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**Karaktärisering av avfall – Bestämning av  
kolväteinnehåll i intervallet C10 – C40 med  
gaskromatografi**

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

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EUROPEAN STANDARD  
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EN 14039

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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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This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

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**EN 14039:2004 (E)**

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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of an identical text or by endorsement, at the latest by March 2005, and conflicting national standards shall be withdrawn at the latest by March 2005.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.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

## EN 14039:2004 (E)

### 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.

## 1 Scope

This document specifies a method for the quantitative determination of the hydrocarbon content (C<sub>10</sub> to C<sub>40</sub>) 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<sub>10</sub>H<sub>22</sub> to C<sub>40</sub>H<sub>82</sub>, 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 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<sub>10</sub>H<sub>22</sub>) and n-tetracontane (C<sub>40</sub>H<sub>82</sub>)

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**,  $(\text{CH}_3)_2\text{CO}$ ;

**6.3 n-Heptane**,  $\text{C}_7\text{H}_{16}$ ;

**6.4 Florisil<sup>1</sup> for the preparation of clean-up column**, particle size 150  $\mu\text{m}$  to 250  $\mu\text{m}$  (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**,  $\text{Na}_2\text{SO}_4$ ;

**6.6 Test solution** of n-octadecanoic acid octadecyl ester,  $\text{C}_{36}\text{H}_{72}\text{O}_2$ ;

Dissolve about  $(100 \pm 1)$  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  $(30 \pm 1)$  mg of n-tetracontane into a 1 l volumetric flask, dissolve completely in an appropriate volume of n-heptane [6.3], add 30  $\mu\text{l}$  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<sup>2</sup>**

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<sup>1</sup> 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<sub>10</sub> to C<sub>40</sub>, 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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<sup>2</sup> 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.

## 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.1 in 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