

Solid recovered fuels — ^{14}C -based methods for the determination of the biomass content

ICS 75.160.10

National foreword

This Draft for Development is the UK implementation of CEN/TS 15747:2008.

This publication is not to be regarded as a British Standard.

It is being issued in the Draft for Development series of publications and is of a provisional nature. It should be applied on this provisional basis, so that information and experience of its practical application can be obtained.

Comments arising from the use of this Draft for Development are requested so that UK experience can be reported to the international organization responsible for its conversion to an international standard. A review of this publication will be initiated not later than 3 years after its publication by the international organization so that a decision can be taken on its status. Notification of the start of the review period will be made in an announcement in the appropriate issue of Update Standards.

According to the replies received by the end of the review period, the responsible BSI Committee will decide whether to support the conversion into an international Standard, to extend the life of the Technical Specification or to withdraw it. Comments should be sent to the Secretary of the responsible BSI Technical Committee at British Standards House, 389 Chiswick High Road, London W4 4AL.

The UK participation in its preparation was entrusted to Technical Committee PTI/17, Solid biofuels.

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

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 cannot confer immunity from legal obligations.

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English Version

**Solid recovered fuels - ^{14}C -based methods for the determination
of the biomass content**

Combustibles solides de récupération - Méthodes basées
sur le ^{14}C pour la détermination de la teneur en biomasse

Feste Sekundärbrennstoffe - ^{14}C -Verfahren zur
Bestimmung des Gehaltes an Biomasse

This Technical Specification (CEN/TS) was approved by CEN on 11 May 2008 for provisional application.

The period of validity of this CEN/TS is limited initially to three years. After two years the members of CEN will be requested to submit their comments, particularly on the question whether the CEN/TS can be converted into a European Standard.

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Foreword

This document (CEN/TS 15747:2008) has been prepared by Technical Committee CEN/TC 343 “Solid Recovered Fuels”, the secretariat of which is held by SFS.

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According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to announce this Technical Specification: 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 the United Kingdom.

Introduction

The determination of the biomass carbon content using the ^{14}C method is based on the well established analytical procedures that are used for the determination of the age of carbon containing objects. It can be used for normal sample types, sample types that cannot be analysed accurately with the methods described in CEN/TS 15440 (1) (see Annex D), samples with a biomass carbon content below 5%, and for reference measurements.

For the determination of the biomass carbon content based on the ^{14}C method a general sample preparation and the three common used methods for the determination of the ^{14}C content are described. With this modular approach it will be possible for normally equipped laboratories to prepare samples for the ^{14}C content, and to determine the ^{14}C content with their own equipment or to outsource the determination of the ^{14}C content to laboratories that specialize in this matter.

For the collection from the sample of the ^{14}C content, generally accepted methods for the conversion of the carbon present in the sample to CO_2 are described. For the measurement of the ^{14}C content, methods are selected that are already generally accepted as methods for the determination of the age of objects.

1 Scope

This Technical Specification specifies the test methods for the determination of the biomass carbon content in solid recovered fuels based on the ^{14}C content. The biomass fraction by weight and by energy are calculated from the biomass carbon content.

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.

CEN/TS 15400, *Solid recovered fuels — Methods for the determination of calorific value*

CEN/TS 15413, *Solid recovered fuels — Methods for the preparation of the test sample from the laboratory sample*

CEN/TS 15442, *Solid recovered fuels — Methods for sampling*

CEN/TS 15443, *Solid recovered fuels — Methods for laboratory sample preparation*

3 Terms and definitions

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

3.1

biogenic carbon

mass fraction of total carbon that was produced in natural processes by living organisms but not fossilized or derived from fossil resources

3.2

biomass carbon

equivalent to biogenic carbon

3.3

biomass content

mass fraction of biomass material present in the sample

3.4

isotope abundance

fraction of atoms of a particular isotope of an element

3.5

percentage modern Carbon (pmC)

percent modern carbon relative to the NIST Oxalic acid standard reference material SRM4990B. The internationally accepted radiocarbon dating reference value is 95 percent of the activity, in AD 1950, of this NBS oxalic acid SRM4990B. In 2006 the value of 100% biogenic carbon was set at 107 pmC.

4 Symbols and abbreviations

^{14}C Carbon isotope with an atomic mass of 14

AMS Accelerator Mass Spectrometry

β	Beta particle, electron emitted during radioactive decay
BI	Beta Ionisation
Bq	Bequerel, desintegrations per second
daf	dry ash free
DPM	Disintegrations per minute
CPM	Counts per minute
GM	Geiger Müller
LLD	Lower Limit of Detection
MOP	3-Methoxy 1-propyl amine
LSC	Liquid Scintillation Counter or Liquid Scintillation Counting
REF	Reference value of 100% biogenic carbon
PSM	Proportional Scintillation-counter Method
pmC	percentage modern Carbon, carbon mass fraction from biogenic origin
RSD	Relative Standard Deviation
SRF	Solid Recovered Fuel
UHV	Upper Heating Value

5 Equipment and reagents

- Carbamate solution (e.g. Carbasorb® E)
- Scintillation cocktail (e.g. Permafluor® E+)
- Glass bottle (standard glass sample bottles with plastic screw caps that are resistant to 4M NaOH)
- 4 M NaOH absorption liquid

For the preparation of a carbonate free absorption liquid, preparation using freshly opened NaOH pellet containers is sufficient. Dissolve the NaOH pellets in a small amount of water (the heat produced during the dissolution process will enhance the dissolution process. Small amounts of precipitation are an indication of the presence of Na_2CO_3 . By decanting the clear phase the almost carbonate free solution can be diluted to the desired volume. As the dissolution of NaOH is an exothermic process extra care should be taken as boiling of the concentrated solution during dilution can occur.

For high precision measurements the following procedure can be used to produce a carbonate free NaOH solution.

- 6700 ml demineralised water
- 1120 g NaOH pellets
- 300 ml saturated $\text{Ba}(\text{OH})_2$ solution. (± 25 g $\text{Ba}(\text{OH})_2$ in 300 ml demineralised water)

- Dissolve the NaOH pellets in the demineralised water (use magnetic stirrer)
- Heat the solution and the saturated Ba(OH)₂ solution to 80 °C, and mix the two solutions. Cool down the solution to -8 °C, stop the stirring and leave the solution overnight at -8 °C. After filtration the solution is ready for use. Keep stored in a well-sealed container.

A list of equipment and reagents necessary for conversion and for the different measurements is presented in the Annexes.

6 Principle

The methods for the determination of the biomass carbon content specified in this Technical Specification are based on the determination of the ¹⁴C content. The amount of biomass carbon in solid recovered fuel is proportional to this ¹⁴C content.

Complete combustion is carried out in a way to comply with the requirements of the subsequent measurement of the ¹⁴C content. This measurement is carried out according to one of the three methods, Proportional Scintillation Method (PSM), Beta Ionisation (BI) or Accelerated Mass Spectrometry (AMS). These methods are considered equivalent, giving the same results within the scope of this Technical Specification. The results are expressed as the percentage biomass carbon in the total carbon content. The fraction of biomass content by weight and the fraction of biomass by energy content are calculated from the biomass carbon content, using the biomass carbon content and the energy content of the biomass fraction that is present in the sample.

7 Procedure

7.1 Sampling

Sampling, transport, storage of the solid recovered fuel shall be conducted according CEN/TS 15442 and CEN/TS 15443. Preparation of the test sample shall be conducted according to CEN/TS 15413.

7.2 Conversion of the carbon present in the sample to a suitable sample for ¹⁴C determination

For the conversion of the sample to a form that can be used for the determination of the ¹⁴C content, three methods are allowed: combustion in a calorimetric bomb (see 7.3), combustion in a tube furnace (see 7.5) and combustion in a laboratory scale combustion apparatus (see 7.6). The carbon dioxide formed is then absorbed in a suitable solution, which depends on the combustion method and the selected method for the subsequent ¹⁴C measurement. For the PSM detection method two absorption solutions are possible. However when substantial chemical or optical quenching is foreseen (high NO_x values, formation of coloured substances) collection of the CO₂ shall be done in the NaOH solution. The use of pure oxygen or a mix of oxygen and argon during combustion will reduce the formation of nitrous oxides to an acceptable level.

7.3 Combustion of the sample in a calorimetric bomb

For the determination of the calorific value of the sample, CEN/TS 15400 shall be used. After the complete combustion in the oxygen bomb the combustion gases are collected in a gas bag as described in 7.4. For the determination of the ¹⁴C content by PSM the carbon dioxide shall be collected in a cooled mixture of carbamate solution and a suitable scintillation liquid. For the determination of the ¹⁴C content by AMS or BI the carbon dioxide shall be collected in a 4 M NaOH solution. For AMS, alternatively ca. 2 ml of the CO₂ gas can be taken from the bag using a glass syringe and the gas can be transferred to the AMS target preparations system. As the bomb volume is released to atmospheric pressure, there will be a residual amount leftover in the bomb that is directly related to the pressure in the bomb after the combustion (with a residual pressure of 25 bar 4% of the combustion gas will be left after release to atmospheric pressure).

To overcome this artefact: