DIN

Voting begins on:
2015-10-22

Voting terminates on:
2015-12-22

Soil quality — Gas chromatographic determination of the content of volatile aromatic hydrocarbons, naphthalene and volatile halogenated hydrocarbons — Purge-and-trap method with thermal desorption

Qualité du sol — Détermination par chromatographie en phase gazeuse des teneurs en hydrocarbures aromatiques volatils, en naphthalène et en hydrocarbures halogénés volatils — Méthode par purge et piégeage avec désorption thermique

Please see the administrative notes on page iii

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Reference number
ISO/FDIS 15009:2015(E)

ISO/CEN PARALLEL PROCESSING

This final draft has been developed within the International Organization for Standardization (ISO), and processed under the **ISO-lead** mode of collaboration as defined in the Vienna Agreement. The final draft was established on the basis of comments received during a parallel enquiry on the draft.

This final draft is hereby submitted to the ISO member bodies and to the CEN member bodies for a parallel two-month approval vote in ISO and formal vote in CEN.

Positive votes shall not be accompanied by comments.

Negative votes shall be accompanied by the relevant technical reasons.

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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 Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

This third edition cancels and replaces the second edition (ISO 15009:2012) which has been technically revised.

Soil quality — Gas chromatographic determination of the content of volatile aromatic hydrocarbons, naphthalene and volatile halogenated hydrocarbons — Purge-and-trap method with thermal desorption

1 Scope

This International Standard specifies a method for quantitative gas-chromatographic determination of volatile aromatic hydrocarbons, naphthalene and volatile halogenated hydrocarbons in soil.

This International standard is applicable to all types of soil.

NOTE In the case of unsaturated peaty soils, absorption of the extraction solution may occur.

The lower limit of quantification is dependent on the equipment used and the quality of the methanol grade used for the extraction of the soil sample.

Under the conditions specified in this International Standard the following limits of quantification apply (expressed on basis of dry matter):

Typical limit of quantification when using GC-FID:

Volatile aromatic hydrocarbons: 0,1 mg/kg

Typical limit of quantification when using GC-ECD:

Volatile halogenated hydrocarbons: 0,01 mg/kg

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

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 4799, *Laboratory glassware — Condensers*

ISO 10381-1, *Soil quality — Sampling — Part 1: Guidance on the design of sampling programmes*

ISO 10381-2, *Soil quality — Sampling — Part 2: Guidance on sampling techniques*

ISO 10381-5, *Soil quality — Sampling — Part 5: Guidance on the procedure for the investigation of urban and industrial sites with regard to soil contamination*

ISO 11465, *Soil quality — Determination of dry matter and water content on a mass basis — Gravimetric method*

ISO 15680, *Water quality — Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption*

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

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

3 Principle

Test samples are taken from an untreated field moist soil sample. To prevent losses of the volatiles, samples are taken as undisturbed as possible in the field with a tube corer or by adding methanol immediately in the field.

The test sample is extracted with methanol. After centrifugation, if necessary, part of the methanol extract is brought into a purge vessel filled with water. The volatile compounds are purged with nitrogen or helium and adsorbed on a suitable adsorbing agent. The adsorbed compounds are desorbed thermally and by means of a carrier gas flow, whether or not via a cold trap, brought into a gas chromatograph. The various compounds are separated by using a capillary column with an immobile phase of low polarity. Volatile organic compounds are detected with appropriate detectors such as: mass spectrometric detector (MS), flame ionization detector (FID), electron capture detector (ECD), photo ionization detector (PID) or electrolytic conductivity detector (ELCD). Identification and quantification takes place by comparison of retention times and peak heights (or peak areas) towards internal standard added with the corresponding variables of an external standard solution. The efficiency of the procedure depends on the composition of the soil that is investigated. The described procedure does not take into account incomplete extraction caused by structure and composition of the soil sample.

When using non-specific detectors such as FID and ECD, the confirmation of the identity of the detected compounds and their concentrations should be done by repeating the gas chromatographic analysis using a column of different polarity. When using gas chromatography-mass spectrometry (GC-MS), the identity confirmation and the quantification can be done in a single run.

NOTE This International Standard follows the description of an 'off-line purge and trap' method. The use of commercially available online instruments is allowed provided that equivalent results are obtained during validation of this equipment. With such an instrument purge and trap occurs on line with gas chromatography and detection. Follow the manual of the manufacturer especially regarding the items [5.2.1](#) to [5.2.9](#).

4 Reagents

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

4.1 Water, free of volatile aromatic and volatile halogenated hydrocarbons

Usually boiler water with a temperature of at least 80 °C and 1 day old can be applied. Purging with an inert gas, e.g. a flow of 10 ml/min of nitrogen for 30 min, is another means of removing interfering compounds from water. A sufficient amount of water from the same batch should be available to complete each batch of analyses, including all preparations.

4.2 Internal standards

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

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

Compound name	CAS-RN ^a	EC-N ^b
Toluene-D8	2037-26-5	218-009-5
Ethylbenzene-D10	25837-05-2	247-292-8
2-Bromofluorobenzene	1072-85-1	214-018-3
^a Chemical Abstracts Service Registry Number		
^b EC-Number		

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

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

Compound name	CAS-RN ^a	EC-N ^b
1,4-Dichlorobutane	110-56-5	203-778-1
α,α,α -Trifluorotoluene	98-08-8	202-635-0
2-Bromofluorobenzene	1072-85-1	214-018-3
^a Chemical Abstracts Service Registry Number ^b EC-Number		

4.3 Standard compounds

4.3.1 Volatile aromatic hydrocarbons

[Table 3](#) contains volatile aromatic hydrocarbons for use as standard compounds.

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

Compound name	CAS-RN ^a	EC-N ^b
Benzene	71-43-2	202-753-7
Toluene	108-88-3	203-625-9
Ethylbenzene	100-41-4	202-849-4
<i>o</i> -Xylene	95-47-6	202-422-2
<i>m</i> -Xylene	108-38-3	203-576-3
<i>p</i> -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
^a Chemical Abstracts Service Registry Number ^b EC-Number		

Table 4 (continued)

Compound name	CAS-RN ^a	EC-N ^b
1,2-Dichloropropane	78-87-5	201-152-2
1,2,3-Trichloropropane	98-18-4	202-486-1
<i>cis</i> -1,3-Dichloropropene	10061-01-5	233-195-8
<i>trans</i> -1,3-Dichloropropene	10061-02-6	208-826-5
<i>cis</i> -1,2-Dichloroethene	156-59-2	205-859-7
<i>trans</i> -1,2-Dichloroethene	156-60-5	205-860-2
3-Chloropropene	107-05-1	203-457-6
Trichloroethene	79-01-6	201-61-04
Tetrachloroethene	127-18-4	204-825-9
Monochlorobenzene	108-90-7	203-628-5
1,2-Dichlorobenzene	95-50-1	202-425-9
^a Chemical Abstracts Service Registry Number ^b EC-Number		

4.4 Methanol

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

Table 5 – Registration data

Compound name	CAS-RN ^a	EC-N ^b
Methanol	67-56-1	200-659-6
^a Chemical Abstracts Service Registry Number ^b EC-Number		

4.5 Adsorbing agent

Polymer of 2,6-diphenyl-p-phenoxide (40 mesh to 60 mesh) of a grade suitable for thermal desorption.

NOTE 1 2,6-diphenyl-p-phenylene oxide (CAS-RN 24938-68-9) is commercially available as Tenax TA¹⁾.

NOTE 2 Other adsorbing agents may be used provided that their suitability has been tested.

4.6 Cooling water for purge and trap

The temperature of the cooling water depends on the dimensions of the purge and trap equipment ([5.2](#)). A temperature of about 10 °C is recommended. A cryostat shall be used if the temperature of the cooling water is too high.

4.7 Inert gas for the gas chromatograph

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

4.8 Nitrogen or helium as inert gas for the purge equipment

1) Tenax TA is an example of a suitable product available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

4.9 Standard solutions

4.9.1 Standard stock solutions for volatile aromatic and halogenated compounds in methanol, 4 g/l

Weigh about 100 mg of the individual standard compounds (4.3) with an accuracy of 0,1 mg into a closed septum flask containing 25 ml methanol. Transfer the standard compounds into the flask by using a syringe.

NOTE The stock solution is stable for about 6 months when stored at -18°C .

4.9.2 Internal standard solutions in methanol, 4 g/l

The containers containing the solutions shall be marked or weighed so that any evaporation losses of the solvent may be recognized. The solutions shall be stored at a temperature of $(4 \pm 2)^{\circ}\text{C}$ in the dark. Prior to use, they shall be brought to ambient temperature.

Weigh about 100 mg of the individual internal standards (4.2.1 and 4.2.2) accurate to 0,1 mg into a closed septum flask containing 25 ml of methanol. Using a syringe, transfer the standard compounds into the flask.

4.9.3 Calibration solutions

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

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

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

Table 6 — Example for preparation of calibration solutions

Calibration solution	Internal standard solution (4.9.2) in ml	Standard stock solution (4.9.1) in ml	Concentration in the calibration solution mg/l	Quantity in $\mu\text{g}/5\ \mu\text{l}$ calibration solution in 100 ml (sample) water
1	5	0	0	0
2	5	1	40	0,2
3	5	2	80	0,4
4	5	3	120	0,6
5	5	4	160	0,8
6	5	5	200	1,0

The total volume of the methanol used for calibration shall be the same as that which will be taken for the methanol extract of the soil sample (see 7.3).

4.10 Methanol containing internal standards

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

5 Apparatus

5.1 General

Usual laboratory glassware, free of interfering compounds.

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

5.2 Purge and trap apparatus

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

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

5.2.2 Gas inlet tube with a tip of sintered glass.

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

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

5.2.5 Inlet tube for the thermocouple.

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

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

5.2.8 Adsorption tubes made of glass or stainless steel, filled with at least 240 mg of adsorbing agent ([4.5](#)).

The adsorbent is kept in place by using inert material, e.g. silanized glass fibre. The tubes shall be suitable for direct use in connection with the apparatus for thermal desorption. The tubes shall be marked on one side. The tubes shall be provided with caps of inert material, e.g. polyethylene or metal, with screw caps and PTFE ring, allow tight closing after purging.

Before use, the adsorbent shall be activated and purified by slowly heating the tubes to 250 °C and keeping them at that temperature for 3 h while a nitrogen flow of 10 ml/min is maintained. The adsorbent shall be cooled under nitrogen and the tubes analysed. The result of a blank determination shall not exceed the equivalent of 1 ng of a compound to be analysed. When the result is higher than this, the adsorbent shall be desorbed once more.

The use of commercially available tubes is recommended.

Tubes that are used should not be used again unless the blank determination meets the above mentioned requirements.

Care should be taken to avoid cross-contamination. A heavily loaded tube can contaminate a lightly loaded tube in the sample change platform.

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

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

5.4 **Centrifuge tubes** with a volume of 200 ml.