SLOVENSKI STANDARD
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Solid recovered fuels - 14C-based methods for the determination of the biomass content

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

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

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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

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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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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

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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 $Ba(OH)_2$ solution. (± 25 g $Ba(OH)_2$ in 300 ml demineralised water)

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— 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 ^{14}C content. The amount of biomass carbon in solid recovered fuel is proportional to this ^{14}C content.

Complete combustion is carried out in a way to comply with the requirements of the subsequent measurement of the ^{14}C 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 ^{14}C determination

For the conversion of the sample to a form that can be used for the determination of the ^{14}C 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 ^{14}C 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 CO$_2$ 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 ^{14}C 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 ^{14}C 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 CO$_2$ 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:

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a) Perform the calibration and the analysis taking account of this residual amount by using the pressure correction factor.

b) Use the vacuum pump to remove the residue.

c) Flush the bomb with Argon and collect the CO_2 in the rinsing gases as well.

7.4   Adsorption of the gas sample

The gas sample bag is connected to a small pump with a connection line into a 20 ml "Packard" Scintillation vial, filled with a mixture of 10 ml of Carbosorb E sorption liquid and 10 ml of Permafluor E+ Scintillation cocktail, placed in an ice bath, to remove the heat of the exothermic carbamate formation reaction. The pumping speed is low, typical 50 ml.min^{-1} to 60 ml.min^{-1}.The transfer of the gas from the bag takes about 2 h to 3 h. After the sample is collected it can be counted on a Liquid Scintillation Counter. Blank samples should also be counted at the same time to allow that small day-to-day variations in the background can be accounted for.

7.5   Combustion of the sample in a tube furnace

Using a tube furnace only a complete combustion of the sample is acceptable. For the determination of the ^{14}C content by PSM the carbon dioxide shall be done using a suitable impinger filled with a cooled mixture of Carbosorb and a suitable scintillation liquid or a 4 M NaOH solution. For the determination of the ^{14}C content by AMS or BI the carbon dioxide shall be collected using a suitable impinger filled with a 4 M NaOH solution.

As an alternative the CO_2 can be trapped by means of a cryogenic trap. In that case the cryogenic trap shall consist of a water trap (dry ice in ethanol or acetone) followed by a cryogenic trap. Care shall be taken to avoid formation of liquid oxygen, which can be achieved by heating the trap slightly above the boiling point of oxygen, using liquid argon or by performing the separation at diminished pressure.

7.6   Combustion of the sample in a laboratory scale combustion apparatus

The lab-scale combustion apparatus shall be able to combust the SRF at a constant rate, with a complete conversion of the carbon present to CO_2. For the determination of the ^{14}C content by PSM the carbon dioxide shall be collected using a suitable impinger filled with a cooled mixture of Carbosorb and a suitable scintillation liquid or a 4 M NaOH solution. For the determination of the ^{14}C content by AMS or BI the CO_2 shall be collected using a suitable impinger filled with a 4 M NaOH solution. As a result of the absorption of the CO_2 a large volume reduction of the gas volume will be observed after trapping. Therefore the gas pump is to be positioned in front of the impinger, and the gas pump used shall be gas tight.

As an alternative the CO_2 can be trapped by means of a cryogenic trap. In that case the cryogenic trap shall consist of a water trap (dry ice in ethanol or acetone) followed by a cryogenic trap. Care shall be taken to avoid formation of liquid oxygen, which can be achieved by heating the trap slightly above the boiling point of oxygen, using liquid argon or performing the separation at diminished pressure. As an alternative, when AMS is being used, CO_2 may be collected by mixing homogenized SRF with cupric oxide (CuO) in a sealed, evacuated quartz or Vycor glass tube. 20 mTorr water can be added to the tube prior to introduction of the CO_2 to help remove sulfur compounds. The tube is heated to 900 °C for 3 h to 5 h. The CO_2 is collected by breaking the tube using a tube-cracker connected to an evacuated glass collection line.

8   Measurements

The measurement of the ^{14}C content of the sample shall be done according to one of the methods as described in the Annexes of this TS. When collected samples are sent to specialized labs, the samples should be stored in a way that no CO_2 from air can enter the absorption solution. A check on the in leak of CO_2 from air shall be performed by preparing laboratory blank's during the sampling stage.

For the determination of the 0% biomass content the combustion of a coal standard (e.g. BCR 181) can be used.

For the 100% Biomass content the NIST Oxalic acid primary standard (SRM 4990b) can be used. For routine checks a wood standard calibrated against the oxalic acid will be sufficient.

For the determination of the radiocarbon content in SRF material the following performance characteristics shall be met.

Range   5 pmC to 120 pmC corresponding to 5% to 100% Biogenic Carbon content

RSD   5% in the range 5 pmC to 10 pmC

            corresponding to 0% to 10% Biogenic Carbon (e.g. 7,0% +/- =<0,35%)

RSD   2% in the range 10pmC to 120 pmC

            corresponding to 10% to 100% Biogenic Carbon.

NOTE 1   The BI and AMS techniques can be used in the lower range (0% – 5 % Biogenic carbon) or if higher precision is demanded.

NOTE 2   The upper limit of 120 pmC is the working range of common biomass components, with optional extension to higher levels (e.g. for the measurement of bomb activity levels)

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9   Calculation

Before the above-ground hydrogen bomb testing (started around 1955 and terminated in 1962) the atmospheric ^{14}C level had been constant to within a few percent, for the past millennium. Hence a sample grown during this time has a well defined 'modern' activity, and the fossil contribution could be determined in a straightforward way. However, ^{14}C created during the weapons testing increased the atmospheric ^{14}C level to up to 200 pmC in 1962, with a decline to 107 pmC in 2006. The ^{14}C activity of a sample grown since 1962 will be elevated according to the average ^{14}C level over the growing interval. However in the already existing ASTM standard ASTM D-6866-5 (2) the 100% biogenic C value of 107 pmC is used. This value shall be the base of calculations; other values are only acceptable if they are based on experimental evidence. From the 107 pmC value the correction factor of 0,93 is derived.

For the calculation of the biomass carbon content a ^{14}C content of 100/0,93 pmC or 13,56/0,93 DPM per gram C will be regarded as a 100% biomass carbon content. (as of the writing of this Technical Specification, November 2006)

This correction value of 0,93 is in accordance with the value that is given in ASTM D 6866-05.

For high precision pmC measurements the ^{14}C/^{12}C and ^{13}C/^{12}C isotopic ratios must be determined as correction for isotopic fractionation should be done. During working up of the sample this fractionation can occur if only a part of the combusted sample is analysed. In biomass small variations in carbon isotope ratio's occur as well, it depends on the type of photosynthesis that formed the biomass. Most biomass (e.g. wood) is of the so-called C3 type photosynthesis, some tropical plants (corn, tropical grasses) are of the C4 type photosynthesis. For SRF applications the maximum error is estimated to be well below 1% as for 100% C4 biomass a value of 99% biomass will be measured if no isotope correction is done.

The fraction of biomass content by weight and the fraction of biomass by energy content shall be calculated using the biomass carbon in the solid recovered fuel and the carbon and energy content of the biomass fraction. The default mean values for SRF, as calculated in Table 1, shall be used. The table is composed of materials that are expected to be present in the commonly used SRF materials, where the bark values in the table also represent mixed wood materials like wood cuttings and the hard wood values represent the wood fraction in general. The averages calculated assume equal fractions of all categories. With a total biomass