
Trda goriva - Določitev vsebnosti biomase na osnovi metode 14C

Solid recovered fuels - Determination of the biomass content based on the 14C method

Feste Sekundärbrennstoffe - Bestimmung des Gehaltes an Biomasse nach der 14C-Methode

Combustibles solides de récupération - Détermination de la teneur en biomasse, basée sur la méthode du C14

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English Version

**Solid recovered fuels - Determination of the biomass content
based on the ¹⁴C method**

Combustibles solides de récupération - Détermination de la
teneur en biomasse, basée sur la méthode du C¹⁴

Feste Sekundärbrennstoffe - Bestimmung des Gehaltes an
Biomasse nach de ¹⁴C-Methode

This Technical Report was approved by CEN on 1 January 2007. It has been drawn up by the Technical Committee CEN/TC 343.

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Foreword

This document (CEN/TR 15591:2007) has been prepared by Technical Committee CEN/TC 343 “Solid recovered fuels”, the secretariat of which is held by SFS.

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0 Introduction

0.1 General

This document has been prepared as a result of the CEN/TC 343/WG 3 meeting in Amsterdam in April 2005. It summarizes the state of the art in ^{14}C -based methods applied to determining the biomass content of SRF; as of yet no technical CEN standards for the application of ^{14}C -based methods to determine biomass content are available. The purpose of this Technical Report is to present the information available on this subject at this moment to assess if an extension of the available methods for determining the biomass content of SRF is required, wanted and technically possible.

Analytically proven standards exist for determining the biomass content of SRF by manual sorting and by selective dissolution (CEN/TS 15440 [1]). In the Netherlands these methods are available as NTA (National Technical Agreement) and have been in use for some years. Important advantages of these standards are their applicability using basic laboratory equipment and available personnel. However, they are not applicable to all kinds of solid recovered fuels. The manual sorting method fails if the constituents of the sample are shredded too finely, if they are strongly intertwined or compressed or if they cannot be recognized visually. The selective dissolution method fails if biomass constituents are present that do not dissolve, or fossil components that do. Both methods fall short if fossil and biomass carbon are mixed at the molecular level. ^{14}C based methods do not use chemical or morphological properties of the sample but physical properties of the carbon atoms themselves. Because ^{14}C based methods are based on these physical properties they avoid the problems of manual sorting and selective dissolution methods. On the other hand they need more instrumentation and skilled personnel. They are proposed here as an addition to the manual sorting and selective dissolution methods because they resolve analytical problems that are otherwise irresolvable.

The application of ^{14}C based methods for similar purposes are not new [2] [3]. In this document the information available in Europe and the USA concerning biomass carbon content determination in solid recovered fuels with ^{14}C based methods is presented to give the reader background information about possibilities and drawbacks of these methods.

0.2 Basis of the ^{14}C method

The ^{14}C method is a well-known method in global use, for determining the age of carbon containing matter. ^{14}C is a radioactive isotope; its presence in the air is a result of the interaction of cosmic radiation and the nitrogen in the atmosphere (see Figure 1). Fossil carbon contains no ^{14}C , however a trace amount of ^{14}C is present in living matter. The ^{14}C isotope is quickly converted to $^{14}\text{CO}_2$ after formation and enters living matter when atmospheric $^{14}\text{CO}_2$ is converted in the biosphere by photosynthesis to sugars and further converted to e.g. cellulose. The concentration of ^{14}C in air is considered constant all over the world. In living material the concentration of ^{14}C is stable and in equilibrium with the air concentration. In dead material the concentration of ^{14}C slowly diminishes to zero as the radioactive ^{14}C isotope decays. Measuring the amount of ^{14}C in solid recovered fuels is the basis for determining biomass content based on the ^{14}C method.

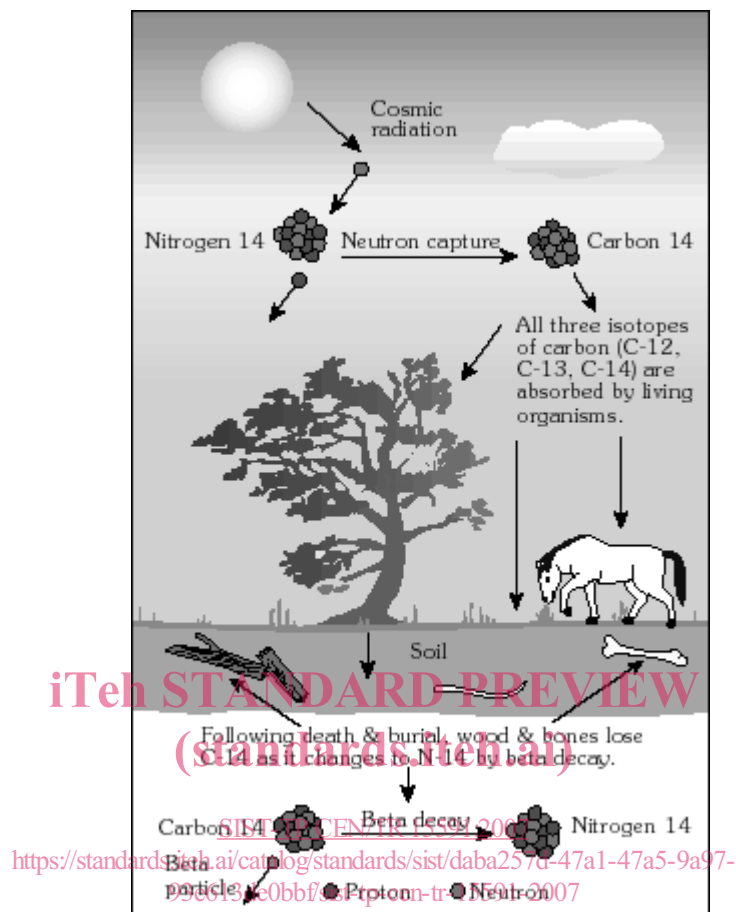


Figure 1 – Illustration of the basis of the ^{14}C method

Organic material is used for many purposes. One of the objectives is direct use as a fuel which is outside the scope of this report. However, after completing their primary use, many of these organic materials may ultimately be used in the form of solid recovered fuels.

Examples of organic materials in solid recovered fuels are:

- Packaging materials;
- Paper;
- Wood used in buildings;
- Kitchen waste;
- Waste (dung and offal) from the bio industry;
- Plastics;
- Car tires.

Carbon present in material produced by living organisms, immobilized as fuel in present times is called biomass. Carbon present in material produced by living organisms immobilized as fuel in a past geological era is called fossil fuel. The difference between the two is that CO_2 from biomass or biomass origin does not

contribute to a higher concentration of CO₂ in the atmosphere as its carbon has been recently extracted from the atmosphere.

In solid recovered fuels, the combustible carbon originates from fossil (mainly in the form of plastics), mixed sources like rubber tyres and packaging materials, and from biomass origin (e.g. wood, paper). Authorities require that emissions of CO₂ from fossil origin by companies is made known, thus, in order to determine these companies, knowledge about the biomass content by total carbon content of mixed fuels should be acquired. For this reason, methods such as the solid dissolution method and ¹⁴C method were developed.

International acceptance of a ¹⁴C based method can be expected, as can be illustrated by the recent publication of ASTM, ASTM D 6866-05, Standard Test Method for determining the Bio based Content of Natural Range Materials Using Radiocarbon and Isotope Ratio Mass Spectrometry Analysis [2].

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1 Scope

This Technical Report gives an overview of the suitability of ^{14}C -based methods for the determination of the fraction of biomass carbon in solid recovered fuels, using detection by scintillation, gas ionization and mass spectrometry.

2 Terms and definitions

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

2.1

biodegradable carbon

mass fraction of the total carbon that is capable of undergoing biological anaerobic or aerobic decomposition under conditions naturally occurring in the biosphere

2.2

biogenic carbon

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

2.3

biomass carbon

equivalent to biogenic carbon

2.4

isotope abundance

fraction of atoms of a particular isotope of an element

2.5

repeatability

extent of the agreement between the results of subsequent measurements of the same quantity, performed under the same measuring conditions

2.6

reproducibility

extent of the agreement between the results of measurements of the same quantity, performed under variable measuring conditions.

3 Symbols and abbreviations

This Technical Report uses the following 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

BP	Before Present (before 1950)
CPM	Counts per minute
DPM	Disintegrations per minute
ETS	Emissions Trading Scheme
GM	Geiger Müller
LSC	Liquid Scintillation Counter or Liquid Scintillation Counting
PSM	Proportional Scintillation-counter Method
PMT	Photo Multiplier Tube
RSD	Relative Standard Deviation
SDM	Selective Dissolution Method
SRF	Solid Recovered Fuel
STP	Standard Temperature and Pressure (273,15 K (or 0 °C) and 101,325 Pa (or 760 mmHg))

4 Methods of measurement

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4.1 Principle

The principle of the ^{14}C method is to determine the biomass content by total carbon by measuring the amount of ^{14}C present in the sample. This method utilizes the isotope abundance of ^{14}C similar to the way the age of objects is measured for archaeological purposes. In all organisms living ashore, ^{14}C has a known isotope abundance equal to its isotope abundance in atmospheric CO_2 . As soon as an organism dies, the isotope abundance of ^{14}C in its organic material starts to decrease because ^{14}C is an unstable isotope with a half-life of 5 730 yr. The isotope abundance of ^{14}C may be considered zero after ten half lives or 60 000 yr. The biomass content by total carbon of a material is calculated as the proportion of the isotope abundance of ^{14}C in that material and the isotope abundance of ^{14}C in the atmosphere at the time when the biomass was laid down.

The method is especially useful for determining biomass carbon content, however, the relationship between biomass carbon content and biomass content should be determined for every type of waste; a limitation that is also valid for other existing methods. When information is available about how carbon atoms are chemically bound, the amount of bio energy can be calculated.

4.2 Sampling

For the ^{14}C based methods sampling procedures that are similar to those for determining major elements [4] are used. As carbon is one of the major components in solid recovered fuel, problems with homogeneity are not to be expected with laboratory samples. Typical particle size of the sample material should be $\leq 0,2$ mm.

4.3 Transport and storage

For transport and storage of the samples, the same requirements are fulfilled as for normal lab samples. As part of the solid recovered fuel consists of organic material, dry and cool storage is applied to prevent conversion of the biomass part by microbiological activities.

4.4 Preparation of the test portion from the laboratory sample

For the PSM and BI methods sample sizes of 1 g or more are used. However at the 1 g level problems still arise with homogeneity of the sample; the use of a lab scale combustion device (e.g. rotary kiln) is recommended, allowing sample amounts of 5 g to 20 g.

The AMS method only needs a few milligrams of sample. In this case combustion of samples at a scale of approximately 1g is necessary. After combustion the carbon is present in a gas phase as CO₂, and the next step is preparing a mg size sample from the gaseous combustion products.

4.5 Analysis by Proportional Scintillation-counter Method (PSM)

PSM (also called Liquid Scintillation Counter method, LSC) determines the isotope abundance of ¹⁴C indirectly through its emission of β (beta, electron) particles. The β particles are detected through interacting with a solution of a scintillation molecule. This is possible only if the carbon is homogeneously distributed in the solution, as the β particles must be able to interact with the solution instead of being quenched in the solid fuel. Homogeneous distribution may be attained by four different methods:

- Conversion to CO₂, followed by absorption in an organic amine and mixing this absorbent with the scintillation fluid. The amine is produced using fossil carbon, in order not to cause a blank signal.
- Conversion to CO₂, followed by absorption in a BaCl₂ or CaCl₂ solution, and
 - after drying and grinding, transfer of BaCO₃ or CaCO₃ into the scintillation fluid forming a suspension; or
 - regeneration of CO₂ from the precipitate, which is absorbed in an organic amine, and mixing this absorbent with the scintillation fluid.
- Conversion to CO₂, followed by adsorption on a solid medium, regeneration of CO₂ which is absorbed in an organic amine, and mixing this absorbent with the scintillation fluid.
- Liquid fuels may be directly mixed with the scintillation fluid.

The scintillation fluid consists of a solvent and a dissolved fluorescent agent, the fluor. When a β is emitted, it rapidly transfers its energy to solvent molecules (< 5 ns) in the form of heat, ionisation and excitation. A part of the excited solvent molecules transfers energy to fluor molecules; the remaining energy is lost as heat by various quenching processes. A part of the excited fluor molecules release their energy in the form of photons in the blue part of the visible spectrum; again, the remaining energy is lost as heat by various quenching processes. A part of the photons are detected in the form of a light flash; the intensity is proportional to the β's initial energy. The remaining photons are lost by quenching, by reabsorption by the fluor, or by not being detected because of geometry. The standard addition technique can be used to determine quenching effects.

In practice, a pair of light detectors – classically, PMT's – are used for two reasons:

- It is necessary to compensate for geometry effects: an event close to a detector will produce a stronger signal because more photons will reach the detector. This is done by adding the signals of the detectors;
- Events caused by background radiation should be excluded, by admitting only those pulses that are seen by both detectors simultaneously (window size approximately 20 ns). A predefined intensity ratio threshold is set in order to exclude most events that occur outside the sample vial.

The remaining background counts occur mainly by decay of other naturally radioactive isotopes such as ⁴⁰K, ²¹²Bi, ²¹²Pb, ²¹⁴Bi, and ²¹⁴Pb and / or ¹³⁷Cs.

The overall *a priori* efficiency of the detection is unknown. Therefore, the method has to be calibrated with samples of known ^{14}C isotope abundance.

4.6 Analysis by B-ionisation (proportional gas counting) (BI)

The B Ionisation method determines the isotope abundance of ^{14}C indirectly. This method employs the emission of β particles by ^{14}C , like PSM. It detects β particles by means of discharge current pulses between high-voltage electrodes in a proportional gas counter. Those pulses are initiated by the β particles. The detection principle resembles the way a Geiger-Mueller (GM) counter works, the difference being details of the electron avalanche in the counter.

To use this method, the sample has to be in the form of CO_2 or converted to CO_2 , as is also the case for most applications of PSM.

The sensitivity of the gas counter is proportional to the contained gas quantity, and therefore to the specific mass/pressure of the gas and to the volume of the detector. In practice, 1,4 g carbon may be loaded (up to 10 l CO_2 at STP (Standard Temperature and Pressure)). Assuming a counting efficiency of 80 %, the performance based on counting statistics may be in the same order of magnitude as the performance of the liquid scintillation method. However, it is not necessary to absorb the CO_2 in a liquid, the method may be more manageable than PSM and use less consumables.

4.7 Analysis by Accelerator Mass Spectrometry (AMS)

The accelerator mass spectrometry method determines the presence of ^{14}C directly. The atoms in the sample are converted into a beam of ions. Accelerating them in an electric field, deflecting them in a magnetic field and detecting them in an ion detector determine the relative isotope abundances of these ions.

AMS is a form of mass spectrometry that uses a high potential electrostatic field, which serves not only to accelerate them but also to specifically form only C^{4+} ions that are allowed into the spectrometer, excluding all other ionic species. This greatly enhances sensitivity without compromising selectivity.

AMS uses only a few mg of sample, and the sample processing and counting time is considerably less time consuming compared with β counting. Logistic turnaround times of two weeks or less are possible. Due to the complex accelerator system cost is presently still higher but this issue may change in the near future due to the rather mature state of small accelerators. AMS may be even more attractive if reliable gas-ion-sources (now under development) may become routinely available, because the CO_2 can be fed directly into the accelerator.

5 Equipment and reagents

5.1 For the preparation of the test portion

5.1.1 Oxygen bomb

Commercially available oxygen bombs for determining the caloric values are used for the combusting the test portion.

In some cases intermediate storage of the combustion gases in a tedlar gas bag is used. The combustion gases from the oxygen bomb can then be released in a short time, and afterwards the combustion gases can be processed at the desired flow rate using a small gas pump. For longer storage of combustion gases gasbags with an aluminium layer are advised, as losses are observed in other types of materials.

If the carbon content in the sample is calculated from the amount of CO_2 present in the combustion gases, impingers filled with concentrated phosphoric acid and zinc pellets are used to remove water, and sulphur and halogen oxidation products, prior to the absorption of the CO_2 .