BRITISH STANDARD

BS EN 14345:2004

Characterization of waste — Determination of hydrocarbon content by gravimetry

The European Standard EN 14345:2004 has the status of a British Standard

ICS 13.030.01

British Standards

National foreword

This British Standard is the official English language version of EN 14345:2004.

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

- aid enquirers to understand the text;
- present to the responsible international/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.

Cross-references

The British Standards which implement international or European publications referred to in this document may be found in the *BSI Catalogue* under the section entitled “International Standards Correspondence Index”, or by using the “Search” facility of the *BSI Electronic Catalogue* or of British Standards Online.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 1 November 2004

Summary of pages

This document comprises a front cover, an inside front cover, the EN title page, pages 2 to 16, an inside back cover and a back cover.

The BSI copyright notice displayed in this document indicates when the document was last issued.

Amendments issued since publication

Amd. No.	Date	Comments

ISBN 0 580 44701 4

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 14345

September 2004

ICS 13.030.01

English version

Characterization of waste - Determination of hydrocarbon content by gravimetry

Caractérisation des déchets - Détermination de la teneur en hydrocarbures par gravimétrie

Charakterisierung von Abfällen - Bestimmung des Kohlenwasserstoffgehalts mittels Gravimetrie

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

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

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.

CEN members are the national standards bodies of 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.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36 B-1050 Brussels

Ref. No. EN 14345:2004: E

Contents

Foreword

This document (EN 14345:2004) 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.

Introduction

Hydrocarbons 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 the new standard is to provide an analytical method for the determination of hydrocarbon content by gravimetry avoiding the use of such solvents.

The user of this standard should be aware that the results obtained with the new method might not be comparable with those obtained when using infrared spectroscopy.

This document is restricted to waste samples containing large amounts of relatively high boiling hydrocarbons (boiling point above 250 °C) and may be used as a test that is easy to perform.

1 Scope

This document specifies a gravimetric method for the determination of the hydrocarbon content in solid waste. It is applicable to hydrocarbon content greater than 0,5 % (m/m) on dry matter basis. This method does not permit to provide qualitative information on the nature and the source of the hydrocarbons.

NOTE Aqueous liquid waste samples can be analysed in accordance with prEN ISO 9377-1 or the procedure specified in Annex B.

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)*

3 Terms and definitions

For the purposes of this document, the following term and definition applies.

3.1

hydrocarbon content by gravimetry

sum of compounds extractable with acetone/petroleum ether (2+1) which do not adsorb on Florisil and do not evaporate during the drying process.

For practical reasons, the term "hydrocarbon content by gravimetry" is abbreviated "hydrocarbon content" in the following text

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

NOTE 2 This definition differs from that given in EN 14039.

4 Principle

Depending on the type of waste, a known amount of the homogenised waste sample is extracted by mechanical shaking twice with acetone/petroleum ether (2+1). The combined extracts are washed twice with water. Polar compounds are removed by chromatography on Florisil. The final extract is evaporated to dryness after which the mass of the residue is determined by weighing.

5 Hazards

Acetone and petroleum ether 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. Due to its toxicity, the contact with the skin and eyes and the inhalation of petroleum ether vapours shall be avoided.

6 Interferences

High concentrations of more polar compounds, e.g. animal and vegetable fats and oils, may exceed the adsorption capacity of the Florisil used. A mass fraction of up to 1,0 % of such compounds will not interfere with the determination of hydrocarbon content.

7 Reagents

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

7.2 **Acetone**, $(CH_3)_2CO$;

7.3 **Petroleum ether**, (boiling range 40 °C to 60 °C);

NOTE Other hydrocarbon solvents, boiling range 36 °C to 69 °C can be used providing extraction efficiencies are proven to be comparable.

7.4 **Florisil**[1], 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 Forisil cartridges containing 2 g of Florisil and 2 g of sodium sulfate are also applicable.

7.5 **Anhydrous sodium sulfate**, Na_2SO_4, heated for at least 2 h at 550 °C;

7.6 **Test solution** of n-octadecanoic acid octadecyl ester, $C_{36}H_{72}O_2$. Dissolve about 2 g of n-octadecanoic acid octadecyl ester in 100 ml petroleum ether [7.3].

7.7 **Hydrocarbon standard solution for recovery check**

Dissolve about 2 g of an heavy mineral oil such as a lubricating oil, without any additives, in 100 ml of petroleum ether [7.3].

7.8 A plug of pre-washed glass wool or a PTFE frit is pushed down into the column [8.10]. Then, successively 2 g of Florisil [7.4] and 2 g of sodium sulfate [7.5] are added. The column shall be prepared immediately before use.

8 Equipment

8.1 **Standard laboratory glassware**, which shall be heated or rinsed with acetone [7.2] and dried before use;

8.2 **Mechanical shaker,** e g. horizontal or rotary shaker;

8.3 **Evaporation device**, e.g. a rotary evaporator;

8.4 **Analytical balance** (Accuracy equal or better than 0,1 mg);

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

---

[1] Florisil is the trade name of a prepared diatomaceous substance, mainly consisting of anhydrous magnesium silicate. This information is given for the convenience of users of this European Standard 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.

8.6 **Conical flask**, 100ml or 250 ml, with ground glass stopper;

8.7 **Separating funnel** of at least 500 ml, with ground glass stopper;

8.8 **Glass evaporation vessel**, e.g. 100 ml or 250 ml round bottom flask;

8.9 **Glass beaker**, 25 ml;

8.10 **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 pre-treatment

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, the 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 exceed 0,1 % (20 mg for a typical mass of the test portion of 20 g), every step in the procedure shall be checked to find the reason for these high blanks.

10.2 Dry matter

Determine the dry matter on a separate sub-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

Weigh to the nearest 0,1 g about 20 g of the homogenised sample into a glass extraction vessel [8.5], add 40 ml ± 1 ml of acetone [7.2]. After short shaking by hand add 20 ml ± 0,1 ml of petroleum ether [7.3]. Extract the sample for 10 min to 15 min on a mechanical shaker [8.2]. After settling of the solid material transfer as much as possible of the supernatant into a separating funnel [8.7]. Repeat extraction with the same volumes of fresh solvent. Combine the extracts and remove the acetone by washing with 100 ml of water twice. Collect the organic layer in an conical flask [8.6]. Add sufficient amount of sodium sulfate [7.5] so that no lumps are formed anymore.

NOTE 1 Alternative extraction procedures, e.g. ultrasonic or accelerated solvent extraction (ASE) can be used provided they give comparable extraction performances.

NOTE 2 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.

10.4 Clean-up

Fill the clean-up column with Florisil in accordance with [7.8.]. Transfer the extract quantitatively to the top of the column. Rinse the conical flask containing the sodium sulfate twice with about 5 ml of petroleum ether and add this to the column. Collect the entire eluate in the evaporation vessel [8.8]. Rinse the column twice with about 5 ml of petroleum ether and add that eluate to the evaporation vessel [8.8]

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

10.5 Gravimetric determination of the hydrocarbon content

Concentrate extract using an appropriate evaporation device [8.3] to a small volume, but do not evaporate to dryness. Transfer the concentrated extract into a previously weighed 25 ml beaker [8.9]. Rinse the evaporation vessel with 3 small portions of the petroleum ether [6.3] and add the washings to the beaker. Place the beaker on a heating bath and cautiously evaporate the solvent under a hood to 1 ml to 2 ml. Heat the beaker in an oven at (80 ± 2) °C for (15 ± 0,5) min. Remove the beaker and allow to cool in a desiccator and reweigh. Calculate the mass m_2 of the extraction residue by difference.

NOTE If semi-volatile hydrocarbons, e.g. diesel fuels, should be included, do not dry at 80 °C, but follow the procedure in Annex A.

10.6 Calculation and evaluation

The hydrocarbon mass content for each of the phases is calculated using the equation:

$$w = \frac{m_2 - m_o}{m_1} \times \frac{\%100}{w_{dm}} \times \%100 \qquad (1)$$

where

w is the hydrocarbon of the sample, in per cent on a dry matter mass content basis;

m_o is the mass of extraction residue of the blank determination, in grams, in accordance with [10.1];

m_1 is the mass of the sample taken for analysis, in grams;

m_2 is the mass of extraction residue of the sample, in grams;

w_{dm} is the dry matter mass fraction of the original sample in percent determined in 10.2.

Round the result to 0,1 % . 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 % or as g/kg based on the original material.

10.7 Quality control

10.7.1 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:

Pipette 10 ml of the n-octadecanoic acid octadecyl ester solution [7.6] into an conical flask [8.6] and add 40 ml of petroleum ether [7.3] Continue with [10.4] and [10.5]. The mass of residue m_2 shall not exceed 10 mg (less than 5 % of the fatty ester initial content). If the recovery of n-octadecanoic acid octadecyl ester is above 5 %, activate the Florisil in accordance with [7.4] and repeat the test. If the repeated test again shows that the criterion is not met, discard that batch of Florisil.

10.7.2 Recovery of the hydrocarbon standard solution

The recovery of the hydrocarbon standard solution [7.7] 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:

Pipette 10 ml of the hydrocarbon standard solution [6.7] into an conical flask [8.6] and add 40 ml of petroleum ether [7.3] Continue with [10.4] and [10.5]. The mass of residue m_2 shall be at least 160 mg (recovery rate more than 80 %).

If the recovery of the hydrocarbon standard solution is below 80 %, activate the Florisil in accordance with [7.4] and repeat the test. If the repeated test again shows that the criterion is not met, discard that batch of Florisil.

11 Performance characteristics

The method performance characteristics given in Table 1 have been established in an European intercomparison study, carried out in 2003.

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

Material	l	n	f [%]	*w:w* [%]	CV_r [%]	CV_R [%]
Contaminated soil	21	42	0	1,33	7,44	19,59
Sludge from a chemical-physical treatment plant	21	42	0	8,09	12,16	33,74

l is number of participating laboratories;

n is the number of outlier-free individual analytical results;

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

f) reference to Annex A or B, if used.

Annex A
(informative)

Inclusion of semi-volatile hydrocarbons

When semi-volatile hydrocarbons such as a diesel-oil are present in the sample, the evaporation method described in 10.5 could result in a loss of the lightest part of the hydrocarbon mixture, leading to an underestimation of the hydrocarbon content.

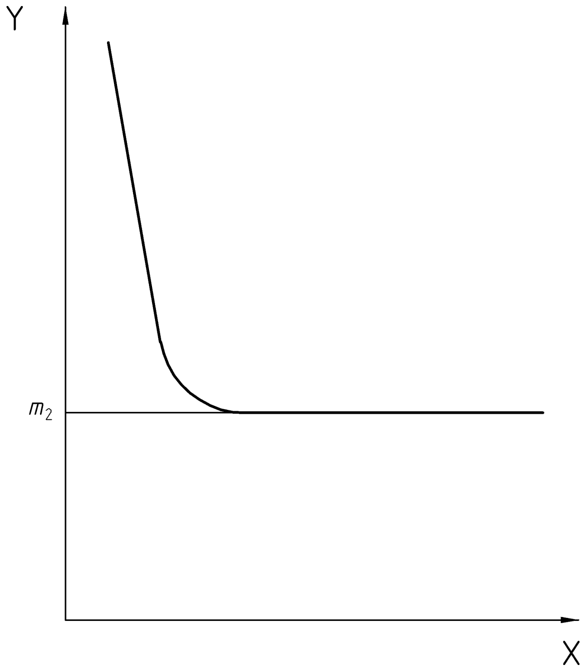
Minimize this error using a variation of this standard, where the final evaporation phase (15 min at 80°C) after reducing the solvent to 1 ml to 2 ml, is replaced by an evaporation step at ambient temperature as follows:

Gently blowing with a stream of inert gas (e.g. nitrogen) on the surface of the liquid for 5 min, then weighing the beaker.

The beaker is placed under the stream of gas for a further 5 min and then weighed again.

If the difference between the two net masses is less than 5 % of the second value, this second value is reported as the dried mass (m_2) [see Figure A.1].

If the difference is higher than 5 % (which indicates the presence of semi-volatile compounds), this operation is repeated noting the masses and then draw a curve of net mass against time. The straight line part of the plot after the inflexion point back onto the y-axis (mass) is projected. The intersection point will give the mass m_2 to be used in calculation (1) in section 10.6 [see Figure A.2]

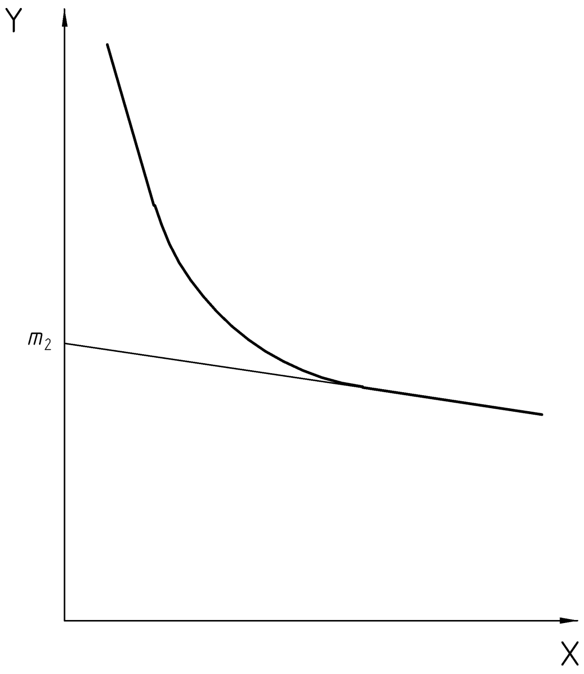


Key

X time

Y mass

Figure A.1 — Sample containing heavy oil



Key

X time

Y mass

Figure A.2 — Sample containing diesel oil

Annex B
(informative)

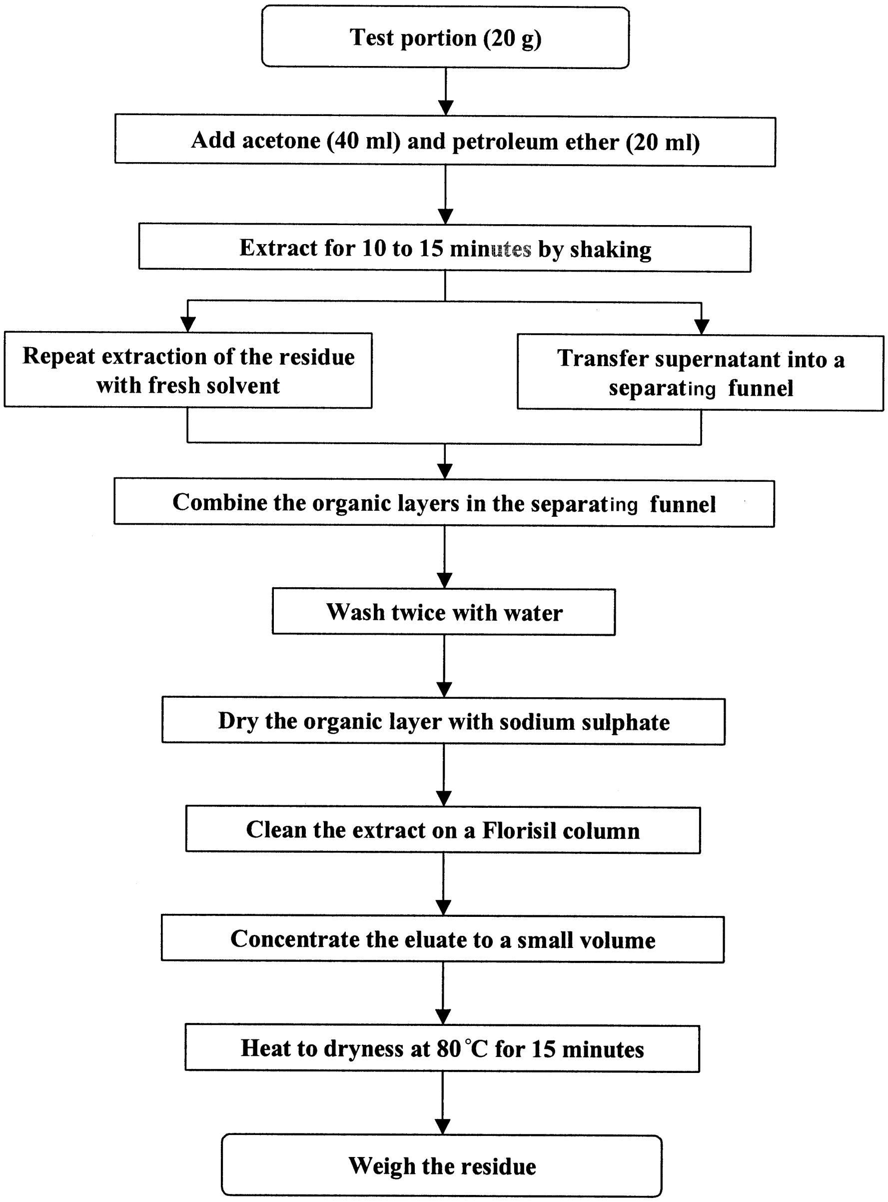
Aqueous liquid waste

A quantity of homogenised liquid waste containing about 20 g of dry matter (e.g. 400 g of liquid waste containing about 5 % of dry matter) is weighed accurately and putted into a separating funnel [8.7]. About 50 ml of petroleum ether [7.3] is added. The sample is extracted by shaking for 10 min to 15 min. After phase separation, as much as possible of the organic layer is transferred into an conical flask [8.6]. Extraction with the same volumes of fresh solvent is repeated and the extracts are combined. Sufficient amount of sodium sulfate [7.5] is added so that no lumps are formed anymore. The extract is cleaned-up and the hydrocarbon content is determined in accordance with [10.4 and 10.5].

NOTE This kind of waste is typically slurry containing a low amount (about 5 % to 10 %) of very fine solid matter that is usually difficult to separate by filtration or centrifugation. When sample contains only small mass fractions of dry matter, e.g. less than 0,5 %, another suitable method should be used.

Annex C
(informative)

Flow diagram



Annex D
(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 document are considered as recommendations.

Matrix restrictions	Only for solid waste
Typical working range	above 0,5 %
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 (GC), TOC[2], halogens and sulphur, dry matter as well. Depending on the number of parameters the sample amount has to be increased.

---

[2] Total Organic Carbon

Bibliography

EN 14039, *Characterization of waste — Determination of hydrocarbon content in the range of* C_{10} *to* C_{40} *by gas chromatography.*

blank

BSI — British Standards Institution

BSI is the independent national body responsible for preparing British Standards. It presents the UK view on standards in Europe and at the international level. It is incorporated by Royal Charter.

Revisions

British Standards are updated by amendment or revision. Users of British Standards should make sure that they possess the latest amendments or editions.

It is the constant aim of BSI to improve the quality of our products and services. We would be grateful if anyone finding an inaccuracy or ambiguity while using this British Standard would inform the Secretary of the technical committee responsible, the identity of which can be found on the inside front cover. Tel: +44 (0)20 8996 9000. Fax: +44 (0)20 8996 7400.

BSI offers members an individual updating service called PLUS which ensures that subscribers automatically receive the latest editions of standards.

Buying standards

Orders for all BSI, international and foreign standards publications should be addressed to Customer Services. Tel: +44 (0)20 8996 9001. Fax: +44 (0)20 8996 7001. Email: orders@bsi-global.com. Standards are also available from the BSI website at http://www.bsi-global.com.

In response to orders for international standards, it is BSI policy to supply the BSI implementation of those that have been published as British Standards, unless otherwise requested.

Information on standards

BSI provides a wide range of information on national, European and international standards through its Library and its Technical Help to Exporters Service. Various BSI electronic information services are also available which give details on all its products and services. Contact the Information Centre. Tel: +44 (0)20 8996 7111. Fax: +44 (0)20 8996 7048. Email: info@bsi-global.com.

Subscribing members of BSI are kept up to date with standards developments and receive substantial discounts on the purchase price of standards. For details of these and other benefits contact Membership Administration. Tel: +44 (0)20 8996 7002. Fax: +44 (0)20 8996 7001. Email: membership@bsi-global.com.

Information regarding online access to British Standards via British Standards Online can be found at http://www.bsi-global.com/bsonline.

Further information about BSI is available on the BSI website at http://www.bsi-global.com.

Copyright

Details and advice can be obtained from the Copyright & Licensing Manager. Tel: +44 (0)20 8996 7070. Fax: +44 (0)20 8996 7553. Email: copyright@bsi-global.com.

BSI
389 Chiswick High Road
London
W4 4AL