TECHNICAL REPORT

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Soil quality — Determination of mineral oil content — Method by infrared spectrometry and gas chromatographic method

Qualité du sol — Dosage des huiles minérales — Méthode par spectrométrie à l'infrarouge et méthode par chromatographie en phase gazeuse

Reference number
ISO/TR 11046:1994(E)

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 main task of technical committees is to prepare International Standards, but in exceptional circumstances a technical committee may propose the publication of a Technical Report of one of the following types:

— type 1, when the required support cannot be obtained for the publication of an International Standard, despite repeated efforts;

— type 2, when the subject is still under technical development or where for any other reason there is the future but not immediate possibility of an agreement on an International Standard;

— type 3, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example).

Technical Reports of types 1 and 2 are subject to review within three years of publication, to decide whether they can be transformed into International Standards. Technical Reports of type 3 do not necessarily have to be reviewed until the data they provide are considered to be no longer valid or useful.

ISO/TR 11046, which is a Technical Report of type 2, was prepared by Technical Committee ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

The following reasons led to the decision to publish this document in the form of a Technical Report of type 2.

Due to the severe impact of chlorofluoro hydrocarbons on the environment, these compounds should not be used for a test method specified in an International Standard. However, at present, no alternative for the extraction agent used in the procedures specified here is available.

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Case Postale 56 • CH-1211 Genève 20 • Switzerland

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Therefore, it was decided to retain the method using chlorofluoro hydrocarbon until alternatives which are applicable in the routine analysis are found, and to publish this document as a Technical Report.

Everybody working in the field of hydrocarbon analysis is encouraged to seek alternative solvents or methods.

Annexes A, B and C of this Technical Report are for information only.

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Soil quality — Determination of mineral oil content — Method by infrared spectrometry and gas chromatographic method

1 Scope

This Technical Report specifies two methods for the quantitative determination of mineral oil content in soil by infrared spectrometry (Method A) and gas chromatography (Method B).

Method A is applicable to mineral oil contents above 20 mg/kg on a dry matter basis. Method B is applicable to mineral oil contents above 100 mg/kg on a dry matter basis.

NOTES

1 It is emphasized that the methods described do not determine the origin of the substances that are considered to be "mineral oil" according to clause 4.

2 The infrared spectrometric method in particular is sensitive to false positive results caused by polar compounds.

3 With the infrared spectrometric method, the boiling range of compounds determined as mineral oil is not defined. With the gas chromatographic method, compounds with a boiling range of 175 °C to 525 °C are determined (*n*-alkanes $C_{10}H_{22}$ to $C_{40}H_{82}$). Petrol cannot be determined quantitatively with these methods, due to loss of volatile compounds during sample pretreatment.

4 Weak polar compounds of recent biogenic origin may be determined as mineral oil.

5 Relatively high contents of polar compounds give interferences in the determination. This applies especially to the infrared spectrometric method.

6 Halogenated hydrocarbons may interfere.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this Technical Report. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this Technical Report are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 3924:1977, *Petroleum products — Determination of boiling range distribution — Gas chromatography method.*

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

3 Definition

For the purposes of this Technical Report, the following definition applies.

3.1 mineral oil: Compounds that are extractable from soil by use of 1,1,2-trichloro-1,2,2-trifluoroethane under the following conditions:

— they do not adsorb on magnesium silicate or aluminium oxide;

— they absorb radiation with a wavenumber of 2 925 cm^{-1}, and/or 2 958 cm^{-1}, and/or 3 030 cm^{-1} (Method A);

— they can be chromatographed with retention times between those of *n*-decane ($C_{10}H_{22}$) and *n*-tetracontane ($C_{40}H_{82}$) (Method B).

NOTE 7 The substances defined are mainly non-polar compounds containing aliphatic and/or C-H groups.

4 Principle

Moist soil taken from the field is chemically dried with a hygroscopic salt, crushed and then extracted with 1,1,2-trichloro-1,2,2-trifluoroethane. Polar compounds are removed either by adding magnesium silicate and shaking or in a closed circuit system containing aluminium oxide.

For spectrometry (Method A), an infrared spectrum of the extract is recorded from 3 125 cm^{-1} to 2 800 cm^{-1}. The CH_2-absorption band at about 2 925 cm^{-1}, the CH_3-absorption band at about 2 958 cm^{-1} and the aromatic CH-absorption band at about 3 030 cm^{-1} are a measure of the mineral oil content. The mineral oil content of the sample is calculated from the determined absorbances using empirically determined absorption coefficients.

For quantitative determination of mineral oil contents (Method B), part of the purified extract is added to hexane and analysed by gas chromatography. For the separation, a column with a non-polar immobile phase is used. For detection, a flame ionization detector (FID) is used. The total area under the peaks from decane ($C_{10}H_{22}$) to *n*-tetracontane ($C_{40}H_{82}$) is a measure of the amount of mineral oil. The mineral oil content of the sample is calculated using an external standard prepared from a standardized oil.

5 Reagents

All reagents shall be of recognized analytical grade and suitable for their specific purpose.

5.1 Reagents used for methods A and B

5.1.1 1,1,2-Trichloro-1,2,2-trifluoroethane, ($C_2Cl_3F_3$)

The suitability of this reagent, for use in infrared spectroscopy shall be verified by recording an infrared spectrum from 3 125 cm^{-1} to 2 800 cm^{-1} in a cell with an optical path length of 4,00 cm, with an identical empty cell as a reference. The solvent is suitable when the transmittance in the range of 3 000 cm^{-1} to 2 900 cm^{-1} is greater than about 30 %.

NOTE 8 This solvent will be referred to in this Technical Report as "CFE".

5.1.2 Magnesium silicate, of particle size 150 µm to 250 µm (mesh: 60 to 100), heated for 16 h at 140 °C and stored in a desiccator.

NOTES

9 Magnesium silicate under the trade name of "Florisil"[1] has been found to be suitable. It is made from diatomae and mainly composed of anhydrous magnesium silicate.

10 The thickness of the layer of the magnesium silicate during the heating shall not be greater than 0,5 cm.

11 The suitability of magnesium silicate is checked by adding 1,0 g to 40 ml of lauric acid solution (5.1.3) followed by shaking for 30 min on a shaking machine (6.1.3). After decanting and measuring, the transmittance in the range from 3 030 cm^{-1} to 2 925 cm^{-1} shall be 35 % to 45 % using cells with and optical path length of 1,00 cm^{-1}.

5.1.3 Lauric acid solution

Dissolve 2,00 g of *n*-dodecanoic acid ($C_{12}H_{24}O_2$) in "CFE" (5.1.1).

5.1.4 Internal standard stock solution

Dissolve exactly 200 mg of *n*-tetracontane in 1 litre of "CFE" (5.1.1). Dilute the solution 10 times to give a concentration of 20,0 mg/l.

5.1.5 Aluminium oxide (Al_2O_3), basic or neutral activity I, particle size 63 µm to 200 µm (mesh 70 to 230).

NOTE 12 The suitability of the aluminium oxide is tested by passing 40 ml of lauric acid solution through the aluminium oxide column. The transmittance of the eluate in the range from 3 030 cm^{-1} to 2 925 cm^{-1} shall be 35 % to 45 % using cells with an optical path length of 1,00 cm.

5.1.6 Anhydrous sodium sulfate, heated for at least 2 h at 550 °C.

5.2 Reagents used for method A

5.2.1 *n*-Hexadecane ($C_{16}H_{34}$)

Dissolve 180 mg of *n*-hexadecane in 1 000 ml of "CFE" (5.1.1).

5.3 Reagents used for method B

5.3.1 *n*-Hexane.

5.3.2 *n*-Alcane standard.

Either

a) a certified mixture of equal amounts, on a mass basis, of the *n*–alcanes with even carbon numbers

1) 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.

of C_{10} to C_{40}, dissolved in *n*-hexane (5.3.1), with a content of 50 mg/l of each *n*-alkane; or

b) an *n*-alkane standard in accordance with ISO 3924.

NOTE 13 This standard is used to verify the suitability of the gas chromatographic system for the separation as well as for the response.

5.3.3 Mineral oil standard.

A mixture of equal amounts, on a mass basis, of two different mineral oil types, dissolved in *n*-hexane, with a mineral oil content of 8,00 g/l and a C_{40} content of exactly 20,0 mg/l.

NOTE 14 This mineral oil standard should consist of two different types of oil. The first type should show discrete peaks in the gas chromatogram as can be seen, for example, in annex A, figure A.1 a) (left part of chromatogram). The second type should have a boiling range higher than the first type and should show a "hump" in the gas chromatogram, as can be seen, for example, in figure A.1 a) (right part of chromatogram). An oil of this type is, for example, a lubricating oil without any additives.

6 Apparatus

6.1 General

Usual laboratory glassware, which shall be washed and rinsed with "CFE" (5.1.1) and then dried before use.

6.1.1 Glass sample containers, of capacity at least 0,5 litre, with screw caps provided with an inlay of polytetrafluoroethylene (PTFE).

6.1.2 Grinding apparatus.

6.1.3 Shaking machine, with a horizontal movement with up to 200 moves per minute.

6.1.4 Glass-fibre filters, with a diameter of 60 mm, heated for 3 h at 500 °C.

6.1.5 Soxhlet extractor, of capacity 150 ml.

6.1.6 Chromatography column, with a closed circuit complying with figure 1.

Dimensions in millimetres

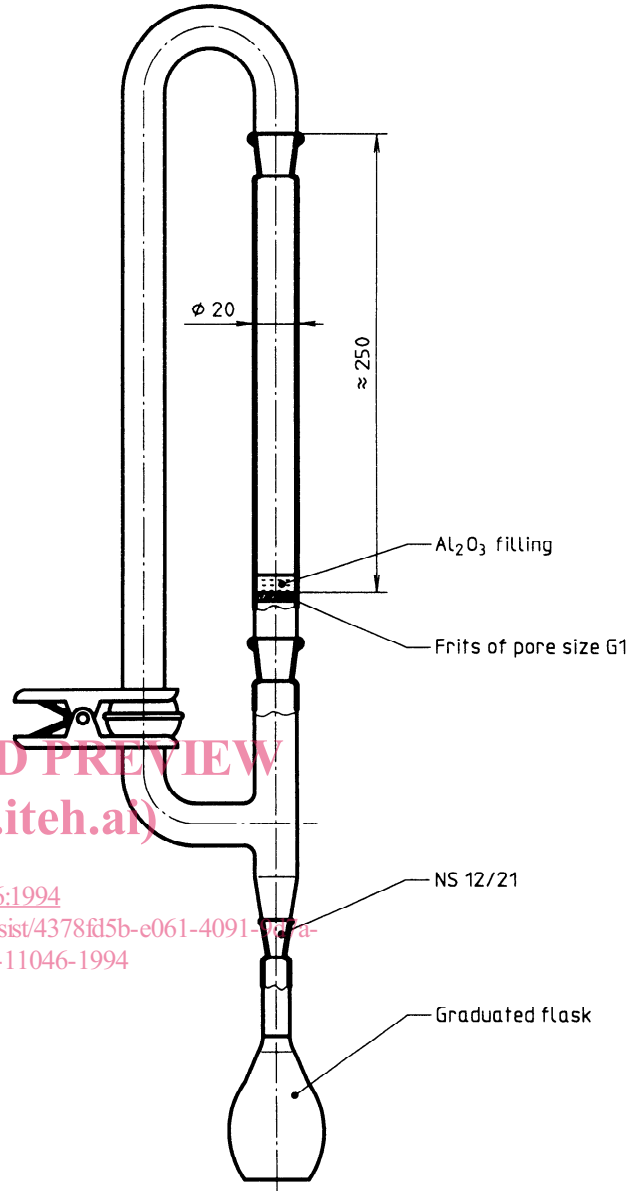

Figure 1 — Closed circuit chromatography column

6.2 Apparatus used for method A

6.2.1 Quartz optical cells, that can be closed and are suitable for infrared measurements, with optical path lengths of 1,00 cm and 4,00 cm (optional 0,2 cm).

6.2.2 Infrared spectrometer, suitable for application in the range of at least 3 200 cm^{-1} to 2 800 cm^{-1}.

NOTE 15 Throughout this Technical Report, the procedure of taking infrared spectra is described for conventional dispersive double beam spectrometers. However, the

use of Fourier-Transform infrared spectrometers (FT-IR) is also possible. All procedures should be adopted to the single beam technique according to the instructions given in the operating manual.

6.3 Apparatus used for method B

6.3.1 Water bath, with a temperature range up to 100 °C.

6.3.2 Concentration apparatus, Kuderna Danish or rotary apparatus.

6.3.3 Gas chromatograph, with a non-discriminating injection system (preferably on-column or ptv injection), a flame ionization detector (FID) and a programmable oven temperature.

6.3.4 Chromatography columns.

The following columns have been found to be satisfactory:

— Glass column: length 1 m, internal diameter 2 mm, immobile phase 3 % polymethylsiloxane on inactive solid support 125 µm to 150 µm (mesh: 100 to 120).

— Fused silica column: length 10 m, internal diameter 0,5 mm, immobile phase polymethylsiloxane, film thickness 1 µm.

— Fused silica column: length 25 m, internal diameter 0,3 mm, immobile phase polymethylsiloxane, film thickness 0,4 µm.

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

7 Sampling, sample conservation and pretreatment

Sampling shall be carried out after coordination with the analytical laboratory.

Keep the samples in darkness at a temperature of 4 °C for no longer than 1 week.

Dry and crush the sample.

8 Procedure

8.1 Blank determination

Before determination of the samples is performed, carry out a blank determination according to 8.2 and 8.3, using all reagents in identical amounts but without a sample.

8.2 Extraction

8.2.1 Shaking procedure

Place 15 g of the dried and crushed sample in a 100 ml conical flask, add 20,0 ml of "CFE" (5.1.1) and close the flask. Place the flask on the shaking machine (6.1.3) and shake for 30 min. Add 1,00 ml of internal standard solution (5.1.4). Shaking shall be performed so that complete dispersion of "CFE" takes place throughout the sample.

NOTES

16 Experience has shown that 150 shaking moves per minute are sufficient if the length of the movement is 7 cm.

17 Internal standard solution is used for the gas chromatographic method only. The concentration is so low that it does not interfere with the infrared screening method.

Allow the solid phase to settle and filter the supernatant "CFE" through a glass fibre filter (6.1.4) into a 100 ml conical flask.

Add another 20,0 ml of "CFE" and repeat the above described extraction procedure. Rinse the glass fibre filter with about 5 ml of "CFE". Add 1,00 ml of internal standard solution (5.1.4).

8.2.2 Soxhlet procedure

Weigh 30 g of dried and crushed sample into a pre-extracted thimble. Place the thimble in a Soxhlet extractor (6.1.5). Fix the sample inside the thimble with pre-extracted glass wool.

Place a 250 ml flask under the Soxhlet extractor.

Choose the amount of solvent applied in a way which ensures that the bottom of the flask will not become dry.

The extraction should take about 5 h. Concentrate the "CFE" extract using an apparatus according to 6.3.2 to a volume of 50 ml. Add 1,00 ml of internal standard solution (5.1.4).

NOTES

18 If the duration of the extraction is too long (e.g. overnight), naturally occurring organic matter will be extracted and false positive results may be obtained.

19 The volume reduction of the extract using a rotary evaporator should be done in a controlled vacuum. The temperature of the water bath should not exceed 40 °C. The recoveries for this procedure should be verified using known amounts of standard compounds over the whole boiling range.

8.3 Clean up

8.3.1 Magnesium silicate clean up

Add 5 g of magnesium silicate (5.1.2) to the combined extract prepared in 8.2.1. Close the conical flask and shake for 30 min on the shaking machine (6.1.3). Filter the purified extract through a glass-fibre filter (6.1.4) into a 50 ml volumetric flask. Rinse the conical flask and the filter with "CFE" (5.1.1). Make up to the mark and mix it if infrared spectrometry is to be used for quantification.

8.3.2 Aluminium oxide clean up

Add, to the extract prepared in 8.2.2, "CFE" (5.1.1) up to the mark, close the flask and mix. Prepare a chromatography column (6.1.6) with 8 g of aluminium oxide (5.1.5) and transfer the extract to this closed circuit system. The extract is passed through the prepared column at atmospheric pressure.

NOTE 20 It may be necessary to repeat the clean up. In all instances in which interferences by non-hydrocarbons cannot be reliably excluded, the extract should be checked by recording a complete infrared spectrum (usually the presence of polar compounds is indicated by the appearance of C=O and O-H bands). If the removal of interfering compounds is not possible, infrared spectrometry cannot be used for a reliable quantification of mineral oil content (false positive result).

8.4 Method A: Determination by infrared spectrometry

8.4.1 Preparation

Ensure that the infrared spectrometer (6.2.2) is working correctly by following the instruction manual of the instrument.

Determine the 100 % transmittance as follows.

Fill two identical cells (6.2.1) with "CFE" (5.1.1) that has been treated according to 8.3 and place these cells in the reference and sample beams of the infrared spectrometer respectively. Adjust the spectrometer to 100 % transmittance at 3 125 cm^{-1} and record the spectrum from 3 125 cm^{-1} to 2 800 cm^{-1}. Determine whether the transmittance in this range is 100 % $\pm$ 1 %.

NOTE 21 Deviations of more than 1 % may be caused by contaminated cells and/or a poorly functioning spectrometer. Repeating the transmittance measurement without cells can give a decisive answer.

Check the accuracy of the absorbance measurements as follows.

Fill two cells (6.2.1) with optical path lengths of 1,00 cm with *n*-hexadecane solution (5.2.1) and "CFE", respectively, and record the spectrum from 3 125 cm^{-1} to 2 800 cm^{-1}. Determine the absorbances at the maxima of about 2 925 cm^{-1} and about 2 958 cm^{-1} and calculate both the absorbance coefficients. The calculated values shall not derivate more than 0,1 ml/mg·cm from the experimentally determined values of 4,0 ml/mg·cm and 1,5 ml/mg·cm.

NOTE 22 Deviations of more than 0,1 ml/mg·cm may be caused by:

— a too high scanning speed and/or too great spectral bandwidth;

— inhomogeneous radiations beams, possibly as a result of ageing of the radiation source, contamination of the optical system and/or damage of the cam in the reference beam. Repeating the measurement with a lower scanning speed and/or smaller spectral band width can give a decisive answer.

8.4.2 Measurement

Measure the absorbance of the purified extract prepared in 8.3 as follows.

Fill a cell (6.2.1), with an optical pathlength of 1,00 cm, with the extract, then close the cell and place it in the sample beam of the spectrometer (6.2.2). Prepare about 50 ml of "CFE" (5.1.1) according to the same clean-up procedure as that used for the extract prepared in (8.3). Fill an identical cell with "CFE", close this cell and place it in the reference beam of the spectrometer. Record the spectrum from 3 125 cm^{-1} to 2 800 cm^{-1}. Draw a straight line through the measured transmittances at 3 125 cm^{-1} and 2 800 cm^{-1} and determine the absorbance at the maxima at about 2 925 cm^{-1}, 2 958 cm^{-1} and 3 030 cm^{-1} with respect to this line. (See figure 2).

If one of the maxima gives an absorbance above 0,8, the extract has to be diluted. Dilute an aliquot of the extract on a mass basis with purified "CFE" (dilution factor, DF) and record the spectrum. Alternatively, a cell with an optical path length of 0,2 cm can be used for both the measuring and reference beam.

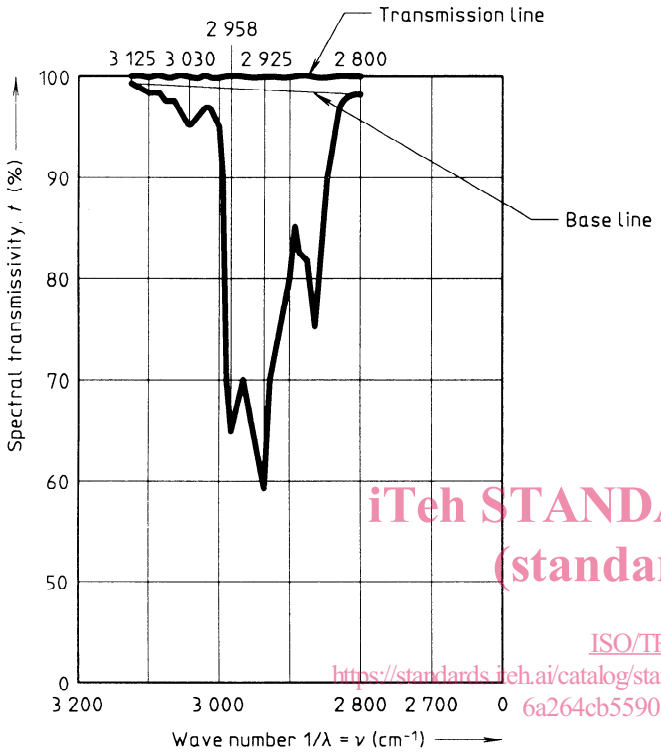

Figure 2 — Example of an infrared spectrum of mineral oil in "CFE"

If none of the maxima gives an absorbance above 0,1, concentrate the extract using an apparatus according to 6.3.2 to a volume of 4 ml to 5 ml (concentration factor, CF). Measure the concentrated extract in a cell with an optical path length of 1,00 cm as described above, using "CFE" that has been concentrated in the same way as a reference.

NOTES

23 Do not adjust the spectrometer to 100 % transmittance at 3 125 cm^{-1} before each new measurement of an extract.

24 A transmittance clearly below 100 % at 3 125 cm^{-1} indicates the presence of polar compounds in the extract. This should be mentioned in the test report.

25 Pipettes are not suitable for measuring the "CFE" accurately, because "CFE" flows from a pipette closed at the top, due to its high specific gravity.

8.4.3 Calculation

Calculate the mineral oil content using the formula

$$w_O = \frac{DF \cdot SF \cdot V}{CF \cdot m \cdot l} \times \left(\frac{a_1}{C_1} + \frac{a_2}{C_2} + \frac{a_3}{C_3} \right) \times \frac{100}{w_{dm}}$$

where

w_O is the mineral oil content, in milligrams per kilogram, on a dry mass basis;

CF is the applied concentration factor (CF > 1);

DF is the applied dilution factor (DF > 1);

m is the mass, in kilograms, of pretreated soil taken for analysis;

V is the volume, in millilitres, of the "CFE" extract (5.1.1), (= 50 ml);

SF is the surcharge factor resulting from the pretreatment;

l is the optical path length, in centimetres;

a_1 is the absorbance of the peak at about 3 030 cm^{-1};

a_2 is the absorbance of the peak at about 2 958 cm^{-1};

a_3 is the absorbance of the peak at about 2 925 cm^{-1};

C_1 is the specific absorbance coefficient of the aromatic CH absorption band at about 3 030 cm^{-1}, experimentally determined (see [4]) from several mineral oil products (= 0,68 ml/mg·cm);

C_2 is the specific absorbance coefficient of the CH_3 absorption band at the peak of about 2 958 cm^{-1}, experimentally determined (see [4]) from several mineral oil products (= 5,2 ml/mg·cm);

C_3 is the specific absorbance coefficient of the CH_2 absorption band at the peak of about 2 925 cm^{-1}, experimentally determined (see [4]) from several mineral oil products (= 3,9 ml/mg·cm);

w_{dm} is the dry matter content, expressed as a percentage by mass.

Round the result to one significant figure when the content found is lower than 100 mg/kg.

Round the result to two significant figures when the content found is higher than 100 mg/kg.

Check the relative content of aromatic hydrocarbons as follows.

Calculate the quotient $a_1/(a_2 + a_3)$. If this quotient is greater than 0,12, the sample contains relatively high amounts of aromatic hydrocarbons. This shall be mentioned in the test report.

NOTES

26 Relatively high amounts of aromatic hydrocarbons may be caused by petrol or components present in coal tar.

27 The quotient 0,12 was determined in a mixture of gasoil, benzene, toluene, and *o*-xylene in a ratio of 3:1:1:1 on a mass basis.

28 The surcharge factor, SF, corrects for added substances during the sample pretreatment, e.g. the drying agent for chemical drying, as follows:

SF = Mass of soil taken in pretreatment + Mass of added drying agent/Mass of soil taken in pretreatment

8.5 Method B: Determination by gas chromatography

8.5.1 Concentration of the extract

Weigh the "CFE" extract or the remaining part (m_1) and concentrate it using an apparatus in accordance with 6.3.2 to a volume of 4 ml to 5 ml. Add 1,00 ml of *n*-hexane (5.3.1) and concentrate under a gentle nitrogen flow to a final volume of 1 ml. Concentrate the blank extract (see 8.1) in the same way.

8.5.2 Verification of instrument performance

Use one of the specified columns (6.3.4) for the gas chromatographic analysis. Adjust the gas chromatograph (6.3.3) to provide an optimal separation. The *n*-alkane standard (5.3.2) shall be baseline separated. The relative response of the *n*-alkane C_{40} shall be at least 0,7, with respect to the *n*-alkane C_{20}.

Optimize the gas chromatographic separation starting with the following settings:

Inlet temperature:	depending on the type of injector
Oven temperature:	55 °C during 5 min
	15 °C/min to 30 °C/min to 300 °C
	300 °C to 325 °C during 20 min
Detector temperature:	350 °C carrier gas.

8.5.3 Measurement

Record the gas chromatogram of the column bleeding by injecting a volume of *n*-hexane (5.3.1). Then inject three times the same volume of the mineral oil standard solution (5.3.3) and record the chromatogram. Correct these three chromatograms for column bleeding and calculate the standard deviation of the measured area. The standard deviation shall not be greater than 5 % of the mineral oil standard. Calibrate the detector response by measuring at least four dilutions of the mineral oil standard.

Prepare a calibration graph using these results. Ensure that the detector is operating within its linear range. Within the linear range, select a suitable standard for quantification. Under the same conditions, record the chromatograms of the blank extract and of the sample extract (see 8.3). Correct the sample for the blank.

NOTES

29 An increase in bleeding of the column may indicate contamination of the injector port or the column.

30 An increase in the blank may indicate the use of impure reagents or contamination of the glassware used.

8.5.4 Integration parameters

For integration of the gas chromatogram, determine the total area from *n*-alkane C_{10} to *n*-alkane C_{40}. Start the integration at the retention time of *n*-alkane C_{10} at the signal level before the solvent peak. End the integration of the total area just before the retention time of *n*-alkane C_{40} at the same signal level (see annex B). Integrate the internal standard in the same way as a separate peak.

NOTES

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

32 The presence of peaks on the solvent peak with a retention time less than that of *n*-alcane C_{10}, not originating from "CFE" and/or *n*-hexane, indicate that the sample