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BRITISH STANDARD

BS EN 14039:2004

Characterization of waste — Determination of hydrocarbon content in the range of C10 to C40 by gas chromatography

The European Standard EN 14039:2004 has the status of a British Standard

ICS 13.030.01

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National foreword

This British Standard is the official English language version of EN 14039:2004.

The UK participation in its preparation was entrusted by Technical Committee B/508, Waste management, to Subcommittee B/508/3, Waste management — Characterisation of waste, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
- monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this subcommittee can be obtained on request to its secretary.

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Summary of pages

This document comprises a front cover, an inside front cover, the EN title page, pages 2 to 22, an inside back cover and a back cover.

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EUROPEAN STANDARD
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EN 14039

September 2004

ICS 13.030.01

English version

Characterization of waste - Determination of hydrocarbon content in the range of C10 to C40 by gas chromatography

Caractérisation des déchets - Détermination de la teneur en hydrocarbures par chromatographie en phase gazeuse dans la plage C10 à C40

Charakterisierung von Abfällen - Bestimmung des Gehalts an Kohlenwasserstoffen von C10 bis C40 mittels Gaschromatographie

This European Standard was approved by CEN on 9 July 2004.

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Foreword

This document (EN 14039:2004) has been prepared by Technical Committee CEN/TC 292 “Characterization of waste”, the secretariat of which is held by NEN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by March 2005, and conflicting national standards shall be withdrawn at the latest by March 2005.

Anyone dealing with waste and sludge analysis should be aware of the typical risks of that kind of material irrespective of the parameter to be determined. Waste and sludge samples may contain hazardous (e.g. toxic, reactive, flammable, infectious) substances, which can be liable to biological and/or chemical reaction. Consequently these samples should be handled with special care. Gases which may be produced by microbiological or chemical activity are potentially flammable and will pressurise sealed bottles. Bursting bottles are likely to result in hazardous shrapnel, dust and/or aerosol. National regulations should be followed with respect to all hazards associated with this method.

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Introduction

Hydrocarbons are important constituents of many types of waste and contaminated soils. They have been determined up to now mainly by infrared spectroscopy after extraction with halogenated solvents such as 1,1,2-trichloro-1,2,2-trifluoroethane or tetrachloromethane. The objective of this standard is to provide an analytical method for the determination of hydrocarbon content by capillary gas chromatography avoiding the use of such solvents. The user of this document should be aware that the results of this standard might not be comparable with those obtained when using the infrared spectroscopy.

A mixture of acetone and n-heptane is the preferred extraction solvent.

For waste samples containing large amounts of relatively high boiling hydrocarbons the gravimetric method (see EN 14345) can be used.

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1 Scope

This document specifies a method for the quantitative determination of the hydrocarbon content (C_{10} to C_{40}) in solid waste by gas chromatography.

It is applicable to hydrocarbon content between 100 mg/kg and 10 000 mg/kg expressed as dry matter basis.

Using this standard all hydrocarbons with a boiling range of approximately 175 °C to 525 °C, e.g. n-alkanes from $C_{10}H_{22}$ to $C_{40}H_{82}$, isoalkanes, cycloalkanes, alkyl benzenes, alkyl naphthalenes and polycyclic aromatic compounds are determined as hydrocarbons, provided they do not adsorb on the Florisil column during clean-up. Volatile hydrocarbons cannot be quantitatively determined using this standard. This will affect the determination of some common hydrocarbon fuels, e.g. petrol.

NOTE 1 On the basis of the peak pattern of the gas chromatogram (see Annex A) and of the boiling points of the individual n-alkanes listed in Annex B the approximate boiling range of the hydrocarbons and some qualitative information on the nature of the hydrocarbons can be obtained.

NOTE 2 At the moment there is no sufficient information on how to handle organic liquid wastes for the analysis of hydrocarbons.

NOTE 3 Aqueous liquid waste samples can be analysed in accordance with EN ISO 9377-2 or the procedure specified in Annex E.

2 Normative references

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

prEN 14346, *Characterization of waste — Calculation of dry matter by determination of dry residue and water content*

EN ISO 3696, *Water for analytical laboratory use - Specification and test methods (ISO 3696:1987)*

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*

3 Terms and definitions

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

3.1
hydrocarbon content by gas chromatography
sum of compounds that are extractable with with acetone/n-heptane (2+1), provided that

- they do not adsorb on Florisil;
- they can be chromatographed on a non-polar capillary column with retention times between those of n-decane ($C_{10}H_{22}$) and n-tetracontane ($C_{40}H_{82}$)

NOTE 1 Substances that comply with this definition are mainly non-polar long chain or branched aliphatic, alicyclic, alkyl substituted aromatic or polycyclic aromatic compounds.

NOTE 2 This definition differs from that given in EN 14345.

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4 Principle

A known amount of the homogenised waste sample is extracted by mechanical shaking or sonication with acetone/n-heptane. The organic layer is separated and washed twice with water. Polar compounds are removed by chromatography on Florisil. An aliquot of the purified extract is analysed by capillary gas chromatography with flame ionisation detection.

The total peak area between the retention time window standards n-decane and n-tetracontane is measured and the amount of hydrocarbons 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 hydrocarbons from waste has to be proven.

5 Interferences

High concentration of more polar compounds, e.g. animal and vegetable fats and oils, may exceed the adsorption capacity of the Florisil used. A mass concentration of up to 10 000 mg/kg of such compounds will not interfere with the determination of hydrocarbon content.

6 Reagents

6.1 In general all reagents shall be of recognized analytical grade and suitable for their specific purposes. Use water complying with at least EN ISO 3696, grade 3.

6.2 Acetone, $(CH_3)_2CO$;

6.3 n-Heptane, C_7H_{16};

6.4 Florisil[1] for the preparation of clean-up column, particle size 150 µm to 250 µm (mesh 100 to 60), heated for at least 16 h at 140 °C and stored in a desiccator over a molecular sieve. Alternatively, commercially available Florisil cartridges can be used.

6.5 Anhydrous sodium sulfate, Na_2SO_4;

6.6 Test solution of n-octadecanoic acid octadecyl ester, $C_{36}H_{72}O_2$;

Dissolve about (100 ± 1) mg of n-octadecanoic acid octadecyl ester in 100 ml n-heptane [6.3]. The solution is stable for 6 months when stored in a refrigerator between 1 °C and 5 °C.

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

Weigh (30 ± 1) mg of n-tetracontane into a 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 and homogenise.

This solution shall be used for all dilution steps of the hydrocarbon standard [6.8] and be stored at room temperature.

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

6.8 Hydrocarbon standard solution for calibration[2]

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[1] Florisil is a trade name for a prepared diatomaceous substance, mainly consisting of anhydrous magnesium silicate. This information is given for the convenience of users of this document and does not constitute an endorsement by CEN of this product. Equivalent products may be used if it can be shown to lead to comparable results.

Mix approximately equal masses of two different types of mineral oil. Weigh to the nearest 0,1 g this mixture and dissolve in the RTW standard solution [6.7] to give a hydrocarbon content of about 8 g/l.

Preparation of the calibration solutions can be done by diluting an aliquot of this standard solution [6.8] with the RTW standard solution [6.7]. The first oil type should show discrete peaks in the gas chromatogram as can be seen in Figure A.1 (left part of the chromatogram) of Annex A. A suitable oil of this type is a diesel fuel without any additives. 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). A suitable oil of this type is a lubricating oil without any additives.

6.9 Control solution

Prepare an independent control solution in accordance with 6.8 with a hydrocarbon concentration of about in the middle of the working range.

6.10 System performance standard solution

Prepare a mixture of equal amounts, on a mass basis, of the n-alkanes with even carbon numbers from C_{10} to C_{40}, dissolved in n-heptane [6.3], to give a concentration of about 50 mg/l of each n-alkane. Store at room temperature.

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 characterize the hydrocarbons in the samples.

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[2] General purpose hydrocarbon standards for calibration can be obtained from many commercial organisations. Calibration standards specific to this European Standard can be purchased from Bundesanstalt für Materialforschung und -prüfung, Fachgruppe I.2, Richard-Willstätter-Strasse 11 D-12489 Berlin, Germany. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

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6.11 Preparation of the clean-up column

A plug of pre-washed glass wool or a PTFE frit is pushed down into the column [8.9]. Then, successively 2 g Florisil [6.4] and 2 g sodium sulfate [6.5] are added. The column shall be prepared immediately before use.

7 Hazards

Acetone and n-heptane are highly flammable solvents and shall therefore be handled with caution. Special care is required during centrifugation. During extraction substantial pressure can built-up in the extraction vessel. This pressure shall be released by occasional venting of the vessel in a fume hood.

8 Equipment

8.1 Standard laboratory glassware, which shall be heated or rinsed with acetone [6.2] and dried before use.

8.2 Devices for extraction, mechanical shaker or ultrasonic bath.

8.3 Gas chromatograph, equipped with a non-discriminating injection, a flame ionisation detector (FID) and a temperature programmable oven.

8.4 Capillary column, fused silica column with suitable stationary phase and dimensions, e.g.

stationary phase: non-polar, e.g. immobilised 100 % dimethyl polysiloxane, 95%-dimethyl-5%-diphenyl polysiloxane, modified siloxane polymer, etc.;

length: at least 5 m;

internal diameter: 0,1 mm to 0,32 mm;

film thickness: 0,25 µm to 1,0 µm.

The column should give a base-line separation of the n-alkanes when the system performance standard solution [6.10] is run.

NOTE 1 Thermally stable low bleed columns should be preferred.

NOTE 2 The use of a pre-column, e.g. wide-bore (0,53 mm internal diameter) deactivated fused silica of at least 2 m of length that suits to the analytical column and connected to it using zero-volume connector is recommended.

8.5 Data system, capable of integrating the total area of the chromatogram, compensating for column bleed and re-integrating after defining a new baseline.

8.6 Glass extraction vessel of at least 100 ml, with ground glass stopper or screw caps incorporating a septum coated with polytetrafluoroethylene (PTFE).

8.7 Glass tube, 25 ml, with ground glass stopper or screw caps incorporating a septum coated with polytetrafluoroethylene (PTFE).

8.8 Separating funnel, at least 500 ml, with a ground glass stopper.

8.9 Chromatography column for clean-up, glass columns of about 10 mm internal diameter shall be used. The upper part of the column should be widened to use as solvent reservoir and the lower part to be narrowed to form a tip.

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9 Sample conservation and pretreatment

The samples shall be kept sealed in darkness at a temperature of about 4 °C and extracted within a period of one week. If this is not possible samples shall be stored at -18 °C or lower. Before analysis the samples shall be homogenised.

10 Procedure

10.1 Blank

With each series of samples a blank determination has to be carried out in accordance with 10.3 using all reagents in identical amounts but without a sample. If blank values are unusually high (more than 10 % of the lowest value of interest) every step in the procedure shall be checked to find the reason for these high blanks.

10.2 Water content

Determine the dry matter content in the sample or each of the phases when phase separation has taken place in accordance with prEN 14346. . When stable emulsions exist, the sample shall be analysed without phase separation.

10.3 Extraction and clean-up

Weigh to the nearest 0,1 g about 20 g of the homogenised sample into a glass extraction vessel [8.6], add (40 ± 1) ml acetone [6.2]. After short shaking by hand add (20 ± 0,1) ml of the RTW standard solution [6.7]. Extract the sample by shaking or sonication for one hour. After settling of the solid material transfer as much as possible of the supernatant into a separatory funnel [8.8]. To remove the acetone wash the organic phase twice with 100 ml of water. Collect the organic layer in a glass tube [8.7]. Add sufficient amount of sodium sulfate so that no lumps are formed anymore.

Transfer 10 ml of the extract to a clean-up column filled with Florisil [6.11]. Do not pre-wash the column with organic solvent. Collect the entire eluate. Transfer an aliquot of the purified extract to a GC-vial and analyse by gas chromatography.

NOTE 1 If appropriate test portions of (5 to 30) g can be used (e.g. smaller test portion should be used if samples adsorb the major portion of the extraction solvent added, sample intake should be increased if high sensitivity is required).

NOTE 2 Alternative extraction procedures e.g. accelerated solvent extraction (ASE) can be used provided they give comparable extraction performances.

NOTE 3 To improve and accelerate phase separation centrifugation can be applied provided that the necessary safety precautions, especially with regard to inflammable solvents, are taken into account.

NOTE 4 Alternatively, commercially available Forisil cartridges containing 2 g of Florisil and 2 g of sodium sulfate are applicable.

NOTE 5 It is very important that the Florisil is freshly prepared and active and the extract is free of acetone (less than 0,1 volume %), especially when the sample contains polycyclic aromatic hydrocarbons (PAH) besides mineral oil hydrocarbons. Make sure that PAH´s are adsorbed on the Florisil column. If the distinct peaks of PAH´s are observed in the GC-FID chromatogram (see Figure A.1in Annex A), this should be reported.

10.4 Determination by gas chromatography

10.4.1 Test of the performance of the gas chromatographic system

Use a capillary column with one of the specified stationary phases [8.4] for gas chromatographic analysis. Adjust the gas chromatograph [8.3] to provide an optimal separation. The n-alkanes in the system performance standard

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solution [6.10] shall be baseline separated. The relative response of the n-tetracontane (C_{40}) shall be at least 0,8 with respect to n-eicosane (C_{20}). For an example of the gas chromatographic settings see Annex A.

10.4.2 Test of repeatability

Record a gas chromatogram at the analytical operating conditions of the column bleed by injection of an appropriate volume of n-heptane. Inject the same volume of the control solution [6.9] three times and record the chromatogram for each injection. Integrate the chromatograms in accordance with 10.4.5 and calculate the mean of the measured peak areas and the corresponding standard deviation. The relative standard deviation shall not exceed 5 %.

10.4.3 Calibration

When the method is used for the first time and/or when the apparatus or operator is changed, a basic calibration in accordance with ISO 8466-1 including the determination of the limit of detection and limit of determination shall be carried out. A calibration shall be done by analysing a minimum of five dilutions of the hydrocarbon standard solution [6.8] which cover the working range. Calculate a calibration function by linear regression analysis of the corrected peak areas [10.4.5]. From the calculated regression line the current sensitivity of the method is determined.

10.4.4 Validity check of the calibration function

The validity of the calibration function shall be checked within each batch of samples by analysis of one independent control solution [6.9]. The calibration check identifies problems of calibration before real samples are run. Check whether the result is within ± 10 % of the reference value of the control solution. If this is the case the actual calibration function is assumed to be valid. If not, a new calibration in accordance with 10.4.3 shall be performed.

NOTE It is good analytical practice to perform both a calibration check and Analytical Quality Control using an independent solution [6.9] randomly placed during the analysis of the batch of samples. This independent solution can perform both functions.

10.4.5 Measurement

Analyse blanks [10.1], sample extracts [10.2], hydrocarbon standard solutions [6.8] and control solutions [6.9] are measured under identical gas chromatographic conditions.

n-Heptane shall be analysed in each sample batch. The resulting chromatogram is used to correct chromatograms of blanks [10.1], sample extracts [10.2], calibration standards [6.8] and control solutions [6.9] for column bleeding prior to integration.

10.4.6 Integration

Integrate the total area between the n-decane (C_{10}) and n-tetracontane (C_{40}) peaks of the chromatogram. Start the integration at the retention time just after the end of the n-decane peak at the signal level in front of the solvent peak. End the integration of the total area at the retention time just before the beginning of the n-tetracontane peak at the same signal level (see Annex A). Integrate n-tetracontane (C_{40}) as a separate peak for the recovery check.

The presence of peaks on the tail of the solvent peak with retention times less than that of n-decane indicates that the sample contains low boiling volatile hydrocarbons. This should be mentioned in the test report.

A non-horizontal baseline at the end of the chromatogram (retention time greater than that of n-tetracontane), with a signal level greater than the column bleed, indicates that the sample contains high-boiling hydrocarbons with more than 40 carbon atoms. This should be mentioned in the test report. It should be ensured that these compounds elute completely from the column. Otherwise they can cause interferences with the subsequent sample analysis.

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NOTE 1 All chromatograms should be checked visually for correct integration. The start and stop times of the integration should be visible on the chromatogram.

NOTE 2 The range of the carbon numbers of n-alkanes present in the sample is determined by comparing the gas chromatogram of the sample extract with that of the system performance standard solution [6.10]. The corresponding boiling range can be derived from Annex B.

NOTE 3 Peak shape and signal intensity of n-tetracontane are sensitive to changes in the surface properties of the injector and/or the pre-column due to contamination by sample constituents. Therefore, they can be used as an good indication for replacing pre-column and/or liner.

10.5 Calculation and evaluation

The hydrocarbon content of the sample is calculated using equation 1.

$$w = p \times \frac{V_\mathrm{h}}{M} \times \frac{100}{100 - w_w} \qquad (1)$$

$$p = \frac{A_\mathrm{S} - b}{a} \qquad (2)$$

where$w$	is the hydrocarbon content of the sample, expressed in milligrams per kilogram (mg/kg) dry matter;
p	is the hydrocarbon content of the extract calculated from the calibration function, expressed in milligrams per litre (mg/l);
A_S	is the integrated peak area of the sample extract, expressed in instrument dependent units;
b	is the intercept of the y axis, expressed in instrument dependent units;
a	is the slope of the calibration function, expressed in litres per milligram (l/mg);
V_h	is the volume of the n-heptane used for extraction, in millilitres (ml)
m	is the mass of the sample taken for analysis, expressed in grams (g);
w_w	is the water content of the analysed sample determined in 10.2, as mass fraction in percent.

Round the result to two significant figures.

If two or more phases are present in the sample calculate the hydrocarbon content of the original sample in accordance with the dry matter mass ratio of the phases.

NOTE If national regulations require results can be expressed as mg/kg based on the original material.

10.6 Quality control

10.6.1 Suitability check of the clean-up procedure

The clean-up efficiency of each batch of Florisil shall be checked (If Florisil cartridges are used, their suitability for the clean-up procedure shall be checked in the same way) by the following procedure:

Add 10 ml of the n-octadecanoic acid octadecyl ester solution [6.6] to the clean-up column [6.11]) filled with 2,0 g of Florisil and 2 g of sodium sulfate and collect the entire eluate. Analyse a portion of the resulting solution by gas chromatography. Analyse a 1+19 dilution of the untreated n-octadecanoic acid octadecyl ester test solution [6.6] as

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reference. Determine the recovery of the n-octadecanoic acid octadecyl ester after clean-up on the base of the peak area in respect to the untreated n-octadecanoic acid octadecyl ester (equation 3).

$$R_{\mathrm{oo}} = \frac{A_{\mathrm{foo}}}{A_{\mathrm{uoo}}} \times 5 \tag{3}$$

where

R_{oo} is the recovery of n-octadecanoic acid octadecyl ester (1+19), in percent (%);

A_{foo} is the peak area of n-octadecanoic acid octadecyl ester after clean-up on the Florisil column;

A_{uoo} is the peak area of the (1+19) dilution of untreated n-octadecanoic acid octadecyl ester.

The recovery shall not exceed 5 %. If the recovery of n-octadecanoic acid octadecyl ester acid is above 5 %, activate the Florisil in accordance with 6.4 and repeat the test.

10.6.2 Recovery of the hydrocarbon standard solution

The recovery of the hydrocarbon standard solution shall be checked with each batch of Florisil (If Florisil cartridges are used, recovery shall be checked in the same way) by the following procedure:

Add 10 ml of the hydrocarbon standard solution [6.8] to the clean-up column [6.11]) filled with 2,0 g of Florisil and 2 g of sodium sulfate and collect the entire eluate. Analyse a portion of the purified solution by gas chromatography. Analyse the untreated hydrocarbon standard solution as reference. Determine the recovery of the hydrocarbons on the base of the peak area of the purified and untreated standard solutions (equation 4).

$$R_{\mathrm{HC}} = \frac{A_{\mathrm{fhc}}}{A_{\mathrm{uhc}}} \times 100 \tag{4}$$

where

R_{HC} is the recovery of the hydrocarbon standard;

A_{fhc} is the peak area of the hydrocarbon standard following Florisil treatment;

A_{uhc} is the peak area of untreated hydrocarbon standard.

The recovery should be more than 80 %.

If the recovery is less then 80 %, wash out the batch of Florisil with ample water and activate the Florisil in accordance with 6.4. If the repeated test again shows that the criterion is not met, try another batch of Florisil.

10.6.3 Quality control sample

For analytical quality control use the control solution [6.9] randomly placed during the analysis of the batch of samples and document the results e.g. in a control chart. Additionally, the analysis of suitable certified reference materials or internal laboratory control samples (e.g. waste sample of known hydrocarbon content or samples which have been analysed several times in a laboratory so that their approximate hydrocarbon content can be assumed as known) in regular intervals is recommended.

11 Performance characteristics

The method performance characteristics given in Table 1 have been established in a European intercomparison study on two typical waste samples, two contaminated soil samples and one standard solution, carried out in 2003.

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Table 1 — Performance characteristics for the determination of hydrocarbons in waste by gas chromatography

Material	l	n	[%]	Mean [mg/kg $w{:}w$]	CV_r [%]	CV_R [%]
Nickel sludge	20	40	5	780	3,88	26,91
Rubble	20	40	5	7,841	6,05	25,53
Contaminated soil (high)	24	48	0	1,818	8,13	28,52
Contaminated soil (low)	23	46	0	697	9,14	44,86
Standard solution	20	40	0	2,848 mg/l	4,94	8,62

where

$w{:}w$	is mean hydrocarbon mass content, expressed in milligrams per kilogram (mg/kg) dry matter;
l	is the number of participating laboratories;
n	is the number of outlier-free individual analytical results;
f	is the fraction of outliers in per cent;
CV_r	is the repeatability coefficient of variation;
CV_R	is the reproducibility coefficient of variation.

12 Test report

The test report shall contain at least the following information:

a) reference to this document;

b) references to the methods used for extraction (shaking or sonification or other) and clean-up;

c) complete identification of the sample;

d) results of the determination;

e) reference to the occurrence of low ($<C_{10}$) and/or high boiling ($>C_{40}$) compounds in the chromatogram

f) any details not specified in this document or which are optional, as well as any other factors that might have affected the result;

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Annex A
(informative)

Examples of gas chromatograms of hydrocarbon standard and waste samples

Figure A.1 shows the gas chromatogram of the calibration mixture of mineral oil consisting of equal parts of a diesel fuel and a lubricating oil. Figure A.2 shows the same gas chromatogram after correction for the column bleed and integration. The total peak area between n-decane (C_{10}) and n-tetracontane (C_{40}) used for quantification is indicated as hatched area.

The Figures A.3 and A.4 show integrated gas chromatograms corrected for the column bleed of contaminated soil and waste samples, respectively.

Figure A.5 shows the gas chromatogram of a system performance standard solution (6.10).

The chromatograms have been recorded under the following conditions:

Injection technique: on-column

Injection volume: 2 µl

Column: fused silica capillary column

Column length: 12 m

Internal diameter: 0,25 mm

Liquid phase: BPX-5

Film thickness: 1,0 µm

Pre-column: deactivated fused silica capillary, 2 m x 0,53 mm

Carrier gas: Helium

Pressure: 150 kPa

Detector: Flame ionisation detector

Detector temperature: 360 °C

Oven temperature: 80 °C for 1 min

20 °C/min to 360 °C

300 °C for 10 min

360 °C for 15 min

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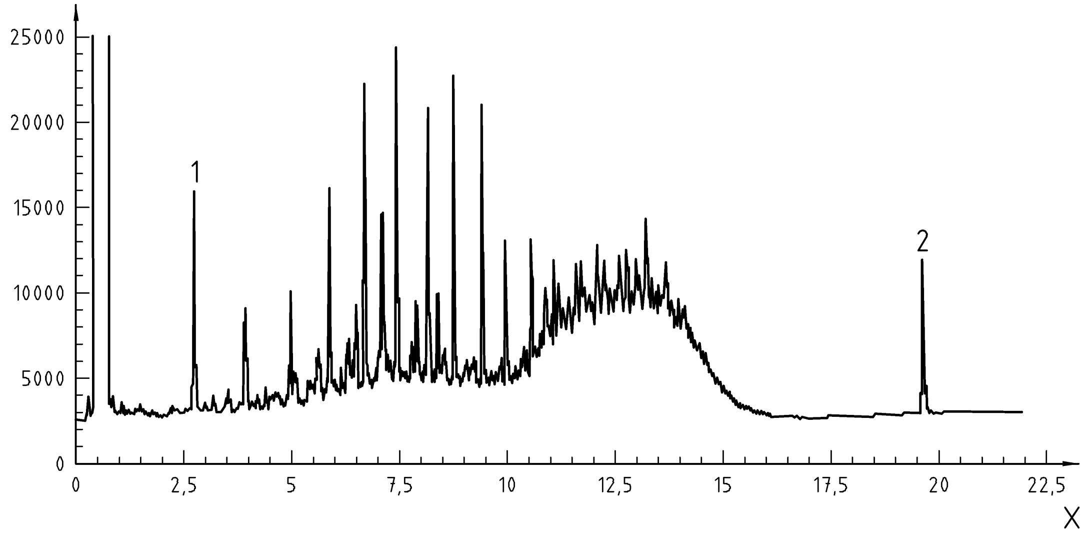
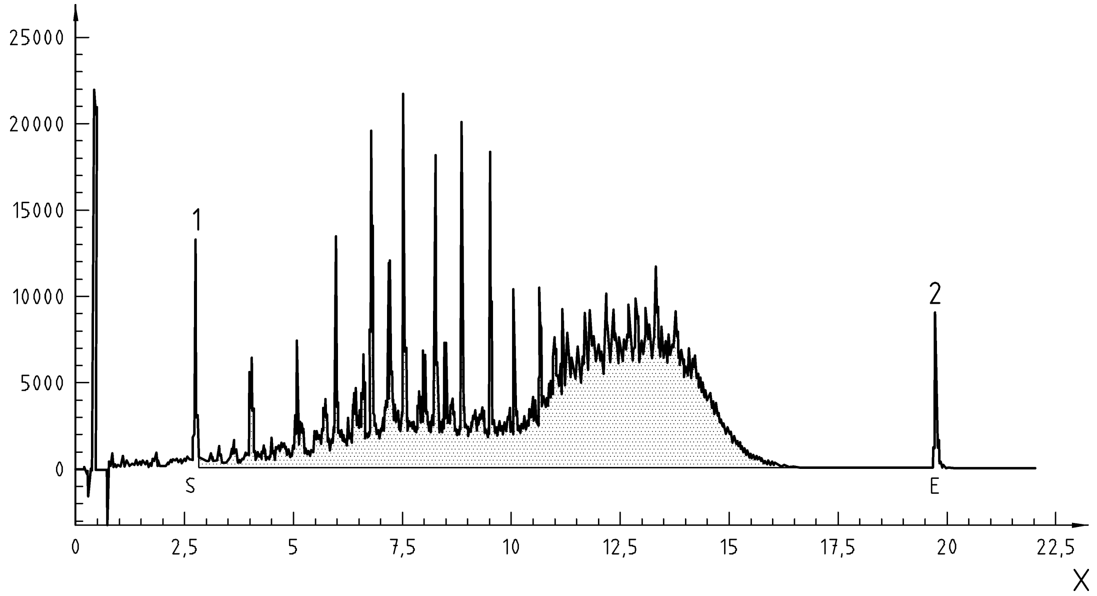


Key

X minutes
1 n-decane
2 n-tetracontane

Figure A.1 — Gas chromatogram of the hydrocarbon standard solution (6.8) consisting of equal parts of diesel fuel and lubricating oil



Key

X minutes
1 n-decane
2 n-tetracontane

Figure A.2 — Integrated gas chromatogram of the hydrocarbon standard solution (6.8) corrected for the "column bleed“

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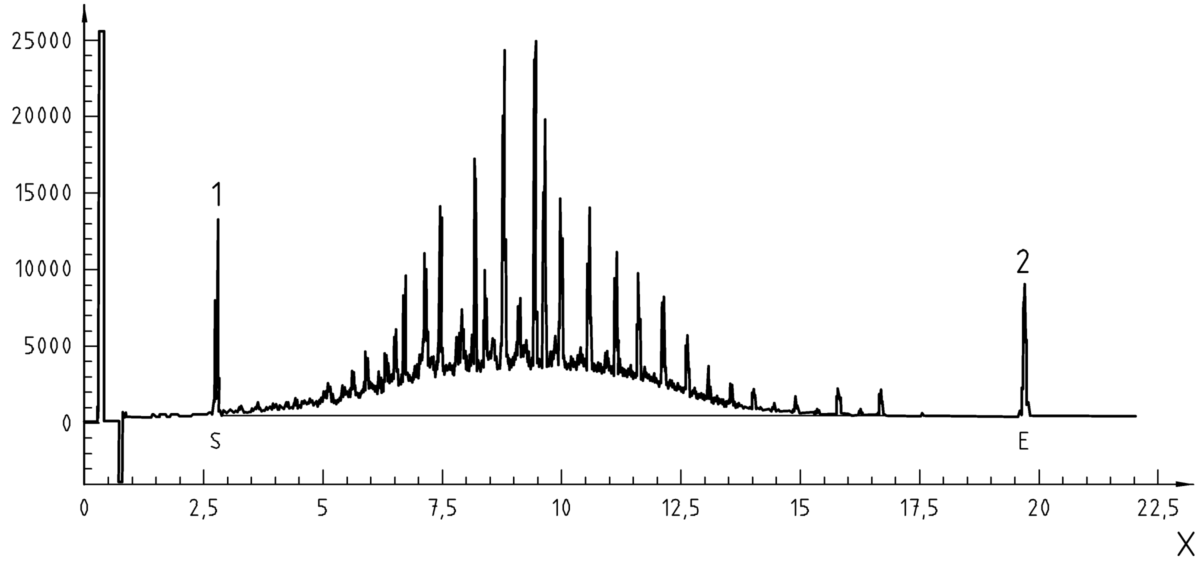
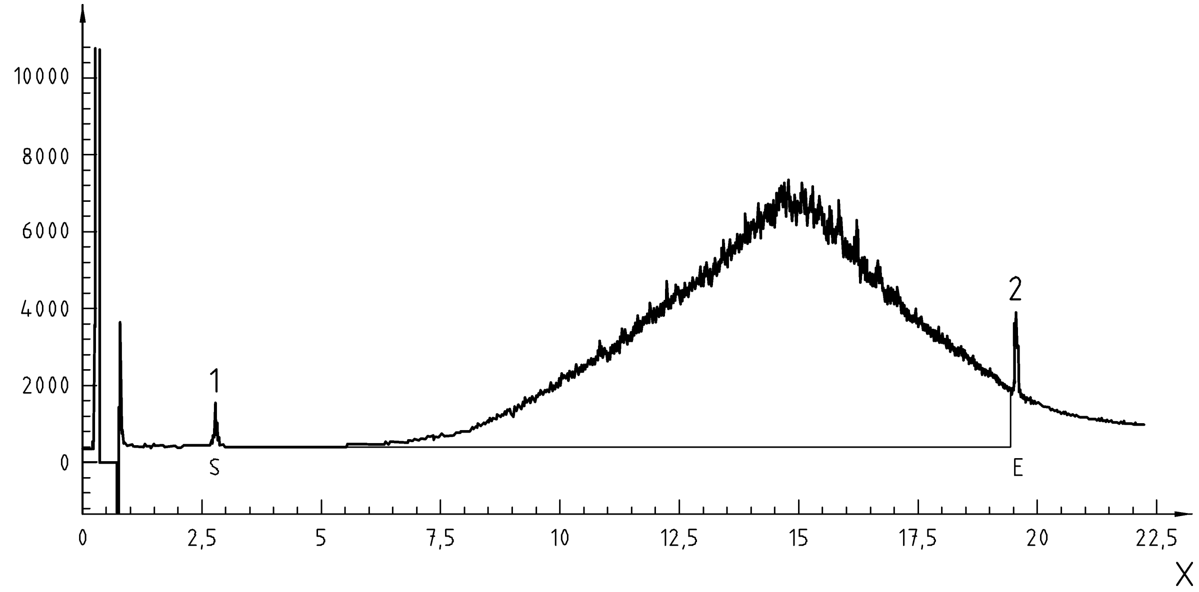


Key
X minutes
1 n-decane
2 n-tetracontane

Figure A.3 — Integrated gas chromatogram of a contaminated soil sample corrected for the "column bleed“



Key
X minutes
1 n-decane
2 n-tetracontane

Figure A.4 — Integrated gas chromatogram of a highly contaminated waste sample corrected for the "column bleed“

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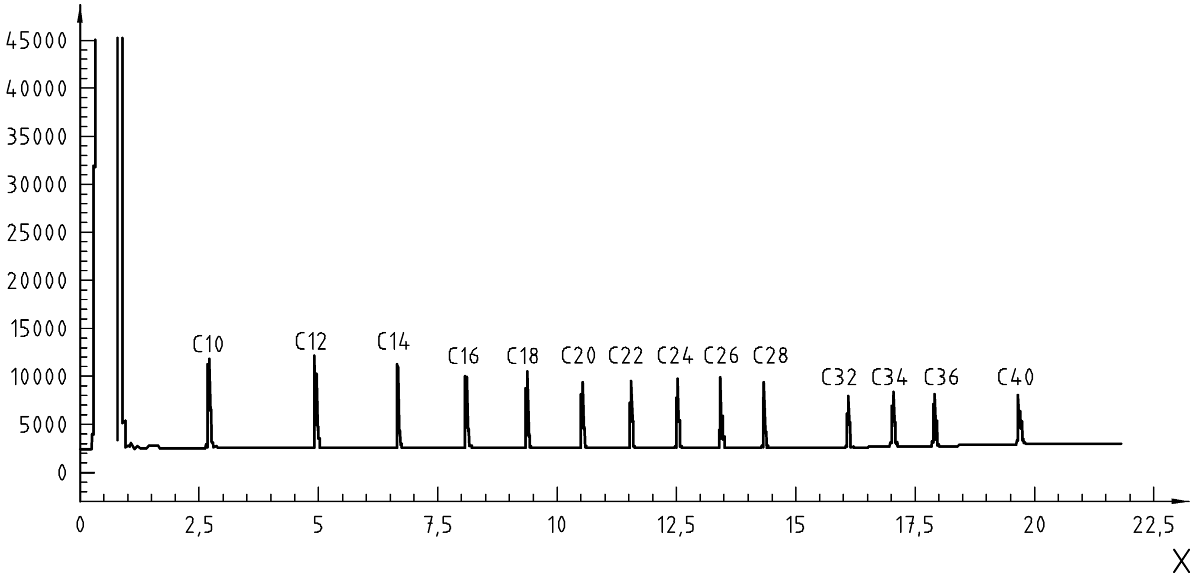

Key

X minutes

Figure A.5 — Gas chromatogram of a system performance standard solution [6.10]

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Annex B
(informative)

Determination of the boiling range of mineral oil hydrocarbons from the gas chromatogram

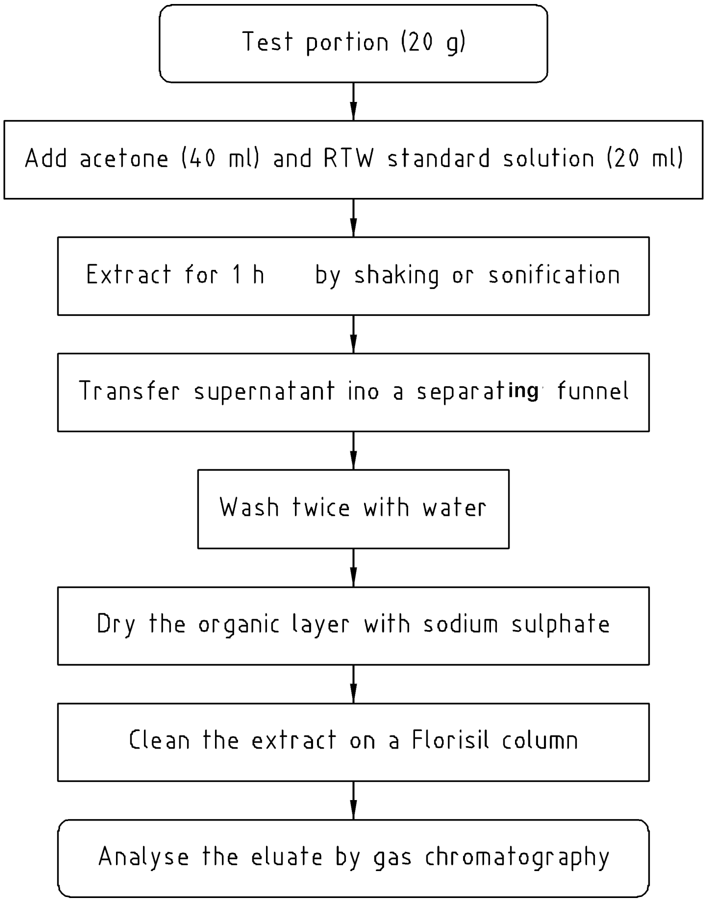
Using the data from Table B.1 the approximate boiling range of the hydrocarbons in the sample can be estimated by comparison of the peak pattern of the sample chromatogram and that of the n-alkane mixture.

Table B.1 — Boiling points of the n-alkanes with from 6 to 44 carbon atoms

Number of carbon atoms	boiling point in °C
6	69
7	98
8	126
9	151
10	175
11	196
12	216
13	235
14	253
15	271
16	287
17	302
18	317
19	331
20	344
21	356
22	369
23	380
24	391
25	402
26	412
27	422
28	432
29	441
30	450
31	459
32	468
34	483
35	491
36	498
37	505
38	512
39	518
40	525
41	531
42	537
43	543
44	548

Annex C
(informative)

Flow diagram



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Annex D
(informative)

Aqueous liquid waste

Weigh to the nearest 0,1 g a quantity of the homogenised liquid waste containing about 20 g of dry matter (e.g. 400 g of liquid waste containing about 5 % of dry matter) and put it into a separating funnel [8.9]. Add (50 ± 0,1) ml of the RTW standard solution [6.7]. Extract the sample by shaking for one hour. Collect the organic layer in a glass vessel [8.6]. Add sufficient amount of sodium sulfate so that no lumps are formed anymore. Transfer 10 ml of the extract to a clean-up column filled with Florisil [6.11]. Do not pre-wash the column with organic solvent. Collect the entire eluate. Transfer an aliquot of the purified extract to a GC-vial and analyse by gas chromatography.

NOTE This kind of waste is typically a slurry containing a low amount (about 5 % to 10 %) of very fine solid matter that is usually difficult to separate by filtration or centrifugation.

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Annex E
(informative)

Summary of general requirements and recommendations

Purpose of this summary is to support the organization of sampling and sample pre-treatment processes. The information given should be helpful to prepare a sampling plan.

Requirements not mentioned in this European Standard are considered as recommendations.

matrix restrictions	Only for solid waste
typical working range	100 mg/kg to 10 000 mg/kg dry mass
sampling instruments	Any instrument that does not release mineral oil. Take care with diesel generators or diesel sampling engines.
bottle pre-treatment	clean and dry; free of solvents
bottle material	wide neck amber glass with grounded stopper
transport conditions	dark and cool
preservation	cooling at about 4 °C
storage conditions	at 4 °C in the dark not longer than 1 week; longer storage at about -18 °C
required amount	about 500 g original sample
test portion	about 20 g of the homogenized original sample
drying procedure	Drying only applies if losses of hydrocarbons can be excluded; if drying is applicable, freeze drying is recommended
sieving (particle size)	Particle sizes < 2 mm are favourable. Size reduction only applies if losses of hydrocarbons can be excluded.
grinding	not applicable
compatibility with	Sample can be used for determination of hydrocarbons (gravimetry), TOC, halogens and sulfur, dry matter as well. Depending on the number of parameters the sample amount has to be increased.

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