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Solid recovered fuels — Methods for the determination of biomass content

Combustibles solides de récupération — Méthode de détermination de la teneur en biomasse

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 300, *Solid recovered fuels*.

This corrected version of ISO 21644:2021 incorporates the following corrections:

— Correction of "4 ml l^{-1}" to "4 mol·l^{-1}" in Annex A.

— Editorial corrections made to several symbols.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The biomass content of solid recovered fuels is relevant for the evaluation of the impact of energy production on greenhouse gas emission. Instrumental methods, wet chemical and manual procedures are available for the calculation of the renewable energy fraction. Instrumental methods are based on the determination of ^{14}C content while manual procedures are based on separation of different fractions by visual inspection. The wet chemical procedure differentiate biomass from non-biomass materials as function of the acid dissolution behaviour.

The fraction of biomass is expressed:

- by mass;
- by energy content (gross or net calorific value);
- by carbon content.

This document is primarily intended for laboratories, producers, suppliers and purchasers of solid recovered fuels, but is also useful for the authorities and inspection organizations.

Solid recovered fuels — Methods for the determination of biomass content

1 Scope

This document specifies three methods for the determination of the biomass content in solid recovered fuels: the ^{14}C content method, the selective dissolution and the manual sorting methods.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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.

ISO 21637:2020, *Solid recovered fuels — Terminology, definitions and descriptions*

ISO 21645[1], *Solid recovered fuels — Methods for sampling*

ISO 21646[2], *Combustibles solides de récupération — Préparation des échantillons*

ISO 21654[3], *Solid recovered fuels — Determination of calorific value*

ISO 21656[4], *Solid recovered fuels — Determination of ash content*

ISO 21663, *Solid recovered fuels — Methods for the determination of total carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) by the instrumental method*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 21637:2020 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

3.1
ash content on dry basis

mass of inorganic residue remaining after ignition of a fuel under specified conditions, expressed as mass fraction in percent of the dry matter in the fuel, also includes removed ash contributors

Note 1 to entry: This is typically expressed as a percentage of the mass of dry matter in the fuel source.

Note 2 to entry: Depending on the combustion efficiency the ash may contain combustibles.

Note 3 to entry: If a complete combustion is realized, ash contains only inorganic, non-combustible components.

[SOURCE: ISO 21637:2020, 3.3]

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[1] Under preparation. Stage at the time of publication ISO/FDIS 21645.

[2] Under preparation. Stage at the time of publication ISO/DIS 21646.

[3] Under preparation. Stage at the time of publication ISO/FDIS 21654.

[4] Under preparation. Stage at the time of publication ISO/FDIS 21656.

3.2
biogenic
produced in natural processes by living organisms but not fossilized or derived from fossil resources

3.3
biomass
material of biological origin excluding material embedded in geological formations and/or fossilized

[SOURCE: ISO 16559:2014, 4.32, modified — Notes 1 and 2 to entry have been removed.]

3.4
calorific value
quantity of heat produced by the complete combustion, at a constant pressure equal to 1 013,25 mbar, of a unit volume or mass of gas, the constituents of the combustible mixture being taken at reference conditions and the products of combustion being brought back to the same conditions

[SOURCE: EN 437: 2018, modified — Second paragraph (the list) has been removed.]

3.5
gross calorific value
calorific value where the water produced by combustion is assumed to be condensed

[SOURCE: ISO 21637:2020, 3.34]

3.6
isotope abundance
fraction of atoms of a particular isotope of an element

3.7
laboratory sample
part of the *sample* (3.13) sent to or received by the laboratory

Note 1 to entry: When the laboratory sample is further prepared (reduced) by subdividing, mixing, grinding, or by combinations of these operations, the result is the test sample. When no preparation of the laboratory sample is required, the laboratory sample is the test sample. A test portion is removed from the test sample for the performance of the test or for analysis.

Note 2 to entry: The laboratory sample is the final sample from the point of view of sample collection, but it is the initial sample from the point of view of the laboratory.

Note 3 to entry: Several laboratory samples may be prepared and sent to different laboratories or to the same laboratory for different purposes. When sent to the same laboratory, the set is generally considered as a single laboratory sample and is documented as a single sample.

3.8
moisture
water removable under specific conditions

[SOURCE: ISO 21637:2020, 3.46]

3.9
net calorific value at constant volume
calorific value where the water produced by combustion is assumed to be in the vapour state

[SOURCE: ISO 21637:2020, 3.47]

3.10
nominal minimum particle size
aperture size of the sieve used for determining the particle size distribution of solid recovered fuels through which no more than 5 % by mass of the material passes

3.11
nominal top size
smallest aperture size of the sieve used for determining the particle size distribution of solid recovered fuels through which at least 95 % by mass of the total material passes through the sieve

[SOURCE: ISO 21637:2020, 3.48]

3.12
percentage modern Carbon
pmC
carbon mass fraction from biogenic origin

Note 1 to entry: The internationally accepted radiocarbon dating reference value is 95 percent of the activity, in AD 1950, of this NBS oxalic acid SRM4990B.

Note 2 to entry: In 2015, the value of 100 % biogenic carbon was set at 102 pmC.

Note 3 to entry: The biogenic origin is expressed in percentage.

3.13
sample
quantity of material, from a larger amount for which the quality is to be determined

[SOURCE: ISO 21637:2020, 3.63, modified — Notes 1–3 to entry have been removed.]

3.14
sample preparation
actions taken to obtain representative *laboratory samples* (3.7) or test portions from the original *sample* (3.13) as received

[SOURCE: ISO 21637:2020, 3.66]

4 Symbols and abbreviations

For the purposes of this document, the following symbols and abbreviations apply.

C	symbol for element carbon
D	diameter (mm)
^{14}C	carbon isotope with an atomic mass of 14 u
LSC	Liquid Scintillation Counter or Liquid Scintillation Counting
M_{sort}	manual sorting method
RSD	relative standard deviation
SDM	selective dissolution method
SRF	solid recovered fuel
TC	total carbon content
u	atomic mass unit
w	mass fraction expressed as a percentage by mass
w_{cal}	content expressed as a percentage of the energy content
w_{TC}	content expressed as a percentage of the total carbon content

The different references used in this document are indicated by the following indices:

- $_{(ad)}$ for air dried (dried at room temperature 20°C to 25 °C for 24 h)
- $_{(ar)}$ for as received
- $_{(d)}$ for dry
- $_{(daf)}$ for dry and ash free, where appropriate.

EXAMPLE $w_{\mathrm{cal,NB}(d)}$ means the fraction of energy content in the non-biomass fraction by calorific value, on dry basis.

5 Principle

The determination of the biomass content is based on selective dissolution, manual sorting or ^{14}C measurement of biomass in solid recovered fuel. The choice for the method to be used is described in Clause 6. The biomass content gives an estimation of the content of the biogenic fraction in solid recovered fuel.

6 Determination of biomass content

6.1 Sampling

Sampling, transport, storage of the solid recovered fuel and sample preparation in the field shall be conducted according to ISO 21645 and ISO 21646.

6.2 Sample preparation

Preparation of the test sample for the ^{14}C or SDM shall be conducted according to ISO 21646. For the M_{sort}, no sample preparation is performed.

Since SRF is considered as a heterogeneous material, the minimum sample amount to be used for each test shall be:

- ^{14}C method: a quantity between 0,4 g and 2 g of the material with a nominal top size of 1 mm or less, depending on the device used for combustion (bomb, combustion tube furnace or elemental analyser) or the quantity indicated by the constructor in the case of the use of a laboratory scale combustion apparatus;
- selective dissolution method (SDM): at least 5 g of the material with a nominal top size of 1 mm or less;
- manual sorting method (M_{sort}): at least as big as the minimum sample size according to ISO 21645 (as received), as calculated in ISO 21646.

6.3 Applicable methods

For the determination of biomass content three methods are available:

1) the instrumental ^{14}C method shall be according to Annex A. This method is based on the determination of the ratio of ^{14}C to the total carbon content; the ^{14}C is proportional to the biomass content of the SRF. This method is suitable for samples of all types of fuel and shall be according to Annex A. A value of 10 % biogenic carbon can be considered as the lower range of application of ^{14}C method by liquid scintillation counter (LSC);

2) the selective dissolution method (SDM) shall be according to Annex B. The determination of the biomass content by the SDM is based on the property of biomass that it can be dissolved in a sulphuric acid / hydrogen peroxide mixture. This method has limitations that makes it less suitable

if the content of natural and/or synthetic rubber in the SRF is more than 10 %, or if the sum of the content of hard coal, coke, brown coal, lignite, degradable plastics of fossil origin, non-degradable plastic of biogenic origin, oil or fat present as a constituent of biomass, wool, viscose, nylon, polyurethane or other polymers containing molecular amino groups and silicon rubber exceeds 5 %. Additional information about these limitations is found in Annex D. The selective dissolution method (SDM) is applicable for the biomass percentage content between 10 % and 90 %;

3) the manual sorting method (M_{sort}) shall be according to Annex C. The determination of the biomass content by the manual sorting method is based on the visual examination of fractions and their separation on the basis of their nature and origin. The method is suitable for samples with a particle size >10 mm.

For the limitations of the three methods see Annex D.

7 Expression of results

Depending on the use of the results, three different dimensions are used to express the biomass content:

a) biomass in percent by mass w_B;

b) biomass in percent by calorific value $w_{B,cal}$;

c) biomass in percent by carbon content $w_{B,TC}$.

The expression of results by ^{14}C method shall be according to Annex A.

The expression of results by SDS method shall be according to Annex B.

The expression of results by M_{sort} method shall be according to Annex C.

8 Performance characteristics

External data for the calculation of the expanded uncertainty of measurements are presented in Annex E where results of round robin and validation studies are summarized. These values should be used in combination with individual laboratory performance characteristics and a desired coverage factor to get the overall uncertainty.

Practical examples of use of the data from Annex E:

EXAMPLE 1

A laboratory wants to determine the expanded uncertainty of measurement of SDM method (% by mass).

The intra-laboratory reproducibility for the laboratory calculated from internal validations studies and control charts was determined to be 2,5 % (RSD).

The round robin results from the QUOVADIS[3] study (Table E.2) give a RSD value of 3,43 % (at 67,79 % level).

$$u_{c,rel} = \sqrt{}(2{,}5^2+3{,}43^2) = 4{,}24\ \%$$

$$U_{rel} = 2 \times u_{c,rel} = 8{,}48\ \%$$

where $u_{c,rel}$ is the combined uncertainty of measurement and U_{rel} is the expanded uncertainty of measurement using a coverage factor of 2 (~95 % confidence interval).

EXAMPLE 2

A laboratory measures the biomass content by ^{14}C method – LSC B (% by TC).

The intra-laboratory reproducibility for the laboratory calculated from internal validations studies and control charts was determined to be 2,4 % (RSD).

The round robin results from the QUOVADIS[3] study (Table E.6) give a RSD value of 2,5 % (at 55,5 % level).

$$u_{c,rel} = \sqrt{(2{,}4^2+2{,}5^2)} = 3{,}5\ \%$$

$$U_{rel} = 2 \times u_{c,rel} = 7{,}0\ \%$$

where u c,rel is the combined uncertainty of measurement and U_{rel} is the expanded uncertainty of measurement using a coverage factor of 2 (~ 95 % confidence interval).

9 Test report

The test report shall contain at least the following information:

a) identification of the laboratory performing the test;

b) date of the test;

c) identification of product (sample) tested;

d) sample preparation (e.g. method of size reduction, drying, subdivision);

e) storage conditions;

f) date of receipt of laboratory sample and dates of the test (beginning and end);

g) a reference to this document (ISO 21644:2021) and the method used;

h) in case of ^{14}C-method, the results of the test including the basis on which they are expressed and application of the isotope correction;

i) the biomass content expressed as a percentage by mass, calorific value and/or carbon content, rounded to the nearest 0,1 %;

j) any operation not included in this document, or regarded as optional;

k) any unusual features noted during the test procedure.

Annex A

(normative)

Determination of the biomass content based on the ^{14}C method

A.1 General

The two proposed methods for ^{14}C measurement, Proportional Scintillation Method (PSM) or Accelerated Mass Spectrometry (AMS), require specialised personnel and instrumentation. However, the preparation step for instrumental analysis can be completed as normal routine laboratory activity. For the collection from the sample of the ^{14}C fraction, generally accepted methods for the conversion of the carbon present in the sample to CO_2 are described.

A.2 Principle

The methods for the determination of the biomass content specified in this annex 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.

The carbon present in the sample is converted to CO_2 by combustion. The 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 two following methods, Proportional Scintillation Method (PSM) or Accelerated Mass Spectrometry (AMS). These methods are considered equivalent, giving the same results within the scope of this document. The results are expressed as the percentage biomass carbon of the total carbon content. The fraction of biomass content by mass and the fraction of biomass by energy content are calculated from the carbon content of biomass, using the carbon content of biomass and the energy content of the biomass fraction that is present in the sample.

A.3 Limitations

For the limitation of this method see Annex D.

A.4 Symbols

For the purposes of this annex, the following symbols apply.

C	symbol for element carbon
^{14}C	carbon isotope with an atomic mass of 14
AMS	Accelerator Mass Spectrometry
β	beta particle, electron emitted during radioactive decay
Bq	Bequerel, disintegrations per second
d	on dry base
DPM	disintegrations per minute
CPM	counts per minute

C_V	coefficient of variation
GM	Geiger Müller
LCV	Low calorific value
LLD	Lower Limit of Detection
m	mass expressed as a percentage by mass
M	moisture expressed as a percentage by mass
MOP	3-Methoxy 1-propyl amine
NCV	Net Calorific Value
LSC	Liquid Scintillation Counter or Liquid Scintillation Counting
REF	reference value of 100 % biogenic carbon
pmC	percentage modern Carbon
PSM	Proportional Scintillation-counter Method
X	fraction expressed as a percentage by mass
RSD	Relative Standard Deviation
SRF	Solid recovered fuel
TC	Total carbon content

A.5 Reagents and materials

CO_2 absorber for LSC (methoxypropylamine or equivalent).

Universal LSC cocktail for aqueous and non-aqueous sample.

2 mol·l^{-1} to 4 mol·l^{-1} KOH or NaOH absorption liquid (standard glass bottles with plastic screw caps that are resistant to alkaline solutions shall be used).

For the preparation of a carbonate free adsorption liquid, preparation using freshly opened KOH or NaOH pellet containers is sufficient. Dissolve the KOH (NaOH) pellets in a small amount of water (the heat produced during the dissolution process will enhance the dissolution process). When NaOH is used, small amounts of precipitation are an indication of the presence of Na_2CO_3. By decanting the clear phase, the almost carbonate free solution shall be diluted to the desired volume. As the dissolution of KOH or 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 shall be used to produce a 0,7 l carbonate free KOH (NaOH) 4 mol·l^{-1} solution.

- 670 ml demineralised water (water from a system producing ultrapure water for laboratory use);
- 156,8 g KOH pellets (112 g NaOH);
- 30 ml saturated $Ba(OH)_2$ solution. [2,4 g $Ba(OH)_2$ ÷ 2,6 g $Ba(OH)_2$ in 30 ml demineralised water];
- dissolve the KOH (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.6 Procedure for the conversion of the carbon present in the sample to CO_2 for ^{14}C determination by PSM

A.6.1 General

Three procedures are allowed for the conversion of the sample to a form that can be used for the determination of the ^{14}C content:

1) combustion in a calorimetric bomb,

2) combustion in a tube furnace,

3) combustion in a laboratory scale combustion apparatus.

NOTE The method mentioned under 3) is not validated.

Other apparatus may be used which provide a complete combustion in the reported experimental conditions. As an example, the combustion may be performed by using elemental analyser. The CO_2 formed is then absorbed in a suitable solution, which depends on the combustion method and the selected method for the subsequent ^{14}C measurement. Two absorption solutions are available: in case 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.

A.6.2 Combustion of the sample in a calorimetric bomb

A.6.2.1 Procedure

For the combustion according to the determination of the calorific value of the sample, ISO 21654 shall be used. The test sample is a general analysis sample passing through a sieve with 1 mm aperture and prepared according to ISO 21646. The test sample mass of less than 1 g is pressed in the form of a pellet by using a suitable pressing device (manual or pneumatic). For SRF materials with high content of plastic or rubber showing higher LCV values, the test sample mass should be reduced to a mass in the range from 0,4 g to 0,8 g to be suitable for safe bomb operation. For materials difficult to combust (e.g. material with high ash content >30 % on dry basis) it is recommended to use a combustion aid.

The appropriate mass of the test sample to be combusted depends on the total carbon content in order to have similar amount of absorbed CO_2 in the scintillation cocktail for subsequent ^{14}C measurement to reduce the measurement bias due to different quenching conditions: for this purpose, the total carbon content of the sample shall be determined before the combustion step.

After combustion, the combustion gases are collected in a suitable mixture. Alternatively, the gases are collected in a gas bag as described in A.6.2.2. For the determination of the ^{14}C content the CO_2 shall be collected in cooled (<10 °C) absorbing solution or a cooled mixture of absorbing solution and scintillation liquid.

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 2,5 MPa 4 % of the combustion gas will be left after release to atmospheric pressure).

To overcome this issue:

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 gases;

c) flush the bomb with Argon or (CO_2-free) N_2 and collect the CO_2 in the rinsing gases as well.

A.6.2.2 Absorption of the gas sample

If a gas sample bag is used, it shall be connected to a small pump with a connection line into a 20 ml glass vial, filled with 10 ml of absorbing solution or a mixture of 10 ml of the absorbing liquid and 10 ml of the scintillation cocktail, placed in an ice bath or cooling device at <10 °C, to remove the heat of the exothermic carbamate formation reaction. The pumping speed shall be about 50 ml·min^{-1}. The transfer of the gas from the bag takes about 2 h to 3 h. After the sample is collected, it is ready to be counted on a LSC. 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.

In case of direct absorption of combustion gases, the outlet of the combustion device (e.g. oxygen combustion bomb) is connected via transfer line, equipped with a valve, to an empty cooled impinger for water removal and a second cooled impinger with 10 ml absorbing solution or scintillation cocktail. Using the proper safe device, the bomb valve is opened and the gases are collected at a low flux rate (optimal value 50 ml·min^{-1} to 60 ml·min^{-1}). The transfer takes about 3 h. 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.

Measurements shall be started after leaving the vial to cool down to the measurement temperature and to reduce any chemiluminescence due to manipulation. Absorbing solution are stable at least for 1 week after sampling: alternatively, the CO_2 shall be collected in a 4 mol·l^{-1} KOH (NaOH) solutions for longer period.

NOTE 1 There are strong indications that the NO_x formed during the combustion reacts with the absorption mixture resulting in yet unexplained errors after a few days of storage.

NOTE 2 The initial and final mass of the absorbing solution is an estimation of the recovery of CO_2 and indicates the possible sources of error in the procedure, such as a leakage in the absorption system.

A.6.3 Combustion of the sample in a tube furnace

A suitable amount of sample (seaved at 1 mm nominal size) is weighed in the boat to be inserted in the combustion tube. The test mass depends on the carbon content of the SRF and the capacity of the absorption solution; generally, up to 2 g are processed in macro instruments and typically 200 mg in microtube furnace. The gas bubbles set is filled with the absorption solution. The temperature of the furnace is raised at the operation value (e.g. 1 100 °C or 1 350 °C): when temperature reaches the set point the oxygen supply is connected and the flow rate is adjusted at the desired value. The sample boat is inserted and combustion is started. At the end of the combustion the impingers are removed and the absorption solutions collected for subsequent analysis. The oxygen flow rate should not exceed the maximum flow rate allowed for the gases to be quantitatively collected in the absorption solution. In case of the use of microtube the representativity of the test sample should be verify according to the grain size.

For the determination of the ^{14}C content the CO_2 shall be collected using an impinger filled with a cooled absorbing solution or a mixture of absorbing and scintillation liquid; alternatively, a 4 mol·l^{-1} KOH (NaOH) solution may be used (see A.6.2.2, NOTE 1 and 2).

As an alternative, the CO_2 may 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 shall be achieved by heating the trap slightly above the boiling point of oxygen, using liquid argon or by performing the separation at diminished pressure.

A.6.4 Combustion of the sample in a laboratory scale combustion apparatus

The combustion condition and test sample amount depend on the apparatus used and manufacturer instructions.

The CO_2 may be trapped using different methods, depending on the laboratory. Some examples are reported below.

The lab-scale combustion apparatus shall be able to combust a suitable SRF-sample at a constant rate, with a complete conversion of the carbon present to CO_2. For the determination of the ^{14}C content the CO_2 shall be collected using a suitable impinger filled with a cooled mixture of absorbing solution and a suitable scintillation liquid or a 4 mol·l^{-1} KOH (NaOH) solution (see A.6.2.2, NOTE 1 and 2). 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 may be trapped by means of a cryogenic trap, which 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 shall 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 high silica, high temperature glass tube. Water vapour (up to 3 Pa) can be added to the tube prior to introduction of the CO_2 to help remove sulphur 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.

A.6.5 Measurements

If collected samples are sent to specialized laboratories, the samples shall be stored in a way that no CO_2 from air can enter the absorption solution. A check on the leak of CO_2 from air shall be performed by preparing laboratory blanks during the sampling stage.

For the determination of the 0 % biomass content the combustion of a coal reference material (e.g. BCR 182) shall be used.

For the 100 % biomass content the Oxalic acid primary standard (SRM 4990c) is available: however, this material is difficult to combust due to its low calorific value and the difficulties in the preparation of a suitable pellet. Other reference materials such as Lichen BCR 482 may be used because their biomass content is 100 % by total carbon by definition (the reported organic C content is 42,1 % and total carbon is 44,7 %). A control by using independent 100 material (laboratory internal reference materials such as collected vegetable prepared for other type o chemical analysis are suitable) is recommended.

NOTE Oxalic acid can be difficult to completely combust under the conditions used in this document for the bomb combustion.

Among the materials which may be used the following are included:

— vegetable, with known TC content, assuming 100 % biomass;

— L-ascorbic acid from natural sources, with known purity and TC content from chemical formula;

— material with recent carbon, with reference biomass content from AMS method.

This aspect regarding uncertainty evaluation should be considered:

— 0 and 100 % biomass reference values should be used without uncertainty since they derive from theoretical consideration and not from accepted averages values from round robin test;

— ^{14}C content should be based on reference method determination such as AMS; or on theoretical consideration from actual CO_2 average level.

A.7 Procedure for the ^{14}C determination by Proportional Scintillation-counter Method (PSM)

A.7.1 General

This procedure describes the determination of the ^{14}C by Proportional Scintillation-counter Method (PSM) in absorbing solutions obtained from the combustion of SRF samples in a calorimetric bomb, a tube furnace or a laboratory scale combustion device as described in A.6.

A.7.2 Principle

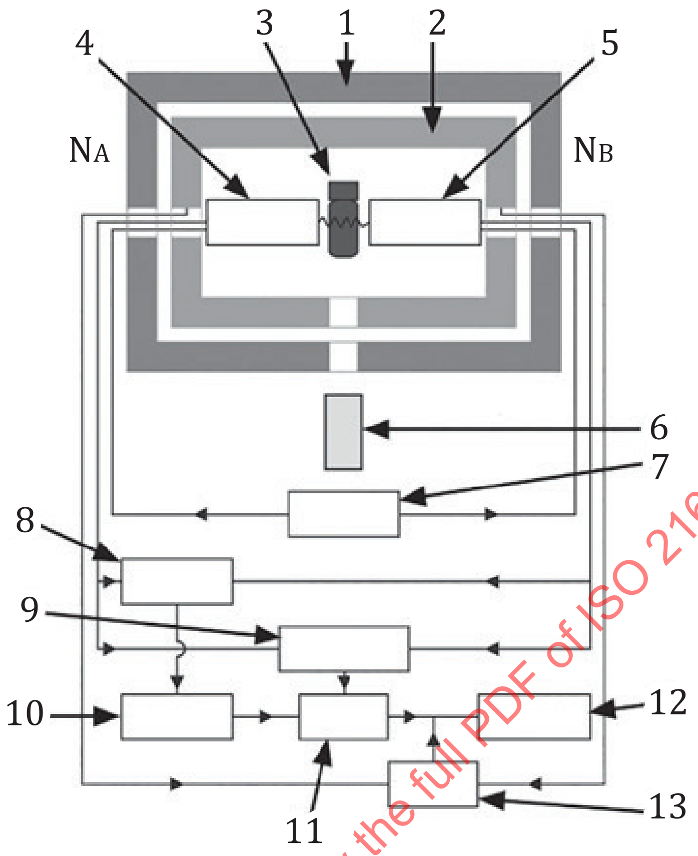
PSM (also called Liquid Scintillation Counter method, LSC) determines the isotope abundance of ^{14}C indirectly, through its emission of β particles due to the radioactive decay of the ^{14}C isotope. The β particles are observed through their interaction with scintillation molecules. The CO_2 formed by the combustion of SRF is trapped in an absorbing solution. This solution is mixed with the organic solution containing the scintillation molecules and the ^{14}C activity of this mixture is measured in a Proportional (Liquid) Scintillation Counter. In case 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 (KOH) solution. As an alternative 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. In this case either absorption solutions may be used.

A.7.3 Reagents and materials

- scintillation liquid;
- absorbing solution (e.g. 100 % ethanolamine or 5M ethanolamine in 2-methoxyethanol or 3-methoxypropylamine);
- commercial ^{14}C labelled substance in solution with known dpm/ml valid to check instrument performances;
- oxalic acid primary standard (SRM 4990c) or other suitable reference material;
- a ^{14}C-free reference material.

A.7.4 Apparatus

The extremely low natural levels of radiocarbon in the earth's atmosphere (about $1{,}10^{-12}$ %) requires extra precautions for accurate measurement of ^{14}C. Care should be taken to eliminate the influence of cosmic and environmental background radiation, other radioisotopes being present, electronic noise and instability. Any LSC used should meet these specifications.



Key

1	lead shield
2	active guard
3	sample
4	photomultiplier tube
5	photomultiplier tube
6	external standard radiation source
7	high-voltage power supply
8	pulse addition circuit
9	fast coincidence analyser
10	pulse height analyser
11	circuit
12	multi-channel analyser
13	command analyser

Figure A.1 — LSC

A.7.5 Procedure

An absorption flask is loaded with a known volume of CO_2 absorbent, e.g. with an absorbing solution. The absorbing capacity of an absorbing solution of about $4{,}8 \times 10^{-3}$ mol/ml shall be taken into account; no more than 80 % of this capacity should be used. The flask shall be cooled in ice or by a cooling device during the absorption process. The sample gas is collected from a flue gas duct or from a gas bag. In either case, the sample has to be dried by passing through dryer or empty cooled impinger and the CO_2 concentration of the dried sample has to be known (either by a flue gas monitor or by the analysis of the solid sample that was used to generate the CO_2) or by measuring the amount of CO_2 absorbed (the absorbing solution absorbs the CO_2 quantitatively) If acquired directly from a flue gas duct, the sample volume has to be measured with a gas meter and corrected for the volume of CO_2 absorbed by the absorbing solution. After absorption of the CO_2, the absorbent is transferred to the measuring vial. An equal volume of the scintillation liquid is added and the mixture is homogenized.

Then the vial containing the mixture is placed in the PSM and measured. Typical counting times are 6 h to 24 h: the total counting time is composed of a suitable number of 30-min counting cycles (for example a total of 24 cycles of 30 min each). The final count (DPM) is the average value from single results from every cycle.

The activity of a sample is compared with the activity of a reference material. The number of ^{14}C registrations (=β counts of ^{14}C decay in radiometric detectors (PSM) is related to the number of registrations of the reference sample under the same conditions.

Standard addition techniques can be used to check for the occurrence of chemical or optical quenching for each sampling or sample type. For that purpose, ^{14}C labelled components shall be used.

Measurement shall be performed together with a measurement of the “background” sample (0 % biomass material, such as coal or equivalent sample) that is counted for the same period of time as the actual sample. The result obtained is the background level for the whole system (apparatus and reagent) given in CPM or DPM. After this the actual sample is counted, which also gives a counting result in CPM or DPM.

The statistical error of counting, background and standard is a result of the decay counting, (Poisson) process; hence the precision of the result depends on the number of counts observed, where the relative error is inversely proportional to the square-root of the number of counts. The total error is then the combination of the analytical errors and the errors of the standard and background determination

The detection limit (LD) is the smallest amount of radioactivity that statistically differs from the background. The LD shall be calculated from the counting time of the sample and the background counting rate assuming the same counting times for background and sample:

$$E\left(R_{n,LD}\right)=\left(k_{1-\alpha}+k_{1-\beta}\right)\cdot\sqrt{E\left(R_0\right)\cdot\left(\frac{1}{t_0}+\frac{1}{t_b}\right)} \qquad \text{(A.1)}$$

where

$E(R_{n,LD})$ is the Limit of Detection (LD);

$k_{1\text{-}\alpha}$, $k_{1\text{-}\beta}$ is the confidence level (1,645);

$E(R_0)$ is the counting rate of blank [cps] (0,316 7 cps);

t_0 is the counting time of blank [s] (16 000 s);

t_b is the counting time of sample [s] (16 000 s).

$$dps=\frac{cps}{\eta} \qquad \text{(A.2)}$$

where

cps counting rate of blank (0,316 7 cps);

dps disintegrations per second [Bq];

η counting efficiency of the apparatus ($0 < \eta < 1$) (0,8).

EXAMPLE The calculation of LD using a counting time of 16 000 s (266,67 min) and 19 CPM (0,316 7 counts per s) background with a counting efficiency of 0,8:

$$LD=\frac{\left(k_{1-\alpha}+k_{1-\beta}\right)\cdot\sqrt{cps\cdot\left(\frac{1}{t_0}+\frac{1}{t_b}\right)}}{\eta}=\frac{(1{,}645+1{,}645)\cdot\sqrt{0{,}316\,7\cdot\left(\frac{1}{16\,000}+\frac{1}{16\,000}\right)}}{0{,}8}=0{,}026\,\text{Bq}=1{,}55\,\text{dpm}$$

A.7.6 Calculation of the results

From the sample count rate, the background count rate of the counter is subtracted (net count rate). The ^{14}C activity (DPM) is obtained by normalizing the net count rate to the count rate of the reference standard (Oxalic acid SRM) or other suitable reference materials.

A.7.7 Example for PSM measurements

In an absorbing solution obtained from a calorific bomb combustion of pure wood (REF = 114 pmC, TC = 48,0 %) an ^{14}C activity of 7,75 DPM is measured. 13,56 DPM/gC is the value of 100 % biomass.

In the bomb an amount of 1,050 g (sm) of sample was combusted (air dry).

Then the biogenic carbon content (on air dry base) will be calculated by the following formula:

$$\text{\% Biogenic Carbon} = [\text{DPM}/(13{,}56 \times \text{REF}/100)/\text{sm}] \times 100$$

$$\text{\% Biogenic Carbon} = \{[7{,}75/(13{,}56 \times 114/100)]/1{,}050\} \times 100 = 47{,}8\ \%$$

$$w_{\text{B,TC}} = \text{\% Biogenic Carbon} / \text{TC} = 47{,}8 / 48{,}0 = 99{,}6\ \%$$

A.7.8 Example for PSM measurements from calibration with reference materials

In an absorbing solution obtained from a calorific bomb combustion of SRF (REF = 107 pmC, TC = 47,5 %) an ^{14}C activity (net value) of 1,36 DPM is measured.

In the bomb an amount of 0,55 gram of sample was combusted (air dry).

In a previous phase, in the same conditions, a reference sample from coal (e.g. BCR 182), after bomb combustion gave an average net activity of 0,22 DPM; similarly, a reference sample from lichen (BCR 482) gave a net average activity of 2,53 DPM. BCR 182 result was used as reference 0 % biomass fraction, while BCR 482 was set as 100 % biomass fraction. As reported in Table A.1, the correction factors were applied:

BCR 182 (0 % biomass) = 100

BCR 482 (100 biomass) = 101

SRF (unknown) = 107

The corrected DPM were: 0,22 (0 % biomass); 2,50 (100 % biomass); 1,27 (unknown).

After combustion, the absorbing solution cocktail was weighted before and after gases collection: from the difference the carbon content was calculated since the recovery can be considered as quantitative. The net DPM/gC were calculated:

0 % = 1,06 DPM/gC

100 % = 10,08 DPM/gC

Unknown = 6,98 DPM/gC

$$w_{\text{B,TC}} = [6{,}98/(10{,}08 - 1{,}06)] \times 100 = 77{,}4\ \%$$

A.8 Procedure for the conversion of the carbon present in the sample to CO_2 for ^{14}C determination by AMS

A.8.1 General

Three procedures are allowed for the conversion of the sample to a form that can be used for the determination of the ^{14}C content:

1) combustion in a calorimetric bomb,

2) combustion in a tube furnace,

3) combustion in a laboratory scale combustion apparatus.

NOTE The method mentioned under 3) is not validated.

Other apparatus may be used which provide a complete combustion in the reported experimental conditions. As an example, the combustion may be performed by using elemental analyser. The CO_2 formed is then absorbed in a suitable solution, which depends on the combustion method.

A.8.2 Combustion of the sample in a calorimetric bomb

A.8.2.1 Procedure

For the combustion according to the determination of the calorific value of the sample, ISO 21654 shall be used. The test sample is a general analysis sample passing through a sieve with 1 mm aperture and prepared according to ISO 21646. The test sample mass of less than 1 g is pressed in the form of a pellet by using a suitable pressing device (manual or pneumatic). For SRF materials with high content of plastic or rubber showing higher LCV values, the test sample mass should be reduced to a mass in the range from 0,4 g to 0,8 g to be suitable for safe bomb operation. For materials difficult to combust (e.g. material with high ash content >30 % on dry basis) it is recommended to use a combustion aid.

The appropriate mass of the test sample to be combusted depends on the total carbon content for this purpose, the total carbon content of the sample shall be determined before the combustion step.

After combustion, the combustion gases are collected in a suitable mixture. Alternatively, the gases are collected in a gas bag as described in A.6.2.2.

For the determination of the ^{14}C content the CO_2 shall be collected in a KOH or NaOH solution. Alternatively, ca. 2 ml of the combustion gas shall be taken from the bag using a glass syringe and the gas shall 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 2,5 MPa 4 % of the combustion gas will be left after release to atmospheric pressure).

To overcome this issue:

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 gases;

c) flush the bomb with Argon or (CO_2-free) N_2 and collect the CO_2 in the rinsing gases as well.

A.8.2.2 Absorption of the gas sample

If a gas sample bag is used, it shall be connected to a small pump with a connection line into a 20 ml glass vial, filled with 10 ml of absorbing solution or a mixture of 10 ml of the absorbing liquid and 10 ml of the scintillation cocktail, placed in an ice bath or cooling device at <10 °C, to remove the heat of the exothermic carbamate formation reaction. The pumping speed shall be about 50 $ml \cdot min^{-1}$. The transfer of the gas from the bag takes about 2 h to 3 h. After the sample is collected, it is ready to be counted on a LSC. 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.

In case of direct absorption of combustion gases, the outlet of the combustion device (e.g. oxygen combustion bomb) is connected via transfer line, equipped with a valve, to an empty cooled impinger for water removal and a second cooled impinger with 10 ml absorbing solution. Using the proper safe device, the bomb valve is opened and the gases are collected at a low flux rate (optimal value 50 $ml \cdot min^{-1}$ to 60 $ml \cdot min^{-1}$). The transfer takes about 3 h. 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.

Absorbing solution are stable at least for 1 week after sampling: alternatively, the CO_2 shall be collected in a 4 $mol \cdot l^{-1}$ KOH (NaOH) solutions for longer period.

NOTE 1 There are strong indications that the NO_x formed during the combustion reacts with the absorption mixture resulting in yet unexplained errors after a few days of storage.

NOTE 2 The initial and final mass of the absorbing solution is an estimation of the recovery of CO_2 and indicates the possible sources of error in the procedure, such as a leakage in the absorption system.

A.8.2.3 Combustion of the sample in a tube furnace

A suitable amount of sample (sieved at 1 mm nominal size) is weighed in the boat to be inserted in the combustion tube. The test mass depends on the carbon content of the SRF and the capacity of the absorption solution; generally, up to 2 g are processed in macro instruments and typically 200 mg in microtube furnace. The gas bubbles set is filled with the absorption solution. The temperature of the furnace is raised at the operation value (e.g. 1 100 °C or 1 350 °C): when temperature reaches the set point the oxygen supply is connected and the flow rate is adjusted at the desired value. The sample boat is inserted and combustion is started. At the end of the combustion the impingers are removed and the absorption solutions collected for subsequent analysis. The oxygen flow rate should not exceed the maximum flow rate allowed for the gases to be quantitatively collected in the absorption solution. In case of the use of microtube the representativity of the test sample should be verify according to the grain size.

For the determination of the ^{14}C content, the CO_2 shall be collected using a suitable impinger filled with a 4 $mol \cdot l^{-1}$ KOH (NaOH) solution.

As an alternative, the CO_2 may 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 shall be achieved by heating the trap slightly above the boiling point of oxygen, using liquid argon or by performing the separation at diminished pressure.

A.8.2.4 Combustion of the sample in a laboratory scale combustion apparatus

The combustion condition and test sample amount depend on the apparatus used and manufacturer instructions.

The CO_2 may be trapped using different methods, depending on the laboratory. Some examples are reported below.

The lab-scale combustion apparatus shall be able to combust a suitable SRF-sample at a constant rate, with a complete conversion of the carbon present to CO_2. For the determination of the ^{14}C content the CO_2 shall be collected using a suitable impinger filled with a 4 $mol \cdot l^{-1}$ KOH (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 may be trapped by means of a cryogenic trap, which 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 shall 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 high silica, high temperature glass tube. Water vapour (up to 3 Pa) can be added to the tube prior to introduction of the CO_2 to help remove sulphur 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.

A.8.3 Measurements

If collected samples are sent to specialized laboratories, the samples shall be stored in a way that no CO_2 from air can enter the absorption solution. A check on the leak of CO_2 from air shall be performed by preparing laboratory blanks during the sampling stage.

For the determination of the 0 % biomass content the combustion of a coal reference material (e.g. BCR 182) shall be used.

For the 100 % biomass content the Oxalic acid primary standard (SRM 4990c) is available: however, this material is difficult to combust due to its low calorific value and the difficulties in the preparation of a suitable pellet. Other reference materials such as Lichen BCR 482 may be used because their biomass content is 100 % by total carbon by definition (the reported organic C content is 42,1 % and total carbon is 44,7%). A control by using independent 100 material (laboratory internal reference materials such as collected vegetable prepared for other type o chemical analysis are suitable) is recommended.

NOTE Oxalic acid can be difficult to completely combust under the conditions used in this document for the bomb combustion, but this does not influence the analytical results in case of use of the AMS apparatus.

Among the materials which may be used the following are included:

- vegetable, with known TC content, assuming 100 % biomass;
- L-ascorbic acid from natural sources, with known purity and TC content from chemical formula;
- material with recent carbon, with reference biomass content.

This aspect regarding uncertainty evaluation should be considered:

- 0 % and 100 % biomass reference values should be used without uncertainty since they derive from theoretical consideration and not from accepted averages values from round robin test.

A.9 Procedure for the ^{14}C determination by Accelerator Mass Spectrometry (AMS)

A.9.1 General

This annex describes the procedure for the determination of the ^{14}C determination by AMS in the carbonate solutions obtained from the combustion of SRF samples in a calorimetric bomb, a tube furnace or a laboratory scale combustion device.

A.9.2 Principle

The accelerator mass spectrometry (AMS) method determines the presence of ^{14}C directly. The atoms in the sample are converted into a beam of ions. The formed ions are accelerated in an electric field, deflected in a magnetic field and detected in ion detectors resulting in the determination of 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^{n+} ions (n = from 1 to 4) that are allowed into the spectrometer, excluding all other ionic species. This greatly enhances sensitivity without compromising selectivity. The ^{14}C is determined in graphite (carbon) that is why all the carbon in the samples has to be converted into graphite before analysing.

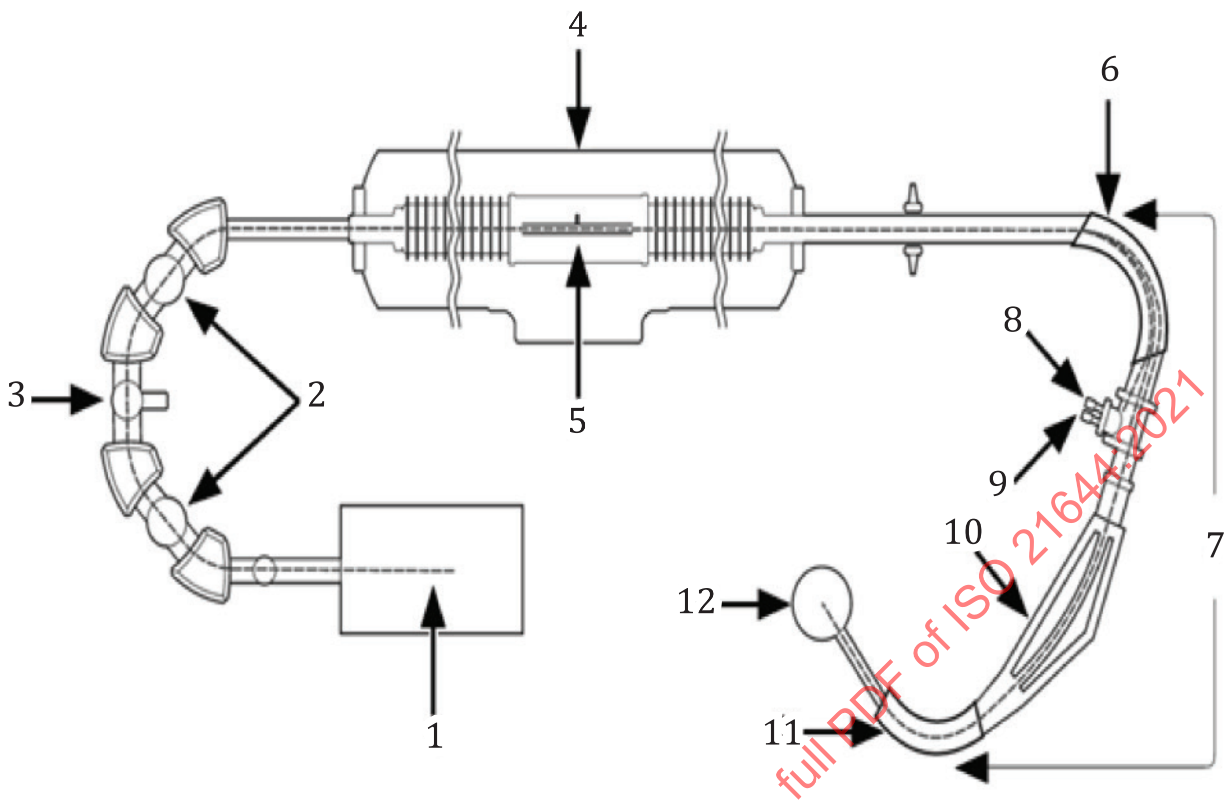
With AMS the modern fraction in the carbon, present in the sample, is determined. The total carbon content is not determined with this technique and shall be determined separately.

A.9.3 Reagents and materials

- oxalic acid primary standard (SRM 4990b). Although not certified other reference materials may be used (e.g. L-ascorbic acid or lichen BCR 482);
- iron catalyst;
- hydrogen;
- HCl solution (5 M);
- dry ice;
- acetone or ethanol;
- liquid N_2.

A.9.4 Apparatus

- sample preparation equipment;
- liquid nitrogen freezing station;
- accelerator mass spectrometer (AMS) (see Figure A.2).



Key

1	59 sample ion source	7	high energy mass spectrometer
2	recombinator	8	^{12}C-cup
3	chopper	9	^{13}C-cup
4	tandem accelerator	10	33° electrostatic deflector
5	stripping canal	11	90° magnet
6	110° magnet	12	ionisation chamber

Figure A.2 — Schematic presentation AMS

A.9.5 Procedures

a) Transfer the carbonate solution to the extraction bottle.

b) Attach the HCl dosing device.

c) Evacuate the bottle and dosing device (degassing, removal of dissolved N_2 and 0_2 from air).

d) Add HCl to the carbonate solution.

e) Remove water vapor using a trap filled with acetone and dry ice.

f) Collect the formed CO_2 in a trap that is submersed in liquid N_2.

g) Take a small sample for ^{13}C determination at this stage.

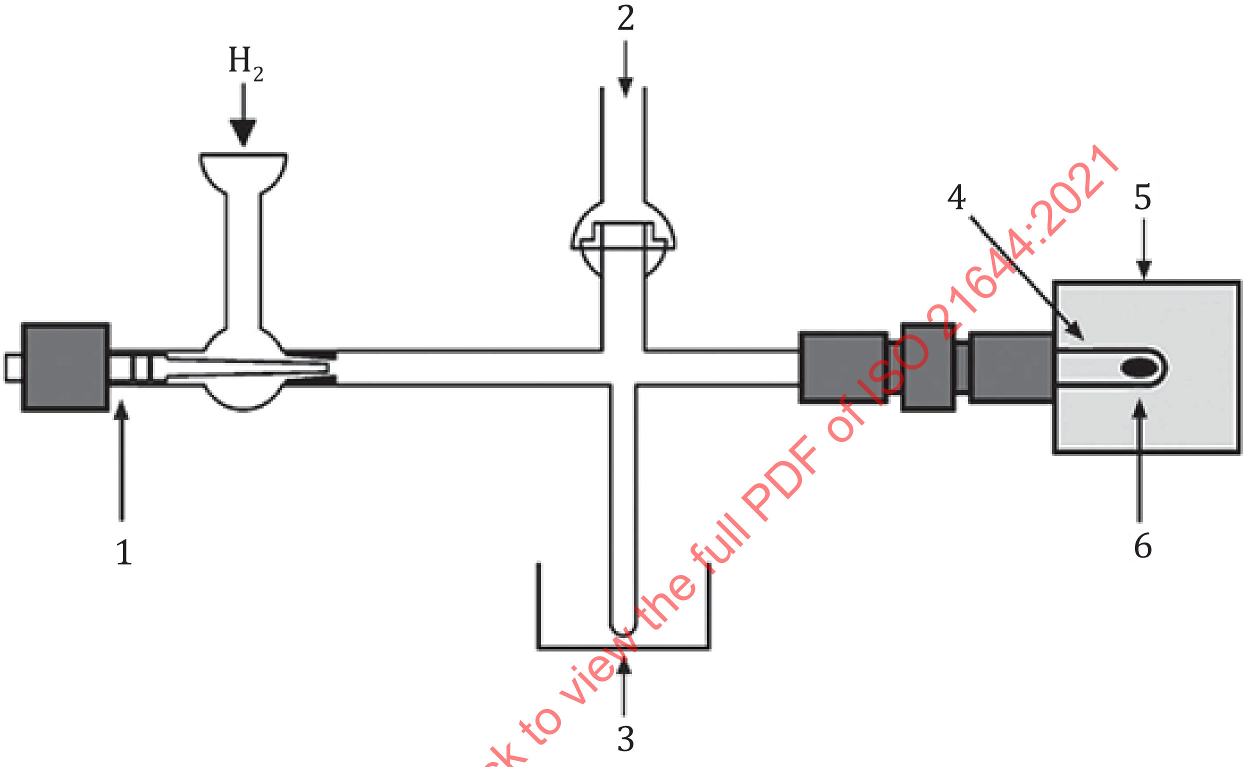
h) Transfer the CO_2 to the graphitizing rig system (see Figure A.3).

Gaseous sample shall be either let in the system released from a quartz tube or after they are trapped in liquid nitrogen followed by subsequent heating. The gas is then converted to graphite using an iron catalyst, according to the following formulae:

$$CO_2 + H_2 \longleftrightarrow H_2O \quad + CO$$

$$CO + H_2 \longleftrightarrow H_2O \quad + C$$

The water produced by this reaction is removed to ensure a complete reduction to graphite. This is particularly important to avoid fractionation.



Key

1	sample ampoule as CO_2
2	pressure sensor
3	electronic cooling element at −18 °C to trap H_2O
4	quartz tube
5	graphite oven at 600 °C
6	Fe powder

Figure A.3 — Graphitization rig

The graphite is pressed into a target and mounted on a wheel before it is loaded into the accelerator mass spectrometer. In the ion source a high current beam of caesium ions (Cs^+) is focused on the target. This liberates negatively charged target atoms, producing a 36 keV beam of C-ions. Targets are kept 10 mm away from each other to avoid cross-contamination and moved during sputtering to avoid cratering, which causes fractionation. The negative ion beam is then focused by a lens into a recombinator. Here a series of magnets remove non-carbon ions from the beam and separate the three carbon isotopes (^{12}C, ^{13}C and ^{14}C). The chopper wheel then physically blocks most of the ^{12}C, allowing a much reduced beam of carbon ions to be recombined for simultaneous injection into the accelerator. In the tandem accelerator the C-ions are accelerated to the terminal (at +2,5 MeV) then changed to C^{3+} ions by collision with Ar atoms in the gas stripper. These positive ions are accelerated to 10 MeV. A charge state of 3+ is chosen because the mass/charge ratio of $^{14}C^{3+}$ is truly unique, allowing its accurate separation in the high-energy mass spectrometer. The first element of the high-energy mass spectrometer is a 110^0 bending magnet, separating in the accelerated ^{12}C, ^{13}C and ^{14}C ions. The ^{12}C and ^{13}C beams are measured in Faraday cups (typical currents 250 nA). The $^{14}C^{3+}$ ions are further purified by a 33° electrostatic deflector a 90° magnet. They are measured in an isobutene-filled ionization chamber, isolated from the accelerator vacuum by a thin metal foil (density 250 µg/cm^2). Typically, a sample is counted for one hour.

A.9.6 Calculation of the results

The isotopic ratios of $^{14}C/^{12}C$ and $^{13}C/^{12}C$ are determined relative to the appropriate primary reference material. All percent modern carbon (pmC) values obtained from the radiocarbon analyses measurements shall be corrected for isotopic fractionation using stable isotope data ($^{13}C/^{12}C$ ratios) obtained on CO_2 derived from combustion of the sample. Do not determine $^{13}C/^{12}C$ ratios on the raw product material itself, since that approach can lead to erroneous results in some cases.

A.10 Calculation of the results

A.10.1 Correction factors

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 102 pmC in 2015. The ^{14}C activity of a sample grown since 1962 will be elevated according to the average ^{14}C level over the growing interval.

In addition, the large emission of fossil C during the last decades contributes to the decrease of the atmospheric $^{14}C/^{12}C$ ratio.

In ASTM D 6866-20[4], the 100 % bio-based C value of 101,5 pmC (for year 2016) is used. This value shall be the base of calculations. Other values are only acceptable if evidence can be given on the pmC value of the biogenic part of the material. From the 101,5 (rounded to 102) pmC value the correction factor of 0,98 (1/1,02) is derived. It is considered that such correction factor is now stable during a period of a few years. For the calculation of the bio-based carbon content, a ^{14}C content of 100/0,98 pmC or 13,56/0,98 dpm per gram C is considered as a 100 % bio-based carbon content for biomass that is grown in year 2015.

NOTE 1 This correction factor of 0,98 is in accordance with the value that is given in ASTM D 6866–20[4]. The fraction of biomass content by dry mass will be calculated using the biomass carbon in the biobased product as for other organic carbon materials. Table 2 lists typical values for such common materials.

NOTE 2 The reference value for 2016 is based on the measurements of CO_2 in air in a rural area in the Netherlands (Lutjewad, Groningen), performed by CIO (Centre for Isotope Research, university Groningen)[7]. Measurement performed in year 2018 resulted in a pmC value of 100,7 (101).

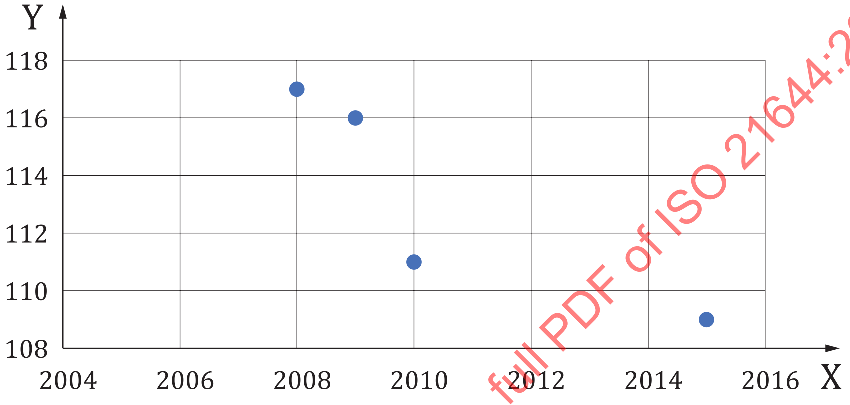
The increase of the CO_2 concentration in air is caused by the increase of combustion of fossil fuels. That this raise of CO_2 concentration (the so-called Suess effect[2]) is caused by the increased emission of fossil fuels is confirmed with ^{14}C measurements in atmospheric CO_2. Measurements in international sites (Schauinsland, Black Forest, Groningen) give values of around 102 pmC in the year 2015. Presently the decline is ca. 0,4 pmC to 0,5 pmC per year, mainly due to fossil fuel combustion.

For high precision pmC measurements, the $^{14}C/^{12}C$ and $^{13}C/^{12}C$ isotopic ratios shall 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 ratios 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 mass and the fraction of biomass by energy content shall be calculated using the biogenic carbon in the solid recovered fuel and the carbon and energy content of the biomass fraction.

According to experimental reported data (ASTM D 6866-20[4]), a consensus value of 101 pmC for biomass may be used for 2019, considering an estimate decrease of 0,3 pmC/year, due to ^{14}C dilution from atmospheric emissions; a value of 100 pmC can be extrapolated for 2022 year. After 2022 a further reduction will probably result in a pmC value lower than 100: a more precise extrapolation will be possible in the future and the new value will be included in the next revision of this document. Extrapolated data should be verified in the future.

For solid recovered fuel (SRF) produced mainly from urban waste, pmC values can be different on a regional base and they may be used if general accepted evidence is provided. A general value reported in this document for European waste material is 116 pmC in 2009. The literature[9] report an extrapolated value of 109 for 2009 and a 2006 value of 113 pmC which is significatively higher than of 108 pmC (as reported in ASTM D6866-20[4]). The literature[8] report 2008 values for different type of SRF ranging from 115 (SRF from urban waste) and 121 (SRF from large wastes): a value close to 117 can be estimated for SRF from mixed waste. In ISO 13833:2013 reference is done to pmC value for 2010 of 111 with a decrease to 109 in 2015. These literature values are reported in Figure A.4.



SRF pmC values (2008-2015)

Figure A.4 — pmC values for SRF from literature

Since pmC values differ on regional values and for different SRF types the reported data are scattered. From the extrapolated value for 2015 and considering the 0,3 pmC/year an extrapolated value for 2020 of 108 pmC can be proposed.

For other fuels composed of single materials, pmC values may be used (UNI/TS 11461[5]):

— paper and cardboard: 117 (2008); 112 (2015) 109 (2020, calculated reported value from ECN database).

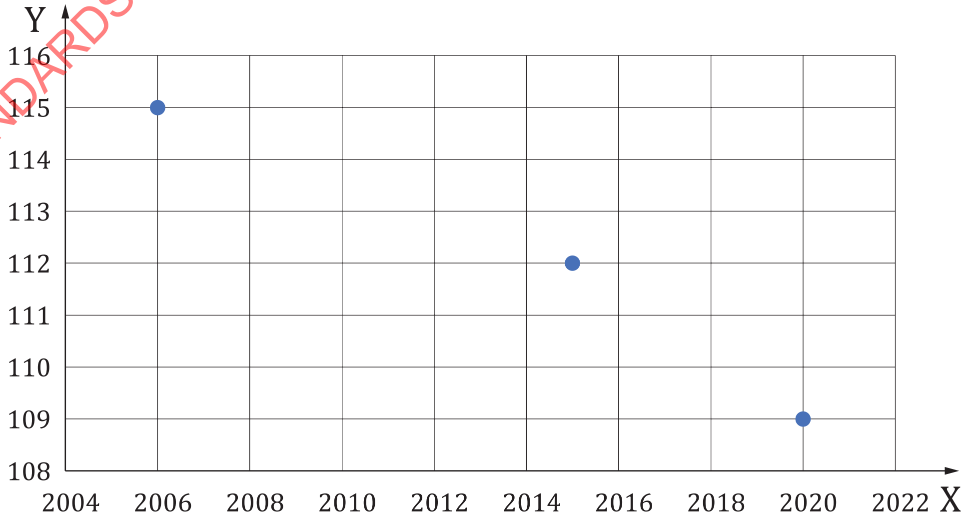


Figure A.5 — pmC values for paper and cardboard

— wood-based material (with the exception of pure biomass): 121 (2015); 122 (2020).

An increase is expected due to increase of the reuse of more recent materials. A consensus value may be proposed to be 122.

From the previous reported data, it is clear that an accurate selection of pmC reference values for fresh biomass and for SRF is of crucial importance for the application of this standard. 101 pmC for fresh biomass and 107 pmC for SRF shall be used on the basis of available literature data.

When available accurate information about the composition of the SRF and the pmC value of the individual fractions a more accurate pmC value for that type of SRF can be obtained, then that pmC value can be used. This value and the method for its calculation shall be included in the test report (Clause 9).

NOTE Calculation example is reported in Table A.1.

Table A.1 — Data used for the calculation

Material	Carbon	Net calorific value	pmC	DPM	Correction factor
	% (daf)	MJ/kg (daf)	%	%	%
Demolition wood	50	19	114	15,4	88
Cardboard	45	17	110	15,1	91
Used paper	47	17	110	15,4	91
Fresh biomass	48	18	101	14,3	99
SRF value	47,5	18,4	107	15,2	93

If for instance the biomass fraction of SRF only would consist of used paper then for that biomass fraction a pmC value of 110, a DPM value of 15,4, a carbon content of 47 % and a net calorific value of 17 MJ/kg has to be used as a basis of the calculation (see Table A.1). Hence a SRF mix containing 50 % used paper (m/m) and 50 % non-biomass fraction a pmC value 114/2 = 57 (or a DPM value of 15,4 / 2 = 7,7) will be measured, resulting in a biomass energy content of 17/2 = 8,5 MJ/kg.

A.10.2 Example of conversion from biogenic carbon content to biomass content

In a SRF sample with a total energy content of 18,1 MJ/kg, an amount of 20,0 % of biogenic carbon was measured.

The biomass fraction of the SRF sample was estimated to be a paper fraction containing 46,6 % of carbon.

The biomass mass fraction (w_B) then will be 20,0 × 100/46,6 = 42,9 %.

A.10.3 Example of conversion from biogenic carbon content to biomass energy content with a mixed biomass fraction

In a SRF sample with a total energy content of 18,1 MJ/kg (ad) and TC = 43 % (ad), an amount of 20 % of biogenic carbon was measured.

The biomass fraction of the SRF sample was estimated to consist of 30 % (m/m) of demolition wood and 70 % (m/m) of paper.

The biomass mass fraction (w_B) then will be 30/100 × 20 × 100/50 (from Table A.1) + 70/100 × 20 × 100/47 (from Table A.1) = 41,8 %.

The biomass energy content will be 30/100 × 20 × 19/50 + 70/100 × 20 × 17/47 = 7,34 MJ/kg ad

$$w_{B,cal} = 7{,}34 / 18{,}1 = 39{,}2\ \%$$

Annex B
(normative)

Determination of biomass content using the selective dissolution method (SDM)

B.1 General

This annex specifies the procedures for the determination of the biomass content expressed in percent by mass, by calorific value and by carbon content using selective dissolution. The selective dissolution method (SDM) is based on the fact that biomass oxidizes significantly more quickly than non-biomass.

B.2 Principle

The SDM for the determination of the biomass content expressed in percent by mass involves the treatment with concentrated sulphuric acid topped with hydrogen peroxide. As a general rule, the biomass in the solid recovered fuel will selectively dissolve and the non-biomass will remain in the residue.

For the determination of the biomass content expressed in percent by mass, the sample shall be weighed before and after selective dissolution. The biomass content by mass is corrected for the content of carbonates by measuring the ash content (according to ISO 21656 Method A) before and after dissolution. Figure B.1 shows which steps are performed when determining the biomass content by percent in mass using the SDM.

The determination of the biomass content by calorific value consists of two procedures. The first procedure determines the calorific values of the total sample and non-biomass fraction. The second procedure calculates the biomass content by energy content. Figure B.2 illustrates the principle by which the fraction specific calorific values shall be determined. Depending on the use of the results, the biomass content may be calculated in percent by net calorific value or by gross calorific value. Before this annex is applied, a choice shall be made whether the biomass fraction shall be determined by net calorific value or gross calorific value. All calorific values in the rest of this annex will then be expressed according to that choice.

The determination of the biomass content by carbon content involves the determination of the TC content before and after the selective dissolution of the biomass fraction. The results are used for the calculations of the biomass content expressed in percentage by TC. The maximum relative error for the biomass content by TC is 0,4 % per 1,0 percent by mass of the ash fraction. Therefore, a correction for carbonate present in the ashes is made if the ash content in the original sample (as determined in this annex is larger than 10 % by mass on a dry basis. Figure B.3 shows which steps are performed when determining the biomass content by using the SDM for the determination of the biomass content in percent by TC.

B.3 Limitations

The minimum sample amount to be used for each test shall be at least 5 g of the material with a nominal top size of 1 mm or less. Other details on limitations of this method can be found in Annex D.

B.4 Symbols

For the purposes of this annex, the following abbreviated terms apply.

A_{SRF}	ash content of SRF sample according to ISO 21656;
C_{ash}	total carbon content of the ash fraction expressed as a percentage by mass;
C_{residue}	total carbon content of the non-biomass fraction expressed as a percentage by mass;
C_{tot}	total carbon content of the total sample expressed as a percentage by mass;
daf	dry and ash free
M	moisture content (percentage by mass)
$m_{\mathrm{residue\text{-}ash}}$	mass of ash of dissolution residue (including filter), burned according to ISO 21656 in g;
m_{SRF}	mass of dry SRF test portion used for dissolution, in g;
m_{residue}	remaining dry mass (including filter) after the test portion has been dissolved, in g;
$q_{\mathrm{B(daf)}}$	calorific value of the biomass fraction on a dry and ash-free basis, in MJ/kg;
$q_{\mathrm{NB(daf)}}$	calorific value of the non-biomass fraction on a dry and ash-free basis, in MJ/kg;
$q_{\mathrm{residue(daf)}}$	calorific value of the residue resulting from the dissolution test on a dry basis, in MJ/kg;
$q_{\mathrm{SRF(daf)}}$	calorific value of the SRF on a dry basis sample, in MJ/kg;
TC	total carbon;
w_{B}	biomass content expressed as a percentage by mass;
w_{NB}	non-biomass expressed as a percentage by mass;
$w_{\mathrm{B,cal}}$	biomass content expressed as a percentage by calorific value;
$w_{\mathrm{NB,cal}}$	non-biomass content expressed as a percentage by calorific value;
$w_{\mathrm{B,TC}}$	biomass content expressed as a percentage by TC;
w_{residue}	amount of dissolution residue, expressed as a percentage by mass.

B.5 Reagents and materials

Reagents and materials needed for performing the SDM are:

- 78 % (g/g) H_2SO_4 (laboratory quality);
- 35 % (g/g) H_2O_2 (laboratory quality);
- glass fibre filter, Ø 10 cm or 12,5 cm, GF 6 (this means that it is a filter which is equipped to block particles larger than 1 µm); in case of high biomass content (>80 %) SRF a filter with a smaller diameter (e. g. 5 cm) may be used. Filters shall be resistant to temperatures of 550 °C;

  NOTE See Table D.1 for examples of high biomass materials.

- water of at least demineralized quality.

B.6 Apparatus

Apparatus needed for performing the SDM are:

- filtration device, for example Büchner funnel;
- conical flask (500 ml);
- desiccator;
- muffle furnace at a temperature over 550 °C (ashing temperature is not important for this document);
- a dish consisting of inert material such as porcelain, silica or platinum;
- cutting grinder or other grinding apparatus that may be used to reduce samples to <1 mm;
- fume cupboard;
- pH measuring device;
- balance, capable of weighing the dish containing the sample to the nearest 0,1 mg.

B.7 Procedure for the determination of the biomass content expressed in percent by mass

B.7.1 General

This procedure specifies the determination of the biomass content expressed in percent by mass, using the SDM. Figure B.1 illustrates the principle by which the percentage by mass is determined.

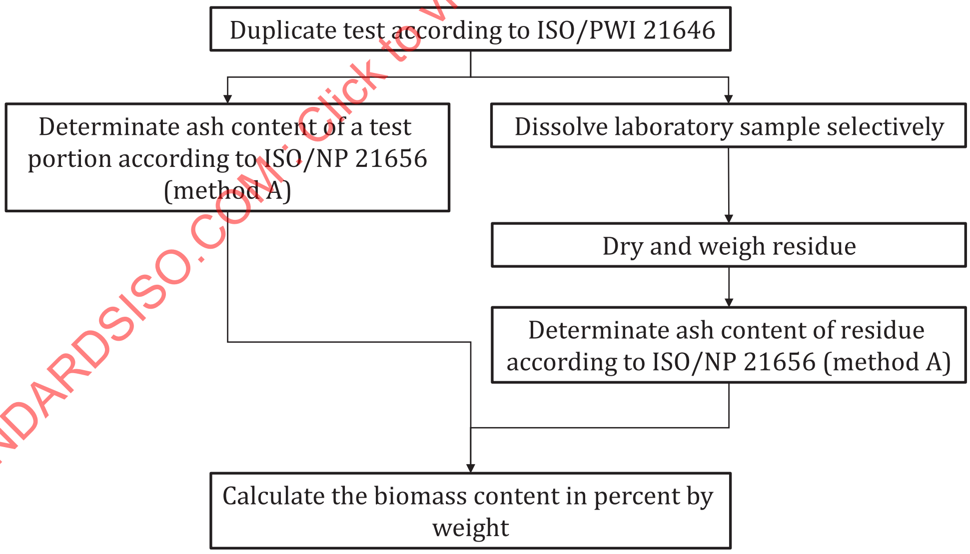


Figure B.1 — SDM for biomass content expressed in percent by mass

B.7.2 Procedure

Sample preparation in the field shall be conducted according to ISO 21645 and to ISO 21646. Preparation of the test sample shall be conducted according to ISO 21646. Perform the following steps for implementing the SDM:

a) take two test portions of 5 g and a nominal top size of 1 mm or less according to ISO 21646. Record the mass of the two test portions;

b) determine the ash content of test portion A, A_{SRF} according to ISO 21656, Method A. When the biomass content expressed in percent by total carbon is to be determined (see B.9), the ash shall be retained;

c) dry and cool the test portion B in a crucible at (105 ± 2) °C to a constant mass according to CEN/TS 15414-1 and cool in a desiccator. In case SRF contains volatile compounds other than water, the Karl-Fischer method is advisable on a different test portion;

WARNING — For some types of solid recovered fuels there can be a risk of self-ignition when drying at 105 °C.

d) weigh the dried test portion B to the nearest 0,1 mg. Record the mass (m_{SRF});

e) place test portion B in an empty 500 ml flask;

f) make sure the crucible is completely empty after emptying into the flask. If not, the mass before and after emptying shall be determined which enables the recalculation of m_{SRF};

g) add 150 ml of 78 % (g/g) H_2SO_4 to the conical flask. Stir carefully, but thoroughly by hand. The sample has to be completely moistened with H_2SO_4. Place the (full) flask away in a fume cupboard for 16 h ± 2 h (cooling may be required);

h) after 16 h ± 2 h, add 30 ml of 35 % (g/g) H_2O_2. Add slowly to control the reaction. Stir carefully, but thoroughly by hand. The sample shall be completely moistened with H_2O_2. Place the conical flask away in a fume cupboard for 5 h ± 1 h (cooling may be required);

i) dry a glass fibre filter and record the mass of the glass fibre filter (m_{filter});

j) after 5 h ± 1 h, dilute the sample B with 300 ml of demineralised water and then filter it over a glass fibre filter in a Büchner funnel or similar device;

k) remove the sulphuric acid by rinsing the residue with 6 doses of 50 ml demineralised water. Make sure the entire 50 ml demineralised water is removed before another dose is added or until the last filtrated volume has a pH of at least 3,0;

l) dry the solid residue from test portion B together with the filter at 105 °C until a constant mass has been achieved;

m) weigh the dried residue B together with the filter to the nearest 0,1 mg. Record the mass ($m_{residue}$);

n) determine the ash content ($m_{residue\text{-}ash}$) of the solid residue from test portion B according to ISO 21656, Method A.

B.7.3 Calculation of the results

The results of the dissolution test and the Formulas (B.1) and (B.2) shall be used to calculate the biomass content, the ash content and the non-biomass content on a dry basis expressed as a percentage by mass.

Use Formula (B.1) for the determination of the biomass content on a dry basis expressed as a percentage by mass:

$$w_{\mathrm{B}}=\left[1-\left\{\frac{m_{\text{residue}}-m_{\text{residue-ash}}}{m_{\mathrm{SRF}}}+\frac{A_{\mathrm{SRF}}}{100}\right\}\right]\times 100 \tag{B.1}$$

Use Formula (B.2) for the calculation of the non-biomass content on a dry basis.

$$w_{\mathrm{NB}}=100-x_{B}-A_{\mathrm{SRF}} \tag{B.2}$$

It should be noted that the result is pure (100 %) biomass, or non-biomass calculated from total dry mass. This means that when calculating e.g. energy content of SRF, calorific values on dry ash-free (daf) shall be used.

EXAMPLE

- An SRF sample has an ash content of 15,0 % (d).
- A test portion of about 5 g is taken (after drying, the dry mass was noticed to be 5,101 3 g).
- A dissolution is carried out for this material.
- After dissolution, the residue is dried and weighed. The mass is noticed to be 2,502 8 g.
- The residue is then ashed and the remaining mass of residue ash was noticed to be 0,411 0 g.

The calculation now gives [according to Formula (B.1)]:

$$w_{\mathrm{B}}=\left[1-\left\{\frac{2{,}5028-0{,}4110}{5{,}1013}+\frac{15{,}0}{100}\right\}\right]\times 100=44$$

The non-biomass content on dry basis can now be calculated [according to Formula (B.2)]:

$$w_{\mathrm{NB}}=100-44-15=41$$

B.8 Procedure for the determination of the biomass content by calorific value

B.8.1 General

This procedure specifies the determination of fraction specific calorific values of biomass and non-biomass. These calorific values can be expressed either as net calorific value or as gross calorific value. Determination of the biomass content of solid recovered fuels is based on the SDM.

B.8.2 Procedure

The determination of the biomass content by calorific value consists of two procedures. The first procedure determines the calorific values of the biomass and non-biomass fraction. The second procedure calculates the biomass content by energy content. Figure B.2 illustrates the principle by which the fraction specific calorific values shall be determined.

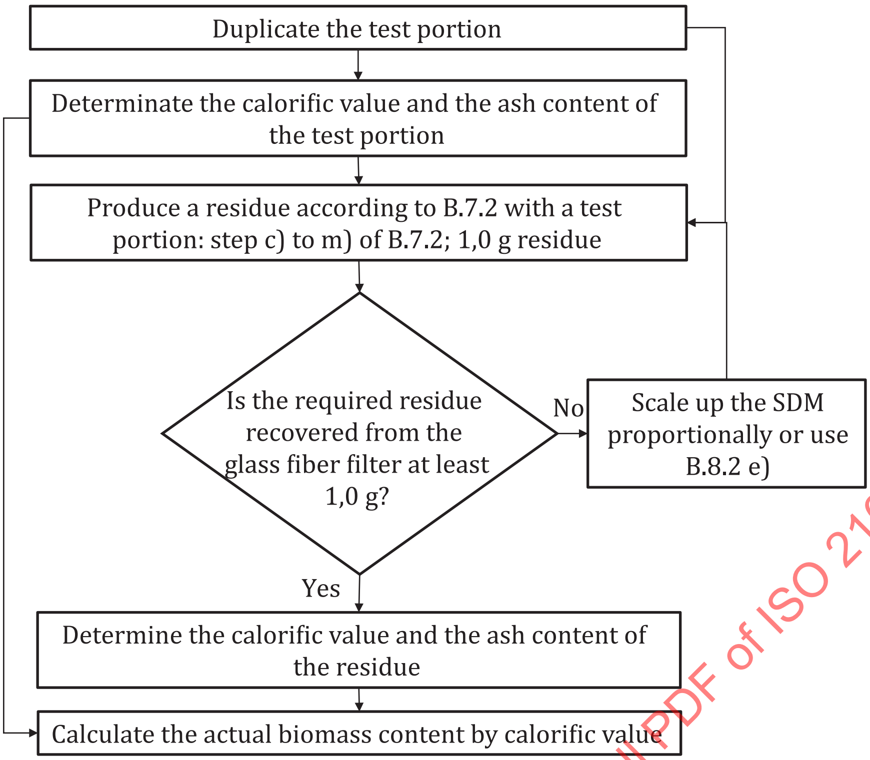


Figure B.2 — Determination of the biomass content by calorific value

Depending on the use of the results, the biomass content may be calculated in percent by net calorific value or by gross calorific value. Before this annex is applied, a choice shall be made whether the biomass fraction shall be determined by net calorific value or gross calorific value. All calorific values in the rest of this annex will then be expressed according to the choice.

The calorific value and the ash content of both the sample and the residue shall be determined according to ISO 21654 and ISO 21656 Method A respectively. With these values the fraction specific calorific values shall be calculated.

In case of gross calorific values, the formulas in Table B.1 can be used for conversion of data from dry base to as received base or dry ash free base:

Given	Wanted			
	As analysed (air-dried) (ad)	**As received**[a] (ar)	**Dry** (d)	**Dry, ash free** (daf)
As analysed (air-dried, ad)		$\frac{100-M_{ar}}{100-M_{ad}}$	$\frac{100}{100-M_{ad}}$	$\frac{100}{100-(M_{ad}+A_{ad})}$
As received (ar)	$\frac{100-M_{ad}}{100-M_{ar}}$		$\frac{100}{100-M_{ar}}$	$\frac{100}{100-(M_{ar}+A_{ar})}$
Dry (d)	$\frac{100-M_{ad}}{100}$	$\frac{100-M_{ar}}{100}$		$\frac{100}{100-A_{ad}}$
Dry, ash free (daf)	$\frac{100-(M_{ad}+A_{ad})}{100}$	$\frac{100-(M_{ar}+A_{ar})}{100}$	$\frac{100-A_{d}}{100}$	

[a] Note that the formulae given for calculating results to the “as received” basis can be used to calculate them to any other moisture bases.

Table B.1 — Formulae for conversion of gross calorific value

In order to determine fraction-specific calorific values the following steps shall be performed:

a) take a sample according to ISO 21645 and prepare the sample according to ISO 21646;

b) determine the calorific value and the ash content of the sample according to ISO 21654 and ISO 21656, Method A;

c) determine the non-biomass content of a test portion according to B.7;

d) take a new test portion and follow steps c) to m) of the instructions in B.7.2. If an estimation of the biomass content indicates that 5 g of a test portion will result in insufficient material to determine the calorific value of the residue, then the volumes shall be scaled up proportionately;

e) determine both the ash content and the calorific value of the residue. When less than 1 g of residue is obtained after selective dissolution or the part of the fines in the residue is high, the residue together with the filter should be crushed for the determination of the calorific value and the contribution of the filter should be deducted in the result.

B.8.3 Calculation of the results

Calculate the dry ash-free fraction-specific calorific value of the non-biomass fraction and the total sample using the values obtained in steps b) to e). To this end, Formulas (B.3) and (B.4) shall be used:

$$q_{\mathrm{NB(daf)}} = \frac{q_{\mathrm{residue}}}{1 - A_{\mathrm{residue}}/100} \tag{B.3}$$

Calculate the ash-free fraction-specific calorific value of the biomass fraction using Formula (B.3):

$$q_{\mathrm{B(daf)}} = \frac{q_{\mathrm{SRF(daf)}} - (x_{\mathrm{NB}}/100) \times q_{\mathrm{NB(daf)}}}{1 - x_{\mathrm{NB(daf)}}/100 - A_{\mathrm{SRF}(d)}/100} \tag{B.4}$$

EXAMPLE In a dry SRF sample, following properties were found: $q_{\mathrm{SRF(daf)}}$ = 18,21 MJ/kg; ash content $A_{\mathrm{SRF(d)}}$ = 8,0 %. In the Selective dissolution test the amount of residue, $x_{\mathrm{NB\ (daf)}}$ was 40 %, ash content A_{NB} = 10,2 % and q_{NB} = 25,03 MJ/kg. We now have:

$$q_{\mathrm{B(daf)}} = \frac{18{,}21 - \left(\frac{40}{100}\right) \times 25{,}03/(1 - 10{,}2/100)}{1 - 40/100 - 8{,}0/100} = 13{,}58\,MJ/kg_{\mathrm{(daf)}}$$

The procedure for determining the biomass content in percent by calorific value consists of four steps:

a) determine the biomass content, x_{B}, and non-biomass content, x_{NB}, according to B.7.3;

b) determine the fraction specific calorific values according to B.8;

c) determine the biomass content in percent by calorific value;

d) The biomass content by calorific value is calculated as follows:

$$w_{\mathrm{B,cal}} = \frac{x_{\mathrm{B}} \times q_{\mathrm{B}}}{q_{\mathrm{SRF}}} \tag{B.5}$$

$$w_{\mathrm{NB,cal}} = 100 - w_{\mathrm{B,cal}} \tag{B.6}$$

B.9 Procedure for the determination biomass content by TC

B.9.1 General

This procedure specifies the procedure for the determination of the biomass content in percent by TC by selective dissolution of the solid recovered fuel. The TC content is determined before and after the selective dissolution of the biomass. The results are used for the calculations of the biomass content expressed in percentage by TC. The maximum relative error for the biomass content by TC is 0,4 % per 1,0 % by mass of the ash fraction. Therefore, a correction for carbonate present in the ashes is made if the ash content in the original sample (as determined in this annex) is larger than 10 % by mass on a dry basis.

Figure B.3 shows which steps are performed when determining the biomass content by using the SDM for the determination of the biomass content in percent by TC.

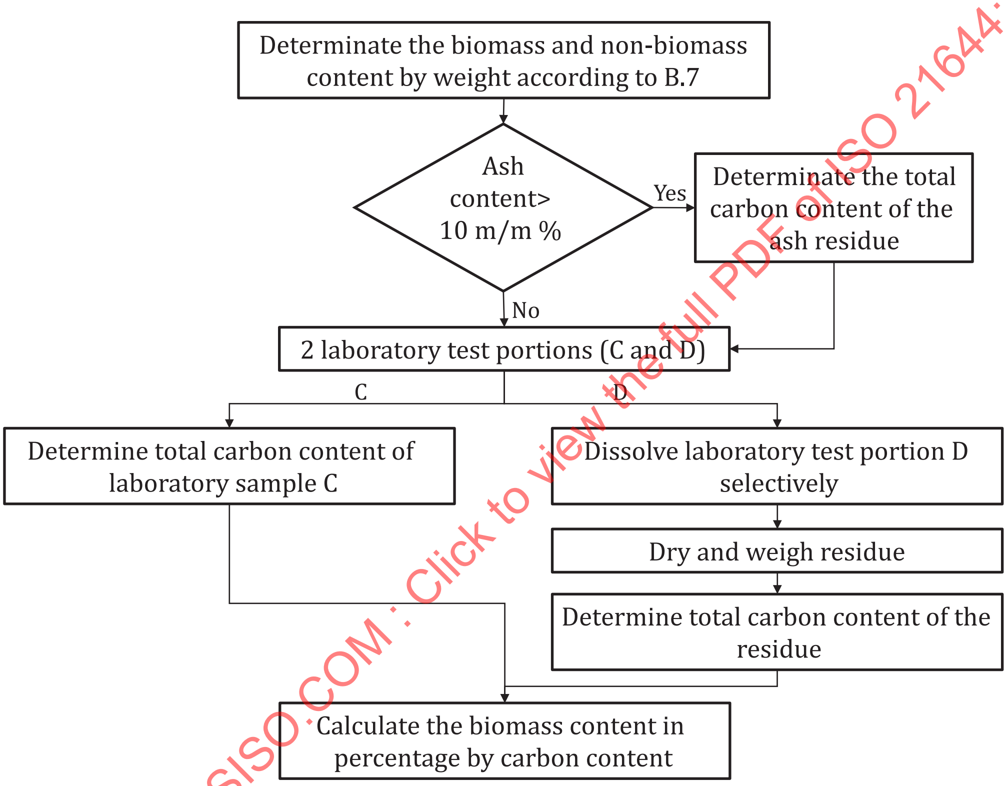


Figure B.3 — SDM for biomass content in percent by TC

The following steps shall be performed for implementing the SDM for the determination of the biomass content in percent by TC:

a) take four test portions A, B, C and D. Test portions A and B shall have a mass of at least 5 g. Test portion C and D shall meet the requirements of ISO 21663; record the mass of all test portions;

b) determine, with test portions A and B, ash (A_{SRF}) and residue fraction ($x_{residue}$) by mass according to procedure B.7.1. Store the ash;

c) if the ash content is larger than 10 % by mass go to step d), otherwise, go to step e);

d) determine the TC content of the ash fraction according to ISO 21663 of the ash residue stored in step b). Record this as C_{ash}. Dependent on the TC analyser, greater sample volumes should be used or analyses be repeated;

e) determine the TC content of test portion C according to ISO 21663. Record this as the TC content of the total sample, C_{tot};

f) take test portion D with a minimum size according to the content of the residue x_{residue};

NOTE In case of micro-methods typical sample mass is 5 mg: if the residue is 40 %, then the minimum size of the test portion is 5/0,4 = 12,5 mg; in case of macro-methods typical sample mass is 500 mg: then the minimum size of test portion is 500/04 = 1 250 mg in case of 40 % residue. When using the micro-methods the representativity should be verified.

g) perform step c) to e) of B.8.2 on test portion D;

h) remove the residue of test portion D from the filter carefully and determine the TC content of the residue according to ISO 21663. The TC content of the residue is equal to the TC content of the non-biomass fraction. Record this as C_{residue}. Dependent on the TC analyser, greater sample volumes should be used or analyses be repeated.

B.9.2 Calculation of the results

If the ash content is larger than 10 % by mass, use Formula (B.7) to calculate the biomass content expressed as a percentage by carbon content.

If the ash content is smaller than 10 % by mass, use Formula (B.8) to calculate the biomass content expressed as a percentage by carbon content.

$$w_{\text{B,TC}} = 100 - \left(\frac{A_{\text{SRF}} \times C_{\text{ash}} + x_{\text{residue}} \times C_{\text{residue}}}{C_{\text{tot}}} \right) \tag{B.7}$$

NOTE In the calculations, it is assumed that there is no inorganic carbon in the biomass fraction. Also, it is assumed that in the selective dissolution test all inorganic carbon is lost i.e. there is no inorganic carbon in the dissolution residue.

$$w_{\text{B,TC}} = 100 - \left(\frac{x_{\text{residue}} \times C_{\text{residue}}}{C_{\text{tot}}} \right) \tag{B.8}$$

Depending on the quality of the ash, a deviation of up to 0,4 % per 1,0 % of ash content may be caused by carbonates present in the ash.

Annex C
(normative)

Determination of biomass content using the manual sorting method ($\mathrm{M_{sort}}$)

C.1 General

In the $\mathrm{M_{sort}}$, a sample of the solid recovered fuel is sorted by hand into sub-fractions, such as plastics, paper/cardboard, wood, vegetable, fruit, garden waste and inert matter.

C.2 Principle

The $\mathrm{M_{sort}}$ for the determination of the biomass content in percent by mass involves the separation of the components into a number of fractions which are either (mostly) biomass or (mostly) non-biomass.

C.3 Limitations

This method is not applicable for solid recovered fuels with a particle size smaller than 10 mm and/or SRF that is pelletized. Other details on limitations of this method can be found in Annex D.

C.4 Symbols

For the purposes of this annex, the following symbols apply.

w_{B}	biomass content on a dry basis, expressed as a percentage by mass;
$w_{\mathrm{B,NB}}$	biomass content in the sorted non-biomass fraction on a dry and ash-free basis, expressed as a percentage by mass;
$w_{\mathrm{i,B}}$	content of component i in the biomass category on a dry basis, expressed as a percentage by mass;
$w_{\mathrm{i,in}}$	content of component i in the ash matter category on a dry basis, expressed as a percentage by mass;
$w_{\mathrm{i,NB}}$	content of component i in the non-biomass category on a dry basis, expressed as a percentage by mass;
w_{in}	inert content on a dry basis, expressed as a percentage by mass;
$w_{\mathrm{B,in}}$	inert content in the sorted biomass fraction on a dry basis, expressed as a percentage by mass;
$w_{\mathrm{NB,in}}$	inert content in the sorted non-biomass fraction on a dry and ash-free basis, expressed as a percentage by mass;
w_{NB}	non-biomass content on a dry basis, expressed as a percentage by mass;
$w_{\mathrm{B,NB}}$	non-biomass content of the sorted biomass fraction on a dry basis, expressed as a percentage by mass;

$w_{\mathrm{B,in}}$	biomass content of the sorted inert fraction on a dry basis, expressed as a percentage by mass;
$w_{\mathrm{NB,in}}$	non-biomass content of the sorted inert fraction on a dry basis, expressed as a percentage by mass;
$w_{\mathrm{in,in}}$	inert content of sorted inert fraction expressed as a percentage by mass.

C.5 Apparatus

Apparatus needed for performing the M_{sort} are:

- screen sieve of 10 mm;
- balance with accuracy of 0,1 g;
- containers for the sorted fractions (14);
- desiccator.

C.6 Procedure

C.6.1 General

The procedure consists of the following two steps:

a) manual sorting;

b) calculation of the results.

C.6.2 Manual sorting

The instructions for implementing the M_{sort} comprise the following steps:

a) take a sample according to ISO 21645. Prepare the sample according to ISO 21646. The test portion for the M_{sort} shall be at least as big as the minimum sample size according to ISO 21645.

b) sort all particles larger than 10 mm of the sample into the fractions mentioned in Table C.1;

NOTE The sample is sieved with a 10 mm sieve to remove all particles below 10 mm which are classified as “fines” fraction.

c) dry all fractions at 105 °C to a constant mass;

WARNING — For some types of solid recovered fuels there can be a risk of self-ignition when drying at 105 °C.

d) allow the dried fractions to cool down in a desiccator (with samples over 100 g it is not feasible to use the desiccator and the samples shall be weighed directly);

e) weigh the dried fractions with four significant digits. Record the mass for each fraction;

f) cluster the masses of the categories according to Table C.1 into biomass, non-biomass and inert fractions and determine the mass per fraction by summing.

NOTE Examples of components/subfractions are given in Table C.2.

For determining the biomass content, the selected sub-fractions concerned shall be clustered into the categories biomass, non-biomass and inert matter. This classification will never be exact, due to e.g. the presence of composite materials. For example, drink cartons contain not only paper (biomass) but also small quantities of plastic (non-biomass) and aluminium (inert).