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Soil quality — Determination of mineral oil content by gas chromatography

Qualité du sol — Dosage des huiles minérales par chromatographie en phase gazeuse

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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.

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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 International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 16703 was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

This second/third/... edition cancels and replaces the first/second/... edition (, [clause(s) / subclause(s) / table(s) / figure(s) / annex(es)] of which [has / have] been technically revised.

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Soil quality — Determination of mineral oil content by gas chromatography

1 Scope

This International Standard specifies a method for the quantitative determination of the mineral oil (hydrocarbon) content in field moist soil samples by gas chromatography.

The method is applicable to mineral oil contents between 100 mg/kg and 1000 mg/kg soil expressed as dry matter.

NOTE If lower detection limits are required petroleum ether can be used as extraction solvent in combination with large volume injection or concentration of the final extract.

With this method all hydrocarbons with a boiling range of 175°C to 525°C, n-alkanes between C₁₀H₂₂ to C₄₀H₈₂, isoalkanes, cycloalkanes, alkyl benzenes, and alkyl naphthalenes and polycyclic aromatic compounds are determined as mineral oil.

Gasolines containing compounds < C₁₀ cannot be determined quantitatively with this method.

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

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2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 8466-1:1990, *Water quality - Calibration and evaluation of analytical methods and estimation of performance characteristics – Part 1: Statistical evaluation of the linear calibration function.*

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

ISO TR 11046, *Soil quality - Determination of mineral oil content - Method by infrared spectrometry and gas chromatographic method.*

ISO 11464:1994, *Soil quality - Pretreatment of samples for physico-chemical analyses.*

ISO 11465:1993, *Soil quality - Determination of dry matter and water content on a mass basis - Gravimetric method.*

ISO/FDIS 14507, *Soil quality - Pretreatment of samples for determination of organic contaminants.*

ISO/FDIS 15009, *Soil quality - Gas chromatographic determination of the content of volatile aromatic hydrocarbons, naphthalene and halogenated hydrocarbons - Purge and trap method with thermal desorption.*

ISO/FDIS 9377/2-2000, *Water quality - Determination of hydrocarbon index - Part 2: Method using solvent extraction and gas chromatography.*

prEN 14039:2000, *Characterization of waste - Determination of hydrocarbon content in the range of C₁₀-C₄₀ by gas chromatography.*

3 Definition

For the purposes of this International Standard, the following definition applies:

3.1

mineral oil:

The sum of compounds extractable with acetone/n-heptane (2+1) which do not adsorb on florisil and can be chromatographed on a non-polar capillary column with retention times between those of n-decane (C₁₀H₂₂) and n-tetracontane (C₄₀H₈₂).

NOTE Substances that comply with that definition are mainly long chain or branched aliphatic, alicyclic, polycyclic- or alkyl substituted aromatic hydrocarbons.

4 Interferences

Non- and weak polar compounds (e.g. halogenated hydrocarbons) and high contents of polar compounds may interfere with the determination.

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5 Principle

A known amount of the homogenized soil sample is extracted by mechanical shaking or sonication with acetone/n-heptane, then water is added and the organic layer is separated. Polar compounds are removed by adsorption on florisil. An aliquot of the purified extract is analysed by capillary gas chromatography with flame ionization detection. The total peak area between the range defining standards n-decane and n-tetracontane is measured and the content of mineral oil in the sample is quantified against an external standard consisting of equal amounts of two different types of mineral oil.

NOTE Instead of heptane, other non-polar solvent (e.g. petroleum ether, cyclohexane, n-hexane) can be used, however its suitability for the extraction of mineral oil from soil has to be proven.

6 Reagents

6.1 In general, all reagents shall be reagent grade and suitable for their specific purposes.

6.2 Acetone, (CH₃)₂CO;

6.3 Heptane, C₇H₁₆;

6.4 Florisil, particle size 150 µm to 250 µm (mesh 60 to 100), heated for at least 16 h at 140 °C and stored in a desiccator over a molecular sieve.

NOTE Commercially available cartridges are also applicable.

6.5 Anhydrous sodium sulfate (Na_2SO_4), heated for at least 2 h at 550 °C.

6.6 Test solution stearyl stearate ($\text{C}_{36}\text{H}_{72}\text{O}_2$).

Dissolve about 100 mg of stearic acid stearyl ester in 100 ml n-heptane [6.3].

6.7 Retention time window (RTW) standard solution, containing n-tetracontane and n-decane.

Weigh exactly about 30 mg of n-tetracontane into an 1 l volumetric flask, dissolve completely in an appropriate volume of n-heptane [6.3], add 30 μl of n-decane (about 21 mg), mix well, fill up to volume with n-heptane.

NOTE 1 n-tetracontane is only moderately soluble in n-heptane. Slight warm up and/or sonication accelerate the dissolution process.

NOTE 2 This solution shall be used for all dilution steps of the mineral oil calibration standard (6.8).

NOTE 3 This solution is to be stored at room temperature.

6.8 Mineral oil standard for calibration

Dissolve equal amounts by weight of two different types of mineral oil in the internal standard solution [6.7] to give a total hydrocarbon content of about 8 g/l and a C_{40} content of about 30 mg/l.

Preparation of the calibration solutions can be done by diluting an aliquot of this standard solution (6.8) with the internal standard solution (6.7).

The first type should show discrete peaks (e.g. a diesel fuel) in the gas chromatogram as can be seen in annex A, figure A.1 (left part of the chromatogram). The second type should have a boiling range higher than the first one and should show a hump in the gas chromatogram, as can be seen in annex A, in figure A.1 (right part of the chromatogram). An oil of this type is for example a lubricating oil without any additives.

NOTE Mineral oil Standards are available from

Fachgruppe I.2
Bundesanstalt für Materialforschung und –prüfung
Richard Willstätter- Str.11
D-12489 Berlin, Germany ¹⁾

6.9 System performance standard solution

A mixture of equal amounts by weight, of the n-alkanes with even carbon numbers from C_{10} to C_{40} , dissolved in n-heptane [6.3], with a content of about 50 mg/l of each n-alkane.

NOTE 1 This solution is used to verify the suitability of the gas chromatographic system for the resolution of n-alkanes as well as for the detector response.

NOTE 2 This solution is used to give information of the retention times of the n-alkanes to characterise the hydrocarbons in the samples.

NOTE 3 Due to the possibility of recrystallisation of n- tetracontane, this solution is to be kept at room temperature.

Annex ZA

¹This Information is given for the convenience of users of this International Standard ISO/DIS 16703 and does not constitute an endorsement by ISO of these products.

7 Apparatus

- 7.1 Standard laboratory glassware, which shall be burnt out or rinsed with acetone [6.2] and dried before use.
- 7.2 **Devices for extraction.** Mechanical shaker, horizontal movement, at least 120 shaking movements per min. Alternatively a ultrasonic bath can be used.
- 7.3 **Laboratory centrifuge**, capable of producing an acceleration of at least 1500 g.
- 7.4 **Gas chromatograph**, equipped with a non-discriminating injection system (preferably on-column or programmable temperature vapourisation injection-PTV), a capillary column and a flame ionisation detector (FID).

NOTE The use of a large volume injection system can improve the limit of detection considerably.

7.5 **Capillary column**, a fused silica capillary column with one of the following stationary phases and dimensions:

stationary phase:	non-polar, e.g. immobilized 100 % dimethyl polysiloxane, 95 %-dimethyl-5 %-diphenyl polysiloxane, modified siloxane polymer, etc.;
length:	10 m to 25 m;
internal diameter :	0,1 mm to 0,32 mm;
film thickness:	0,1 µm to 1,0 µm.

The column shall give a baseline separation for the n-alkanes in the system performance standard solution [6.9].

NOTE Thermally stable low bleed columns should be preferred.

7.6 **Data system**, capable of integrating the total area of the chromatogram, compensating for column bleeding and reintegrating after defining a new baseline.

7.7 **Glass centrifuge tubes**, with a volume of about 80 ml, with screw caps provided with an inlay of polytetrafluoroethylene (PTFE).

7.8 **Test tube**, 25 ml with a ground-glass stopper.

8 Sampling, sample conservation and pretreatment

Sampling shall be carried out according to ISO 10381-1 and in coordination with the analytical laboratory.

The samples should be kept sealed in darkness at a temperature of about 4 °C and extracted within a period of 1 week.

9 Procedure

9.1 Blank

With each series of samples a blank determination shall be carried out according to 9.2 using all reagents in identical amounts but without a sample.

9.2 Extraction procedure

Weigh exactly about 20 g of the homogenized field moist or pretreated soil sample according to ISO 14507 in the 80 ml centrifuge tube (7.7) and add 20 ml of acetone (6.2). After short shaking by hand add 10,0 ml of the RTW-standard solution (6.7). Close the tube and extract the sample for 30 min by mechanical shaking or sonication (7.2).

Add approximately 30 ml of distilled water, shake for 1 min and centrifuge for an appropriate time to get phase separation. Transfer the organic layer free of solid material with a pipette into a 80 ml centrifuge (7.7). Fill the centrifuge tube with water and shake for 1 min. Transfer the organic layer with a pipette into a 25 ml ground-stoppered test tube (7.9) and add 0,25 g to 0,5 g of sodium sulphate (6.5). After a short period of shaking (5 s to 10 s), add 3,0 g of florisil (6.4) and shake again for 10 min on the shaking machine. After settling transfer a portion of the purified extract into a vial and analyse by gas chromatography.

NOTE 1 Accelerated solvent extraction (ASE) with a mixture of acetone/n-heptane (2+1) for 15 min at 14 MPa and 100 °C yields also satisfactory results.

NOTE 2 Instead of shaking the extract with florisil for removal of polar compounds clean-up on florisil mini column will be more effective.

NOTE 3 If there is any indication that the interfering compounds are not removed as may be in case of soils with higher organic contents repeat the clean-up with the same amount of fresh florisil or higher amount of florisil can be used.

9.3 Determination by gas chromatography

9.3.1 Test of the performance of the gas chromatographic system

Use a capillary column with one of the specified stationary phases (7.5) for gas chromatographic analysis. Adjust the gas chromatograph (7.4) to provide an optimal separation. The n-alkanes in the system performance standard solution (6.9) shall be baseline separated. The relative response of the n-tetracontane (C₄₀) shall be at least 0,8, with respect to n-eicosane (C₂₀).

For an example of gas chromatographic conditions see annex A.

9.3.2 Test of repeatability

Record a gas chromatogram of the column bleeding by injection of a volume of n-heptane. Then inject the same volume of a suitable concentration of the mineral oil standard solution (6.8) three times and record the chromatogram for each injection. Correct the three chromatograms for column bleeding and calculate the mean of the measured peak areas and the corresponding standard deviation. The relative standard deviation shall not be greater than 5 %.

9.3.3 Calibration

When the method is used for the first time and/or when the apparatus or operator is changed a basic calibration according to ISO 8466-1 including the determination of the limit of detection and limit of determination shall be carried out.

An external calibration is performed by analysing a minimum of six concentrations of the mineral oil standard solution (6.8) which should be distributed equidistantly over the working range. Calculate a calibration function by linear regression analysis of the corrected peak areas. A chromatogram of n-heptane is used to correct the peak area of the chromatograms of the hydrocarbon standard solutions for the column bleeding. From the calculated regression line the actual sensitivity of the method is determined.

9.3.4 Validity check of the calibration function

The validity of the calibration function shall be checked within each batch of samples by analysis of one calibration standard solution for every ten samples. The concentration of this standard solution shall be between 40 % and 60 % of the working range. Check whether the mean of the results is within the 95 % confidence interval of the actual calibration line. If this is the case the actual calibration function is assumed to be valid. If not, a new calibration according to 9.3.3 shall be performed.